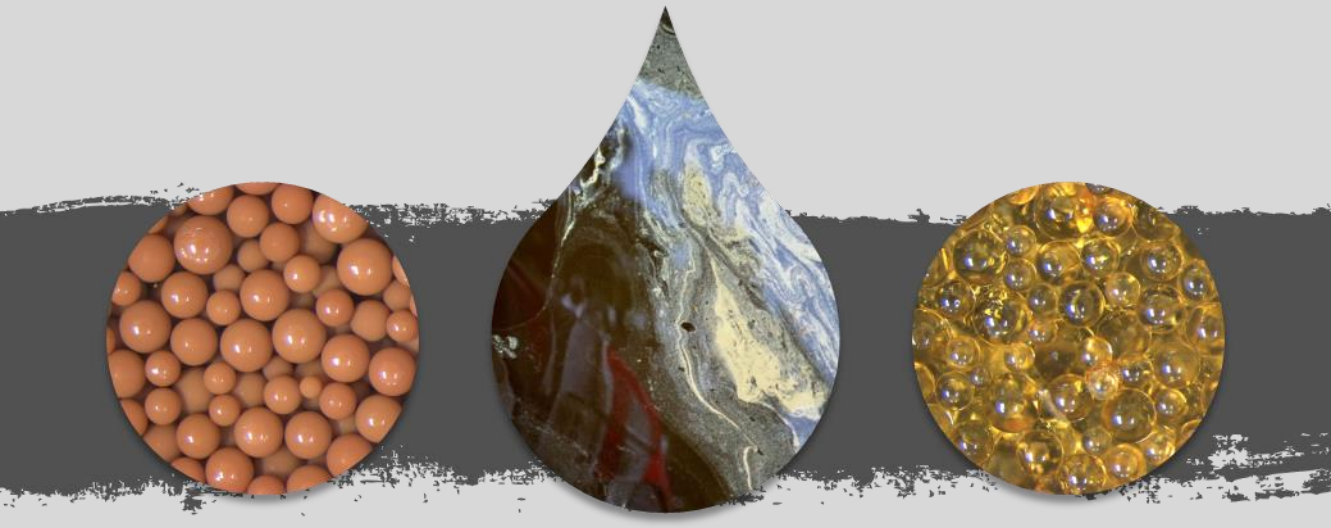
UNIVERSITAT ROVIRA i VIRGILI

Design and optimization of a resin technology system for the elimination of oil from industrial wastewater

M. ÀNGELS TEJERO IBORRA



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Àngels Tejero Iborra

Design and optimization of a resin technology system for the elimination of oil from industrial wastewater

Doctoral Thesis

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Department of Chemical Engineering

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I, Dr. Verónica Gómez, R&D Leader of the Global Water Technology Center by the DuPont de Nemours and Company,

I STATE that the present work entitled "Design and optimization of a resin technology system for the elimination of oil from industrial wastewater", presented by Maria dels Àngels Tejero Iborra for the award of the degree of doctor by the Universitat Rovira i Virgili, has been carried out under my supervision at the Chemical Engineering Department.

Tarragona, 1 November 2020

Doctoral Thesis Supervisor/s

Prof. Dr. Ricard Garcia-Valls

Dr. Verónica Gómez

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Summary

Oily wastewater is ubiquitous in the industrial sector, especially refineries and the petrochemical industry [1]. It poses a huge environmental problem because it includes a broad range of organic compounds that represent a grave threat both to aquatic ecosystems and to human health. Therefore, these waters must be treated for discharge, and must comply with the regulatory limits established by the EU. It is also necessary to treat them for the purpose of reuse, due to the fact that hydrocarbons can have a great impact on other downstream technologies such as reverse osmosis.

The conventional approach for oily wastewater treatment can struggle to deal with this challenging wastewater in an environmentally acceptable manner. Oily waters may contain between 1 and 3% of hydrocarbons up to after treatment with conventional technologies. This oil will be present mainly as suspended microscopic droplets and a dissolved fraction of organic compounds.

This PhD research project has aimed to explore the remediation of oily wastewater through the use of resin technology, with the ultimate goal of being able to design a functional system for the treatment of industrial wastewater.

This project has first focused on the systematic characterization of oily process wastewater, in order to gain a deeper understanding of oily waters and the potential needs of an oil removal system. This has led to the identification of key components that are present in all forms of oily wastewater originating from fossil fuels. It has been found that in spite of their immense variability, most differences are in the relative composition of the oil fraction and the presence of process additives. This has led to the identification of appropriate methods for routine quantitative analysis of components of oil water that are expected to be present in most types of oily water.

This process has also fully characterized different types of resins for the purposes of system design. In particular two resins have been studied, each of them aimed to target the two problematic fractions of oil found in oily wastewater. An oleophilic resin has been studied for the removal of emulsified oil through a coalescence process, and a polymeric adsorbent has been studied for the purpose of removal of oil through adsorption mechanisms.

A fundamental study of the impact of operational variables and wastewater chemical composition on both coalescer and adsorption systems has been performed in a bench-scale experimental set-up in order to determine the operational limits or oil-removal resins. A study has been made of the operation of a coalescer-type unit under different operating conditions that have been shown to have an effect on overall coalescer efficiency. These efforts have allowed us to determine the critical variables for coalescer performance, and to develop a basic predictive model that provides a conservative estimate of performance, as well as design guidelines for this type of system. Similarly, there has been a study on the differential adsorption of common oily-water dissolved components by adsorbent resin media. The isotherms of different components show that there are important differences in the affinity of the adsorbent for the different typical components of oily water, which have important implications in the behavior and recovery of spent adsorbents.

Pilot-scale testing has been used to develop further the concept of oil removal through resin technology and aiding in optimization and troubleshooting of the process. Piloting has allowed a determination of the efficiency of the regeneration process, and the effect of changing wastewater composition on resin loading cycles, resin recovery and fouling.

Using the operational and analytical resources developed in the course of this thesis, it has been possible to carry out an evaluation of the suitability of resin technology for the treatment of a certain types of oily wastewater. The tangible results of this thesis include a set of guidelines for the applications of resins to oil-removal applications.

Objective and thesis outline

The main objective of this project has been the design, validation and optimization of a system for the treatment of industrial wastewater integrating different types of polymeric resins, mainly coalescence and adsorption resins, with the purpose of removing oil and grease from water.

This thesis is divided into different chapters, each of them covering a particular topic of research needed to reach the goal previously outlined. The particular goals of each chapter have been outlined in detail in the main body of the thesis. However, a brief summary of the main goals and contents of each chapter is provided here.

Chapter 1: Introduction to the treatment of hydrocarbon-contaminated industrial wastewater

This chapter provides an overview of oil-removal technologies used for the treatment of oily wastewater. The objective has been to outline the advantages and disadvantages of existing oil-removal technologies in order to better contextualize the existence of resin oil-removal technologies, and better represent their place in the part of oil-removal processes.

Chapter 2: Study of the chemical composition of hydrocarbon-contaminated industrial wastewaters

This chapter addresses the characterization of typical oily industrial wastewaters. The aim of this study is to be able to identify the organic species originating from fossil fuels that are most commonly found in in these types of wastewater. The goal of this exercise has been to be able to identify key components of oily wastewater that are suitable for system monitoring and to identify analytical methods that are both suitably specific and apt for routine analysis.

Chapter 3: Characterization of polymeric resins

The aim of this chapter is to address the physical characterization of the resin materials used in oil removal applications. In order to provide adequate hydraulic characterization of the resin for design purposes, the goal has been to obtain measurements of particle size distribution, void fraction and pressure drop. The intention is to obtain and verify a valid model for the projection of pressure drop as a tool for project development.

Chapter 4: Removal of emulsified oil by coalescence through a particle bed

The focus of this chapter the study of the oil-removal performance of coalescer resin AmberLite™ ROC110 and similar coalescer resin media. The goal of this study has been to develop a standardized testing method for coalescer media, and the study of the effect of changing operating conditions on the performance of a coalescer packed bed. This chapter discusses the development of a model that can predict oil removal efficiency in this type of systems and the establishment of cleaning requirements for the operation of coalescer systems.

Chapter 5: Removal of dissolved oil by adsorption

This chapter focuses on the characterization of the adsorption behavior of resin AmberSorb™ L493 regarding species common in oily water, such as toluene, naphthalene, phenol or acetate. The goal has been the elaboration of single-component isotherms that can allow us to model the adsorption of oily water onto this adsorbent. Additionally, this chapter studies the multi-component adsorption of synthetic oily samples with the aim to determine selectivity and preferential adsorption in this type of system.

Chapter 6: Case study of a de-oiling system for oil removal

This chapter discusses the pilot testing carried out to study the removal of oil in an industrial site in which large amounts of oily waste water are regenerated every year. The main goal of this section has been to test this kind of resin technology on the concept of oil removal in a real wastewater system. The performance of the system has been evaluated on the basis of filtrate water quality, loading cycles and regeneration efficiency, focusing on the optimization of the cleaning and regeneration protocols.

Chapter 7: Conclusions

A final outlook of the main conclusions of this research are summarized in this chapter. An overview od previous chapters as well as a general interpretation of results are included to effectively provide the most important conclusions and to clearly outline the recommendations regarding resin oil-removal technology.

Contents

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Nomenclature

Abbreviations

ANVAR	Agence nationale de valorisation de la recherche
APHA	American Public Health Association
API	American Petroleum Institute
AS	Activated Sludge
BAF	Biologically Active Filters
BOD	Biological Oxygen Demand, mg/L
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
BV	Bed Volume
COD	Chemical Oxygen Demand, mg/L
CPI	Corrugated Plate Interceptors
CWAO	Catalytic We-Air Oxidation
DAF	Dissolve Air Flotation
DVB	Divinylbenzene
EPA	Environmental protection Agency
eSEM	Low-vacuum scanning electron microscopy
FI	Flow indicator
FWKO	Free-water Knockout
GAC	Granular Activated Carbon
GC-FID	Gas Chromatography Flame Ionization Detector
GC-MS	Gas Chromatography Mass Spectrometry
HEM	Hexane-Extractable Material
HIAC	High Accuracy
IAF	Induced Air Flotation
IAST	Ideal Adsorbed Solution Theory
IC	Ion Chromatography
IER	Ion Exchange Resin
IUPAC	International Union of Pure and Applied Chemistry
LC-MS	Liquid Chromatography Mass Spectrometry
LLE	Liquid-liquid Extraction
LOD	Limit of Detection
LOQ	Limit of Quantification
LPG	Liquefied Petroleum Gas
MBR	Membrane Bio-reactor
MF	Microfiltration
MLD	Minimum Liquid Discharge
MPPE	Macro-porous Polymer Extraction
NF	Nanofiltration
NPD	Naphthalene, phenanthrene, dibenzotiophene
O&G	Oil & Grease, mg/L
O/W	Oil-in-water
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PAH	Polycyclic Aromatic Hydrocarbons
PAN	Polyacrylonitrile
PDA	Polydopamine
PEI	Polyethyleneimine
PI	Pressure indicator
PP	Polypropylene
PP1	Parallel Plate Interceptors
PS	Polystyrene
PSU	Polysulfone
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVDF	Polyvinylidene fluoride
RAST	Real Adsorbed Solution Theory
RO	Reverse Osmosis
SAC	Strong acid cation
SBA	Strong base anion
SF	Safety factor, non-dimensional
SPE	Solid-Phase Extraction
sVOC	Semi-volatile Organic Compounds
TDS	Total Dissolved Solids, mg/L
TOC	Total Organic Carbon, mg/L
TOG	Total Oil and Grease, mg/L
TPH	Total Petroleum Hydrocarbons, mg/L
TSS	Total Suspended Solids, mg/L
UC	Uniformity Coefficient, non-dimensional
UF	Ultrafiltration
VOC	Volatile Organic Compounds
WOR	Water-to-oil ratio, non-dimensional
ZLD	Zero Liquid Discharge
HS-GC-MS	Headspace Gas Chromatography Mass Spectrometry
LC-UV-MS	Liquid Chromatography Ultra Violet/Mass Spectrometry

Symbols

ΔC	Gradient of concentration, in mg/L
μ	Arithmetic average in a normal distribution
A	Active surface, in m^2
a_{RP}	Redlich-Peterson isotherm constant, in 1/mg
A_S	Specific surface, in m^2/m^3
BE	Bed Expansion, %
$C_{o,i}$	Feed concentration of solute *i* in the fluid phase, in mg/L
$C_{e,i}$	Equilibrium concentration of solute *i* in the fluid phase, in mg/L
$C_{e,i}^{o}$	Equilibrium concentration of solute i in single-component adsorption, in mg/L

C_i	Outlet concentration of solute i in the fluid phase, in mg/L
C_s	Limit of solubility, in mg/L
d_{oil}	Oil droplet size, µm
d_p	Particle diameter, µm
dP	Pressure drop, bar
$d_{p,10}$	Particle size at accumulated frequency 10%
$d_{p,60}$	Particle size at accumulated frequency 60%
$d_{p,90}$	Particle size at accumulated frequency 90%
$d_{p,AMS,N}$	Particle Arithmetic Mean Size, µm
$d_{p,HMS,N}$	Particle Harmonic Mean Size, µm
$d_{p,MD,N}$	Median Size Diameter, µm
$d_{p,MD,V}$	Volume Median Diameter, µm
E_o	Energy of adsorption. in KJ/mol
e^2	Mean square error, non-dimensional
E_{max}	Maximum Efficiency of Oil Removal, %
E_{OR}	Efficiency of Oil Removal, %
E_{PR}	Efficiency of Particle Retention, %
F	Flowrate, m^3/h or BV/h
$f_{N,i}$	Frequency of beads of i diameter, %
$f_{V,i}$	Volume-weighted frequency of i diameter beads, %
g	Gravitational acceleration on Earth, 9.81 m/s^2
$K_{BET,1}$	First-layer BET isotherm constant, in l/mg
$K_{BET,2}$	Upper-layer BET isotherm constant, in l/mg
K_E	Mass transfer coefficient, in m/s
k_E	Mass transfer rate, in mol/s
K_F	Freundlich isotherm constant, in $(mg/g)/(mg/l)^n$
K_K	Khan isotherm constant, in l/mg
K_L	Langmuir isotherm constant, in l/mg
K_{RP}	Redlich-Peterson isotherm constant, l/g
K_S	Sips isotherm constant, in $(mg/g)/(mg/l)^n$
K_{TO}	Toth isotherm constant, in l/mg
m_e	Mass of solute in the adsorbent at equilibrium, mg
$m_{e,i}$	Mass of solute in the adsorbent at equilibrium, in mg
M_i	Mass of resin, in g
MW	Molar Weight (g/mol)
n	Isotherm model exponent, non-dimensional
NC	Number of components, non-dimensional
N_i	Number of particles of i diameter, non-dimensional
$Øext$	Tubing external diameter, m
$Øint$	Tubing internal diameter, m
q_e	Equilibrium adsorption capacity, mg/g
$q_{e,i}$	Equilibrium adsorption capacity of solute *i*, mg/g
$q_{e,i}^o$	Equilibrium adsorption capacity of solute *i* in single-component adsorption, in mg/g
q_o	Maximum theoretical adsorption capacity, in mg/g
q_o^*	Maximum theoretical adsorption capacity for a multi-component system, in mg/g
$q_{o,i}$	Maximum theoretical adsorption capacity of solute *i*, in mg/g
q_T	Total equilibrium capacity for a multi-component system, in mg/g
R^2	Determination coefficient, non-dimensional
Re	Reynolds Number, non-dimensional
S	Cross-section, m^2
S_D	Standard deviation, non-dimensional
T	Temperature, ºC
t	Time, s
u_0	Linear velocity, m/s
u_r	Rising velocity, m/s
V_i	Volume, L
W_i	Weight, g
x_i	Mole fraction in the adsorbed phase, non-dimensional
Z_i	Bed depth, m
γ_i	Activity coefficient of solute *i*, non-dimensional
ε	Void Volume, non-dimensional
ε_b	VoidD Volume for two-phase flow, non-dimensional
η	Fluid viscosity, kg/(m·s)
π_i	Spreading pressure of solute *i*, in dyn/cm^2
ρ_B	Bulk density, kg/m^3
ρ_F	Fluid density, kg/m^3
ρ_o	Density of oil, kg/m^3
ρ_S	Solid density, kg/m^3
ρ_w	Density of water, kg/m^3
σ	Standard deviation in a normal distribution
Φ	Sphericity, non-dimensional

Chapter 1

Introduction to the treatment of hydrocarbon-contaminated industrial wastewater

The Author of this document, Maria dels Àngels Tejero, is fully responsible for the information included in it. Even though part or the whole work here presented might have been completed in one of the DuPont de Nemours Company ("hereinafter "DuPont") facilities, the content of this document is based on the opinion of the Author. Nothing stated herein is DuPont's opinion and DuPont has not offered to take responsibility for it.

1. Industry drivers, environmental impact and discharge regulations.

The popular refrain saying that "oil and water don't mix" can be quite misleading. Industrial wastewaters often carry large amounts of components derived from crude oil: a complex mixture of free-floating, emulsified, and dissolved organics. Hydrocarbon-bearing wastewaters –which going forward will be referred to as *oily wastewater*– represent a major environmental problem and a management challenge for industrial water treatment plants worldwide. Oily wastewater is quite ubiquitous in the industrial sector, since petroleum products are commonly used as both energy sources and raw materials –this is particularly the case in refineries and the petrochemical industry. The Oil & Gas industry alone generates enormous volumes of contaminated wastewater every year –up to 55.5 million m^3/day according to the Global Water Intelligence (GWI) in 2014 [1]–, both in upstream production and downstream in the petrochemical industry and the petroleum refining sector.

The potential sources of oily wastewater include oil production wells, petroleum refineries, petrochemical industries, transport and storage facilities, and metallurgical sites. The most prevalent form of oil contamination comes from wastewaters generated during the production of Oil & Gas from onshore and offshore oil wells –also known as *produced water*. Produced water is the main by-product in the Oil & Gas industry. The current average water to oil ratio (WOR) in these operations is 3:1; that is to say that there are three barrels of oil-contaminated water extracted for every barrel of oil [2]. However, this varies greatly and can fluctuate from essentially zero to more than 50:1 depending on the age, geological nature of the well and the oil recovery strategy in use. The volumes of contaminated water can even increase in the case of aging wells where water and steam injection is used as a method to enhance oil recovery. With a world production of 1696 million barrels of oil in 2017, produced water can be currently estimated at 800 million m^3 per year [3]. Another very important source of oil contamination is industrial wastewater from the big chemical industry –mainly the petrochemical plants, refineries, and the plastics industry–, where petroleum is transformed for general consumption into fuel and other commodities. The metal industry is also a large source of oil contamination due to the water rinsing typically carried out after the process of galvanization and other various surface treatments. Furthermore, water can be contaminated in other mechanical processes where lubricants are used to reduce the mechanical stress in joints and moving parts in water circuits. Leakages in motors and pumps regularly contaminate closed water circuits.

Many of the components commonly found in oily water are carcinogenic, or at least strongly suspected of being so, and otherwise generally harmful to human health and the environment. The treating of oily wastewater effluents for their disposal or potential reuse is generally determined by the confluence of three motivators: existing regulations, overall treatment costs and intrinsic process demands.

Compliance with existing regulation has historically been the starting point for the design of wastewater treatment systems. Until the turn of the XXIst century, only non-polar oil-in-water (OIW) was regulated in any fashion by governments across the world, and very little attention was given to the accompanying dissolved organics found in oily wastewater. Accordingly, the treatment received by oily wastewaters before discharge used to be very basic, which has in certain areas lead to instances of severe environmental pollution to of soil, coastal waterways, surface and underground waters [4]. As a result, there has been worldwide shift in policy towards prevention, and a progressive toughening of environmental standards. The regulation of the discharge of hydrocarbon-contaminated wastewaters into bodies of water varies worldwide, as they are highly dependent on the industrial sector and the location of the discharge endpoint.

The Oil & Gas Exploration & Production (E&P) industry usually practices direct discharge into the sea whenever possible, particularly in offshore operations. Generally speaking, discharge into the sea has been

less stringently regulated than into freshwater bodies, as contaminants are released into an immense body of water, creating a very powerful dilution effect. As per current international regulations, offshore produced water discharges have a limit of O&G content of 40 mg/L [5]. The United States Environmental Protection Agency (US EPA) is limited to a 29 mg/L as a maximum monthly average with allowable sporadic emissions up to 42 mg/l for offshore discharges of produced water into the Gulf of Mexico. Nonetheless, due to the growing concerns about the cumulative effects that such practices have on the environment, some countries have started to implement more strict regulatory standards. China has set its discharge limit at a monthly maximum average of 10 mg/L. The discharge limits in the Persian Gulf are currently 15 mg/L, below the requirements of international regulations. The Qatar Ministry of Energy also has a standing zero-discharge policy since 2013 [6]. The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) agreed to a maximum of 30 mg/L of O&G and set the goal for zero-discharge by 2020. As the OSPAR contracting parties include Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, The Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom, this policy has also been adopted by the European Union. The EU Water Framework Directive (WFD) adopted in 2000 is committed to 'zero discharge' of hazardous substances –including oil- as a preventive measure against further aquatic pollution [7]. This applies particularly to seawater discharges where member states have agreed to phase out discharges and emissions of priority hazardous substances (Directive 2000/60/EC). Current EU Directives do not directly establish limits for most individual organic contaminants into freshwater bodies except for the case of a few key priority pollutants (Directive 2000/60/EC, Annex IX). Each EU State itself defines the limits for selected organic compounds, based on the fact that the permanence of recalcitrant compounds depends on the local soil characteristics.

Additionally, the above legal considerations sometimes join with the broader concern of water scarcity in water-stressed regions. Water stress is a long-term problem that is expected to be aggravated within the next decades due to both population growth and growing industrialization. The competition of the urban, industrial and agricultural sectors for this resource is set to escalate and has the potential to seriously affect already water-stressed regions such as Spain [8]. Industries need to become more independent of the supply of fresh water for their production processes –whether by law or economic reasons. The combination of water scarcity with the growing environmental concern regarding current discharge practices has resulted in the development of wastewater management practices called Minimum Liquid Discharge (MLD) and Zero Liquid Discharge (ZLD). These processes are designed to either maximize –in the case of MLD– or achieve total recovery –in the case of ZLD– of water from a wastewater source that would otherwise be discharged. For many years, ZLD has been touted as an environmentally friendly way to help the industry sector meet the increasingly strict discharge requirements for their wastewater streams. However, ZLD processes are not only technically complex, but excessively expensive and not necessarily environmentally friendly given the large amounts of energy they require. Therefore, in spite of their great potential for reducing water pollution and augmenting water supply, its implementation is still constrained by high costs and intensive energy consumption [9]. The current trend is towards developing technologies capable of minimizing these issues. MLD is a middle-of the road approach to the industrial wastewater treatment problem. Since usually the recovery of the final 5-10% of total wastewater requires the use of thermal technologies that account for more than 75% of the costs [10]. Coined and heavily developed by DuPont, MLD concept heavily relies on improved and optimized water filtration technologies such as ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF) — with a host of improvements. When such complex water recycling streams are involved, facility operators will seek to reduce the hydrocarbon content in consideration of downstream technologies that might be sensitive to these contaminants.

Downstream demands are an important consideration when designing the treatment of industrial wastewaters. Many technologies used for water purification are adversely affected by the presence of hydrocarbons.

Aliphatic and aromatic hydrocarbons have been found to particularly interfere in membrane-based separation processes such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) by producing fouling and foaming [11]. In the case of reverse osmosis (RO) the presence of hydrocarbons leads to severe fouling, and symptoms manifest as permeate flow decrease and increased transmembrane pressure in cross-flow operation [12]. Their failure is not in failing to provide suitable quality of permeate water, but in sustaining continuous operation in the presence of oil. Furthermore, a progressive degradation of the membrane is observed in membranes exposed to hydrocarbons. It is accepted that membranes chronically exposed to hydrocarbon contaminated waters will take gradual damage by the progressive diffusion of hydrocarbons thorough the membrane; which can end up completely destroying the membrane [13]. Similarly, ion-exchange resins used in water softening experience performance difficulties when face with oil in their feedwater. Typically, oil coats the resin beads forming a film that is difficult to penetrate by the ions, leading to slower kinetics and reduced operating capacity [14]. Hydrocarbon fouling is also a critical problem in boilers and evaporators, both still widely used in ZLD and MLD processes. A build-up of hydrocarbons can lead to significant efficiency loss over time as the heat transfer rate decreases due to the organic film, overheating develops inside the heat exchangers, and the organic matter slowly burns creating a cake of soot and ash. Hydrocarbon fouling inside heat exchangers costs petroleum refineries large amounts of money each year due to energy wasted [15]. Therefore, when plant design requirements demand the implementation of any of these technologies, it becomes necessary to preventively improve on the convectional designs for the treatment of oily wastewater.

2. Treatment of oily wastewater

Because of the inherent complexities of oily wastewater, the design and operation of oily-wastewater treatment plants is complex and challenging. The industrial sector uses a wide array of physical and chemical treatment processes to remove hydrocarbons from water, usually in combination in order to achieve compliance with discharge regulations.

De-oiling technologies can be broadly categorized by their ability to separate oil-in-water based on the average oil droplet size. Therefore, in order to treat the particular combination of oil fractions found at any one site, it is necessary to combine technologies capable of targeting the different fractions (Figure 1-1). The suitability of such technologies is very site-specific, and the treatment system will depend both on feedwater type and conditions, and the level of treatment required, which is governed by local regulations. It should be stated that the classification shown in Figure 1-1 is very basic, by no means exhaustive, and represents only a few token common oil-removal technologies.

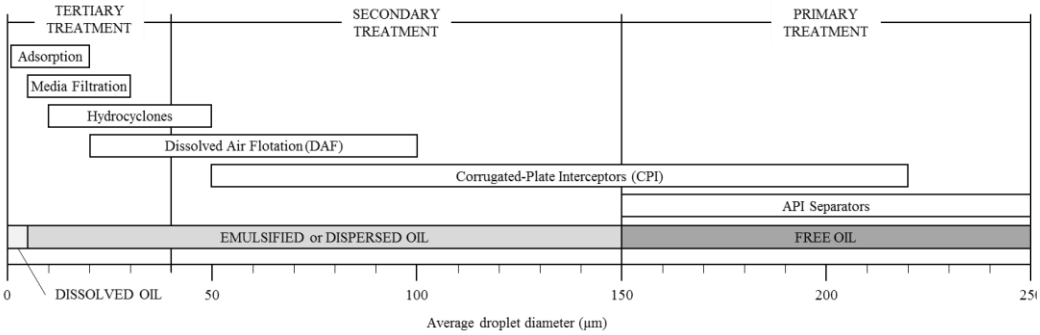

Figure 1-1. Oily water treatment technologies as a function of oil droplet size [16,17].

Typical systems for the treatment of oily wastewater use a combination of different technologies, with a minimum of two consecutive steps for oil removal. The typical produced water treatment includes primary and secondary oil-water separation, normally consisting of technologies that are also capable of addressing the suspended solids (TSS) typically contained in this type of wastewater [1]. The treatment steps up to and including secondary treatment are typically enough for produced water that is disposed of overboard in offshore platforms or in deep injections wells (Figure 1-2). But depending on a reservoir's characteristics and location, an additional tertiary treatment step may be required in order to address the problem of emulsified oil with lower droplet sizes. This is a particularly important consideration for reuse of produced water with reinjection purposes, due to the growing concern of clogging inside reservoirs in waterflooding operations. Tertiary treatment is much more common in the treatment of refinery wastewater. The stricter regulation of hydrocarbon and organic content in onshore industrial discharges means that treatment is also more complex. A typical refinery wastewater treatment plant consists of primary and secondary oil-water separation, followed by biological treatment, and –if at all necessary– tertiary treatment [18].

2.1 Primary treatment

The technologies used in primary treatment are very well-established. The primary treatment of oily wastewater is a physical operation, usually gravity separation in some form. This initial step is aimed towards removing the bulk of contaminants by removing free oil and the floating and settleable material. Such technologies are based on the principle of Stoke's Law and depend on the difference of densities between oil and water to achieve separation. The most typical primary treatment device is the API (American petroleum Institute) Gravity Separator, which uses the difference in specific gravity to allow hydrocarbons to float to the surface be skimmed off, while the water sludge settles to the bottom and is removed periodically. API separators are effective in achieving initial three-phase separation (oil, solids, and water), simple to design and easy to operate [18]. Nonetheless, they can only separate oil droplets of 150μm or larger, and usually, require large amounts of floor space [17,19,20]. This is a disadvantage in some industrial sectors like offshore oil production, where space is at a premium. In such cases, it is not uncommon to have instead other devices such as parallel plate interceptors (PPI) or corrugated plate interceptors (CPI). These use coalescing plates in order to encourage coalescence of oil along plate surfaces. In this way, plate coalescers manage to reduce residence time and footprint, achieving separation of oil droplets as small as 40 μm [21]. Both PPI and CPI separators tend to be smaller than a comparable API and require far less floor space [18]. Produced water primary treatment will often have free-water knockout (FWKO) drum units, where vertical vessels are specially designed to encourage the additional separation of dissolved gas. Usually, FWKO are followed by heater treaters, which provides heat in order to enhance the separation of oil [22–24].

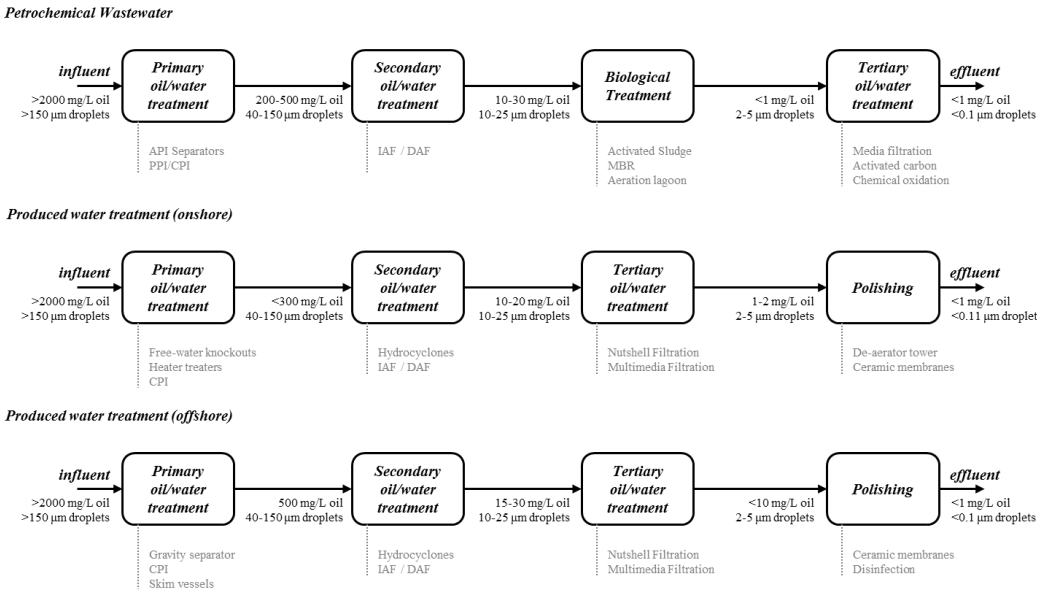

Figure 1-2. Typical oily-wastewater treatment train arrangement for different industrial sectors [1,2,18].

2.2 Secondary treatment

Secondary treatment is designed to achieve further break-down of oil-water emulsions, most commonly through a flotation unit. The general process of flotation systems introduce air bubbles into the waste stream to which oil droplets become attached after initial contact, and through differential density rise to the surface where they are removed [25]. The two major commercial types of gas flotation systems currently used are induced air flotation (IAF) and dissolved air flotation (DAF). In IAF, air bubbles are introduced mechanically using high-speed impellers. In DAF, a gas –normally air– is dissolved in the wastewater under pressure and comes out of solution once pressure is released, creating very small gas bubbles as a result. Making the bubbles as small as possible and evening the size distribution of gas bubbles are key to achieving high removal efficiencies [26]. But unlike gravity settling technologies used in primary treatment, DAF has the advantage of performing well at cold temperatures. DAF can remove particles as small as 25µm and can remove contaminants down 3 to 5 µm in size if coagulation is added as pretreatment, but it cannot remove the dissolved oil fraction [27].

Chemical treatment by coagulation/flocculation is extensively used in large-scale petrochemical wastewater treatment for its ability to de-stabilize stable emulsions and aggregating colloids [28]. In coagulation/flocculation, a coagulant is mixed into the water to precipitate out the treated contaminants in the form of flocculants. Destabilization of oily water emulsions can be achieved by reducing the electrostatic particle surface charges through an adjustment of the pH and the addition of ferric sulfate, zinc silicates, anionic polyacrylamides (A-PAM), aluminum sulfate (alum), poly-aluminum chloride (PAC) or chitosan [29–31]. Under optimized conditions, systems using coagulation/flocculation can improve oil removal efficiencies up to 95-99%. But as the efficiency of chemical coagulation/flocculation depends on a number of factors like the coagulant dosage, pH, temperature, ionic strength, the nature and concentration of organic matter and the amount of total dissolved solids (TDS); it is difficult to predict the best coagulant, and a lot of screening experiments must be carried out to determine suitability. The extensive use of added chemicals is the biggest

drawback of conventional chemical coagulation/flocculation, along with possible downstream effects and processing difficulties. Furthermore, this type of treatment is costly, and poses a severe risk of secondary pollution to water bodies due to the use of metallic salts [32].

In order to overcome the inherent limitations in chemical coagulation, the trend has been to develop alternative technologies like electrocoagulation. In this type of technology, coagulation is accomplished by the in-situ generation of coagulants through an electrolytic oxidation process. Cations are generated by the oxidation of a sacrificial anode, which induces flocculation of the dispersed oil by reducing the electrostatic particle surface charges in the oil droplets. Then, the bubbles generated by electrolysis will carry the oil droplets to the surface. Amongst the anode materials that have been successfully used in oily water de-emulsification are cast iron, stainless steel, aluminum [33]. Among the benefits of electrocoagulation is the fact that it can remove both emulsified oil, some fractions of dissolved oil like phenols, heavy metals and suspended solids [34,35]. However, comparison studies carried out between electro-coagulation and chemical coagulation show that when it comes to oil and grease removal, both technologies are similarly effective [36]. In this light, one of the disadvantages of electrocoagulation is that it is more expensive –an estimated 1.73 $\$/m^3$ compared to 1.11 $\$/m^3$ spent in chemical coagulation [37]. Additionally, dissolved salts like sodium chloride are essential to electrochemical coagulation operations because they provide the needed conductivity to the solution. Therefore, this technology is dependent on the total dissolved solids (TDS) content of the feed solution, as well as pH [38].

While coagulation/flocculation and flotation remain the most common combination for secondary treatment for onshore locations –which include onshore oil-fields, refineries, petrochemical plants, etc.–, it is different in the case of offshore oil production. Because of the incredibly high cost of floor space atop an offshore platform, the oil industry has been turning to the use of much-smaller centrifuges and hydrocyclones to implement secondary treatment. These technologies are based on the application of centrifugal and centripetal forces so that oil droplets –of lower density than water- will migrate to the core of the vortex and travel in the opposite direction than the rest of the treated waste stream [39,40]. Hydrocyclones are suitable to the treatment of oil droplets down to 10-15μm, yielding effluent concentrations of 20-30 mg/L, while centrifuges can deal with oil droplets < 2μm with oil effluent concentrations of 5-25 mg/L [26]. The reduction in size comes at the cost of much higher energy consumption, which is necessary for spinning/pressurizing the system.

Steady-state bed filter coalescers –particle and mesh– are also attractive because of their relatively small footprint. This type of secondary treatment technology has been used as a shipboard oil separator –thanks to their small size– since the decade of 1970s. Particle and fiber coalescers take advantage of the different affinity for the particle/mesh material exhibited by water and oil. Small oil droplets are adsorbed to the surface of the packing materials, and when the oil layer coating them has grown thick enough, the shear forces created by the water flow will drag the larger droplets off. The different settling times of oil and water will result in the formation of an oil layer, which can be easily skimmed off. These units can operate in steady-state almost indefinitely, with only sporadic backwashing to remove suspended solid plugging the solid. Therefore, filter coalescers are an attractive option for oily water treatment owing to the low energy requirements, the simplicity of operation, and their low maintenance costs. Oil wettability is essential in determining good packing materials. Oleophilic materials are the ideal packing materials for the treatment of oil-water emulsions [41]. Materials used for this purpose include natural materials –such as anthracite, quartz, silica sand and granular activated carbon–, synthetic materials –such as stainless steel and glass fibers, ceramic filters, polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyurethane (PU) beads– and functionalized materials like ion exchange resins [41–47]. It was found that some adsorbent resins such XAD-2 and other cationic ion exchange resins performed exceedingly well in particle coalescers [41,48]. The inclusion of specific oleophilic functional groups in polymer beads –in the style of ion exchange resins– results in chemically enhanced oil-water separation, improving the separation of stable emulsions

[42,47,49,50]. Typically, such coalescers treat concentrations in the range of 200-1000 mg/L of Total Petroleum Hydrocarbons (TPH). Concentrations in treated wastewater range of 10-80 mg/L of TPH, and the oil removal efficiency is largely dependent on feed concentration and fluid velocity.

2.3 Tertiary treatment

Tertiary treatment focuses on the treatment of stable micro-emulsions and dissolved organics remaining behind after primary and secondary treatment. Usually, tertiary treatment needs to be considered if the facilities need to meet stringent limits for some contaminants such as a low chemical oxygen demand (COD) and or trace levels of persistent organics such as Polycyclic Aromatic Hydrocarbons (PAHs). Furthermore, although the concentration of oil in the effluent after secondary treatment is quite low in optimized operating conditions, the variability of influent wastewater usually means that quality upsets are frequent. Depending on the local regulations, tertiary treatment can be installed as a polishing step that can act as a preventive stopgap measure against such quality upsets. A wide array of different technologies exists depending on the site capabilities and the problems leading to a need for tertiary treatment. Tertiary oil-removal technologies include air stripping, chemical oxidation, photo-catalytic oxidation, biological treatment, extraction, membrane filtration and adsorption.

2.3.1 Air Stripping

In many countries, there are strict regulations concerning the emission of BTEX (benzene, toluene, ethylbenzene and xylene) and other volatile organic compounds (VOC). Since petrochemical and refinery wastewaters usually contain significant concentrations of these compounds –as discussed in Chapter 2–, air stripping is one of the more common strategies for VOC emission remediation [51,52]. It is in fact, currently considered the best available technology for the treatment of VOCs. Air stripping is a process of physical mass transfer, which removes VOCs from water by increasing the surface area of the contaminated water that is exposed to air [53]. This takes advantage of the high volatility of certain compounds. Therefore, the efficiency of air stripping is determined by the vapor pressure of target contaminants; it is highly efficient in the elimination of lighter hydrocarbons but will have little to no effect upon heavier oil fractions. If there are high concentrations of non-volatile hydrocarbons air strippers will require proper pre-treatment and equalization in order to prevent fouling and plugging of the internal parts of the stripper [18]. Additionally, air strippers are also sensitive to TDS and TSS content, as they frequently become fouled by mineral deposits when calcium exceeds 40 mg/L, iron exceeds 0.3 mg/L, magnesium exceeds 10 mg/L, or manganese exceeds 0.05 mg/L, or from biological growth [53]. On the other hand, there are two points that make strippers an extremely attractive solution for VOC remediation. They are a very simple and cost-effective technology that will operate continuously with little maintenance if properly designed. And it also allows VOCs to be recovered and reused when there is an economic interest. If not reused, the base toxicity of such compounds will require for the vapors to be routed to a gas flare, with its associated direct carbon emissions.

2.3.2 Chemical oxidation and photo-catalytic oxidation

Conventional chemical oxidation –that means oxidation through the addition of an oxidant– is used to remove organics and some inorganic compounds like iron and manganese from wastewater streams. It is not common to have a chemical oxidation system in a refinery wastewater treatment plant, but as one of the best-established technologies for dealing with persistent color, odor, COD and BOD problems caused by the presence of non-biodegradable compounds, they may be implemented when biological treatment proves inadequate or inefficient [5,18]. The oxidants to be used are typically strong oxidants such as permanganate, peroxide, oxygen, ozone, and chlorine. The specific oxidant to use for the best performance will depend on many factors including raw water quality and the specific contaminants present in the water. The removal rate can be controlled through the chemical dose and the contact time between oxidants and water. Generally speaking,

conventional oxidation is a very reliable technology which requires minimal equipment investment and maintenance [27]. The cost of chemicals is usually a concern, but no pretreatment is usually required for oxidation processes. However, the action of most conventional oxidants (Cl_2, ClO_2, H_2O_2, $KMnO_4$ and O_3) is often limited to a partial oxidation of organic matter, which will result in poor TOC and COD removal, particularly when organic acids are involved [54,55]. In more recent years the trend has been to favor processes that can achieve total degradation of organic matter in order to minimize COD at the point of discharge.

Catalytic wet air oxidation (CWAO) is on such process capable of converting all organic pollutants into carbon dioxide and water. One of the strong points of CWAO as a tertiary treatment technique is that it is prepared to deal with both stable micro-emulsions and soluble oil; as water-insoluble organic matter is oxidized into smaller soluble compounds which are in turn oxidized to carbon dioxide [56]. This process uses air –oxygen– as the oxidant, which is mixed with the influent waste stream and passed over a catalyst at elevated temperatures and pressures. Although, if complete COD removal is not required, the air rate, temperature, and pressure can be reduced, therefore reducing the operating costs [57]. CWAO is an attractive technique because it can degrade non-biodegradable organic substances that biological treatment fails to address. The typical operating conditions for conventional CWAO are 180-315ºC and 20-150 bar. The COD removal that can be achieved is of 75–90% [58]. There are several drawbacks to conventional CWAO: it requires harsh operating conditions and the use of noble metals as catalysts, which mean very high energy and operating costs. Despite its virtues, these disadvantages are not insignificant and have restricted implementation of CWAO to developed countries and small enterprises [57].

Another alternative is the enhancement of conventional chemical oxidation by catalysis. Catalytic ozonation uses heterogeneous catalyst in order to overcome the slow reaction rate and inefficient removal of simple ozonation. The use of catalysts such as MnO_2, TiO_2, Al_2O_3 and mixed metal oxides allows the removal of persistent organics. Chen et al. showed that activated carbon-supported manganese oxide was capable of treating heavy-oil refinery wastewater, showing COD and TOC removal as high as 54.6% and 49.1% with contact times between 60-80 min at 60ºC. Wastewater saw a decrease in toxicity of 70%, greatly improving biodegradability. This indicates that such process by itself is not sufficient, but can be more than adequate pre-treatment for biological systems [55]. Some other forms of catalytically enhancement include using UV light to enhance catalysis. Studies have shown that photo-assisted oxidation with hydrogen peroxide obtained 20-45% COD removal with 830-1660 mg/L of H_2O_2. Analysis showed that oil decomposed into organic acids, which are particularly resilient to photo-oxidation, but some compounds like ethylene glycol were unaffected by this process. The process was only enhanced by a decrease and pH and the introduction of Fe(III) [59].

Photo-Fenton processed have also achieved certain popularity in literature in the treatment of toxic and refractory wastewaters. These are often cited due to their rapid and effective degradation of petroleum-derived contaminants. It encompasses a set of cyclic reactions to produce reactive oxygen species –mainly ˙OH radicals- that oxidize persistent chemicals into carbon dioxide (CO_2), water (H_2O), and inorganic ions. Elimination can effectively be very high, but conditions such as catalyst dose, pH and pollutant load can have a very large impact changing removal rates from 98% to 45%. These systems are also costly for their application at industrial scale, especially due to the associated energy and reagent costs. The attempts to reduce the impossible energy costs have so far been unsuccessful [60].

2.3.3 Biological treatment

Biological treatment is the most widely used wastewater treatment technology for removal of dissolved organic compounds in the oil refining industry. In a report from 2011, 94% of the water treatment facilities of refineries in the EU-27, Norway and Switzerland in operation in 2008 had at least one stage of biological

treatment. A majority of them -over 59%- used some combination of gravity separation, some other advanced treatment and full biological treatment on-site [61].

There are numerous -predominantly aerobic- microorganisms such as bacteria, fungi and yeasts, known for their ability to degrade hydrocarbons [62]. Chaillan et al. identified 33 distinct species capable of hydrocarbon degradation. The capacity of such species for the biodegradation of hydrocarbons showed similar trends regardless of taxonomy: the most efficient degradation was that of saturated hydrocarbons -such as n-alkanes, isoalkanes and isoprenoids- whereas aromatic hydrocarbon degradation was considerably lower: 20% removal for smaller aromatic species and 10% removal for PAHs. This seemed to indicate that efficiency of the biodegradation of petroleum hydrocarbons was far more affected by their intrinsic biodegradability than enzymatic particularities of each species. Additionally, it was found that most active strains produced polar metabolites as a result of hydrocarbon biodegradation -mostly aliphatic organic acids and ketones- that can result in the inhibition of microbial metabolism because of their toxicity [63]. Most microorganisms used for hydrocarbon biodegradation are aerobic. Studies of anaerobic degradation have shown that anaerobes are inefficient, which means anoxic treatment conditions -usually cheaper and simpler to implement- are not feasible [64].

The most common biological process in refinery wastewater is a suspended growth process –meaning microorganisms are maintained in suspension and thoroughly mixed with the organics in the liquid– called activated sludge processes. The microbial composition of the activated sludge and its activity are difficult to control and mostly depend on the nature and availability of hydrocarbons, nutrient composition, and other environmental conditions such as pH, temperature, dissolved oxygen, plant configuration, etc. Such systems typically consist of an aeration tank and clarifier provided with sludge recycle system. Removal efficiencies can be as high as 90-95% for COD and TPH in optimized conditions (Table 1-1). Complete removal is not possible: such systems can treat many sources of dissolved oil, but recalcitrant components such as PAHs are not adequately removed. As such, the un-degraded aromatic fraction will tend to accumulate in the biofilm and emerge as residual oil in the effluent [65]. Therefore, achieving complete removal of hydrocarbons with biological systems is difficult. Pilot-scale studies working *in situ* have showed that even in optimized systems, there removal efficiencies can oscillate considerably due to changes in production regime and output of the upstream plant [66]. A look at feed stream characteristics of successful AS systems will show they can only manage organic loads that are in the lower-end of the spectrum for petrochemical wastewaters and other sources of oily wastewater. Oil field produced waters normally carry much larger amounts of COD than petrochemical wastewaters. Early studies of produced water bioremediation with AS processes showed poor removal rates for phenols and COD, unless important dilution was applied to get in a concentration range similar to that found in successful studies of petrochemical wastewater bioremediation [67]. Additionally, a high hydraulic residence time – usually well over 20h– is also necessary to achieve optimum removal conditions and ensure adequate removal efficiencies. The removal efficiencies when the hydraulic residence time is < 10h are usually below 50%. Therefore, the biggest drawback of activated sludge systems is their very high footprint size. This is an important limitation for the application of AS systems to offshore facilities.

Some of the disadvantages of activated sludge processes can be overcome using attached growth processes – where microorganisms are attached to an inert packing material such as rocks, gravel, plastic, etc.– such as biologically active filters (BAF) or membrane bio-reactors (MBR). BAFs consist of a column filled with a biomass carrier –usually either sand or granular activated carbon pellets– where the biomass grows, ands sloughs off on its own once it reaches a certain film growth. These BAF feature a smaller hydraulic retention time –usually between 1-4h– and footprint size (Table 1-1). Some studies have shown that high removal rates are possible with BAF systems: Xie et al. carried out a study where they obtained removal rates as high as 84% of COD and 94% of hydrocarbons [68]. However, in many BAF studies removal efficiency is very variable, and results as low as 20-40% have been reported [69]. MBRs are a more sophisticated technology

where biofilm growth is supported by a permeable membrane through which oxygen is provided for aerobic growth. There are studies as early as 2007 using immersed ultrafiltration fibers to treat petrochemical wastewaters. In MBR removal rates are much improved from BAF, but the hydraulic retention time becomes much higher in compensation (Table 1-1). Bench-scale testing with refinery wastewater (195-590 mg/L COD) obtained stabilized rate of removal of COD in the range of 76–97% with a retention time of 24-36h [70,71]. Membrane-aerated biofilm reactors (MABR) can operate more consistently in the ideal aerobic conditions in which oil-degrading microorganisms can live. A study by Hu et al. in which produced water from an offshore platform was being treated with an MABR set-up, showed that at optimum conditions removal efficiencies of COD and oil, reached 60.3, and 80% respectively. They also found that this technology can be negatively affected by high amounts of suspended solids, that will become attached to biofilm and present a barrier for nutrient adsorption [72]. Li et al. carried out an MABR study with oily wastewater that found a similar efficiency in oil removal (85.7%) but a considerable difference in COD removal, which was as high as 82.3% [73]. Both studies treated wastewater streams with 380-480 mg/L COD and 10-30 mg/L of oil, it is unknown whether such technologies would be viable on more heavily contaminated wastewaters.

There are other less common configurations that use different principles such as the set-up described by Lu et. al where anoxic hydrolysis is followed by aerobic treatment of industrial wastewater. in both cases microorganisms are immobilized in a fixed film over a combined semi-soft medium constructed by plastic ring and synthetic fiber string [74].

2.3.4 Extraction

The solvent extraction of oily wastewater has usually been the go-to treatment option for oily sludge. Typically, it mixes the oil-water waste with a non-polar solvent which extracts the oil fraction, and the solvent-oil mixture is then sent for distillation to separate oil from solvent. Considering the relatively high oil content in sludge, oil recovery is often the most desirable management option: it will not only reduce pollutant concentration, but also generate profit from the value of the recovered oil. Furthermore, it is the best-known option for removing semi-volatile and non-volatile organic compounds from water matrices: phenols, creosols and other phenolic acids, as well as aromatics [75]. Examples of solvents used are carbon dioxide, ethane, propane, n-heptane, ethylene dichloride, toluene, xylene, diethyl ether, methyl ethyl ketone, LPG condensate, naphtha and kerosene cuts [76–78]. Unfortunately, these solvents tend to be either reactive, flammable or toxic in their own right. Solvent extraction is not an energy demanding process, being carried out at low temperature and pressure, but when the distillation used in the solvent recovery stage is accounted for it becomes so. The overall efficiency of solvent extraction, is not very high: 58.5% as reported by Ávila-Chávez et al. and 40% as reported by Hu et al. [76,79]. Zubaidy et al. found that their extraction yields could be much improved by closed system recirculation, obtaining yields of 82.6-90.0. The mixing time reported was 2h [77].

Unfortunately, although useful for recovery of valuable oil fractions, solvent extraction is not entirely apt for waste stream purification. In many cases the waste water fed to the system will be saturated with hydrocarbons and may even contain emulsified hydrocarbons. When a hydrocarbon solvent is used -which are those found most efficient and are also relatively soluble in water- it will only replace the original hydrocarbon pollutants and there will still be hydrocarbon contamination in the water stream [75]. New extraction-based technologies have emerged in the last years that can deal with these disadvantages. The C-Tour is a patented technology by PWA ProSep removes both dispersed oil and water-soluble organics using liquid condensate as extracting agent [80]. What the C-Tour process does is inject a volatile condensate steam from the production process in produced water, allowing contact time between condensate and water. The contaminants and injected condensate coalesce to form oil droplets. Then the process removes the contaminated condensate and recycles it back into the production steam. The pilot trials 2002-2003 showed that removal rates of PAHs and NPDs

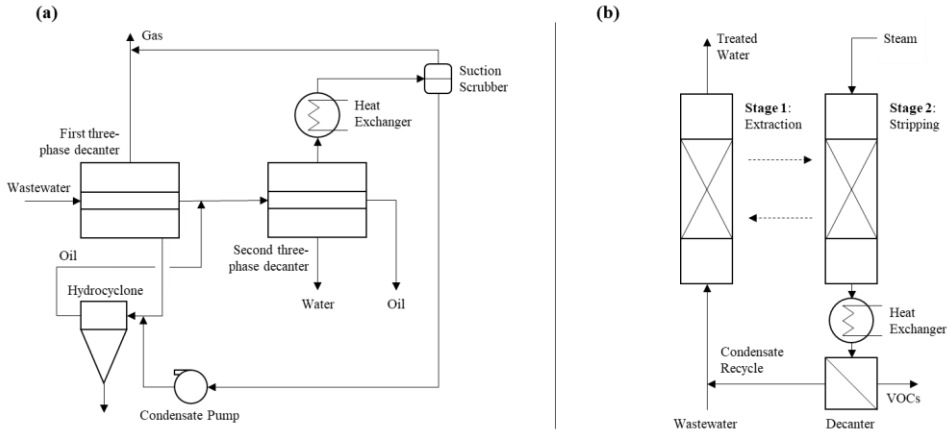

Figure 1-3. Scheme of a C-Tour (a) and a MPPE (b) system for oil-remediation [81,83].

was ~70%, for C6-C9 phenols ~60%, C4-C5 phenols ~55%, and for C0-C3 phenols there was no removal. For BTEX there was actually a negative removal effect due high content of these compounds in the untreated condensate [81].

The Macro-porous polymer extraction (MPPE) technology also manages to solve some classical problems of solvent extraction for oily wastewater treatment [82]. In MPPE systems hydrocarbon-contaminated water is passed through a column packed with MPPE particles. Such particles -typically 400-1000 μm diameter- are made of a porous polymer that encapsulates an extraction liquid. Once the extraction liquid has become saturated, the column is regenerated in situ with low pressure steam. The immobilized non-volatile extraction liquid is retained in the pores of the polymer, but the volatile hydrocarbons are removed. Continuous operation is achieved with the construction of a back-up column that operates while the first one is in operation [83]. MPPE performs very well in the removal of volatile aromatic hydrocarbons, mainly BTEX (> 95% removal). On the other hand, the average removal efficiency for dispersed aliphatic hydrocarbons was 50 wt%, and that of PAHs was 72% [82]

2.3.5 Membrane processes

Membrane technology makes use of a microporous film to physically separate molecules dissolved in water based on molecular size. Membranes can remove the smallest and most stable oil droplets from a water matrix (<10 μm in diameter) and are effective in the treating of stable oil emulsions. Membrane processes are generally cost-effective, have moderate footprint and avoid the use of toxic chemicals. It is not strange that there has been a lot of interest in achieving oil-water separation with membrane-based separation processes for a while, and an abundance of literature on the subject. There are four well-established types of membrane separation: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Of them, MF is typically used for suspended solids removal, UF for macromolecules removal, NF for selective ion removal, and RO for total ion removal. The fundamental limitation to the applicability and economic viability of membrane technology for the treatment of oily wastewater is the phenomenon of flux decline caused by organic fouling of the membrane active surface. Evidently membranes can be cleaned, but this often requires both downtime of the system and an inefficient use of additional chemicals and energy.

The reported rejection of hydrocarbons by RO and NF membranes is very good. Short-run type of experiments have historically shown that the rejection of hydrocarbons by cellulose acetate RO membranes can be as high

as 94.7%. The ability of membranes to reject hydrocarbons is directly related to their solubility: more soluble hydrocarbons have considerably lower rejections [84]. Sometimes, increased rejections can be observed due to the phenomenon of pore size reduction by fouling: the pore-blocking effect is caused by the adsorption of non-polar hydrocarbons onto the membrane surface pores. The issue of fouling is particularly severe in the case of NF and RO membranes, where the presence of hydrocarbons is the cause of severe fouling, flow decrease and increased pressure, even being the cause of membrane decay [11–13]. Mondal et al. studied the treatment of produced water with commercially-available polyamide RO (BW30) and NF membranes (NF270, NF90). Their results indicate that there was important fouling by organic compounds in the treatment of produced water. The NF270 membrane –which has the largest pore size, smoothest and most hydrophilic surface- suffered less from the reduction in permeate flux that characterizes membranes afflicted with organic fouling, but produced lower quality permeate [85].

Ultrafiltration is by far the best membrane technology for oil-removal: typically the rejection of hydrocarbons is better than in Microfiltration –in the range of 90-99%– and transmembrane pressure (TMP) is markedly lower than for Nanofiltration or Reverse Osmosis membranes [86]. However, ultrafiltration is not apt to deal with the small polar organic components that usually accompany hydrocarbons, leading to rejections of COD and TOC in the range of 50-80% [87–89]. Ultrafiltration membranes can be made of different materials, mainly polymers –such as PVDF, PAN and PVC– and ceramic materials –alumina, silicon carbide, titanium oxide, zirconia oxide, etc. Polymeric membranes are better-established in general, but for the implementation of UF in oil-removal systems it is one of the few niche applications where ceramic membranes enjoy a modicum of success. There is some evidence that ceramic membranes can sustain higher flux and the extent of fouling is much lesser than on polymeric systems [90]. Also, they have superior mechanical strength and greater chemical stability, which means that once fouling is present it is usually reversible and less economically draining. However, the total capital expenditure of ceramic membrane systems is considerable, mainly due to manufacturing costs of the membranes, and this has ensured that there is very little accumulated operational experience with this type of technology [91].

The way researchers have tried to get around the problematic of membrane fouling and low permeate flux in oil removal applications is through surface modification. Hu et al. modified alumina ceramic membranes coated with graphene to obtain a flux 27.8% higher, with greater long-term stability and higher oil rejection [92]. Similarly, Zhang et al. created a super-hydrophilic UF PAN membrane by devising a new strategy for membrane preparation that introduced an in-situ alkaline hydrolysis. The resulting membranes exhibited ultra-low oil adhesion, resulting in low fouling levels, a very high permeate flux and oil concentrations in the permeate lower than 10 mg/L [93]. However, surface-modified membranes are still an immature technology and no long-term piloting studies have taken place that validate their economic viability.

2.3.6 Media filtration and adsorption

Amongst tertiary and polishing technologies, adsorption has an important place. This technology is usually contemplated when facilities need to meet stringent limits for the discharge of some contaminants such as Chemical Oxygen Demand (COD), heavy metals and trace organics. In adsorption processes, wastewater is contacted with a solid material, where oil molecules are captured into the solid matrix –which is typically hydrophobic– and separated from the water stream. The process of adsorption presents several advantages in comparison to other processes: it is cost effective in terms of energy (operating at low pressures and temperatures), it has a generally small footprint, it is simple to operate, very efficient in the removal of emulsified and dissolved components of oil down to trace quantities and presents very high-water recoveries. There are disadvantages that limit the use of adsorption: adsorbents can be rapidly saturated at high feed concentrations and regeneration –or waste disposal– of spent media is a necessary consideration. Typically, industrial adsorption processes are carried out in a fixed bed system by granular adsorbents [18]. The selection

of the adsorbent material is important for the overall efficiency of the process: considerations such as pressure drop, surface area, recovery and replacement rate and cost must be accounted for.

A lot of recent research on oil-adsorbing materials has been done outside of the scope of direct wastewater treatment technologies, and with oil spill management applications in mind. The most exciting development have been the development of hydrogel adsorbent materials, with underwater oil adhesion properties. Chitosan-based hydrogels, supported by membranes or fibrous materials have been successfully developed that have been shown to adsorb crude oil at capacities higher than 1g/g [94,95]. These new hydrogel adsorbents have shown potential use for floating oil-spill clean-up, but do not yet have a clear industrial application.

The most commonly used adsorbent material used for the removal dissolved organics in the water treatment sector is granular activated carbon (GAC). GAC is a porous organic material that is extremely good in the adsorption of organic and nonpolar molecules. In accordance with a very large surface area (in the range of 200-1200 m^2/g), GAC adsorption capacities are usually very large: between 370 and 550 mg/g [96–98]. Activated carbon is usually applied as a 'polishing' step (removal of residual organics) for wastewater that has been processed first in a biological treatment system. This is because the use GAC will be prohibitively expensive if directly applied to the refinery wastewater [18]. The most prevalent method for the regeneration of GAC is high-temperature reactivation carried out in furnaces at temperatures of 1000-1100ºC in the presence of an inert gas [99]. Because of the expense of the involved equipment, regeneration of GAC must be subcontracted and carried out offsite. This is inconvenient and expensive for facilities that operate in remote places, especially offshore oil platforms. There are other methods for the regeneration of GAC, and each has some important drawbacks: the use of volatile organic solvents in extractive regeneration or the expense of reactive regeneration [100]. Often, GAC is disposed of after a single absorption cycle because it is cheaper to replace than to reactivate.

Other adsorbents typically cited for their large adsorption capacity for oil include organoclays. Carmody et al. reported adsorption capacities of 1.2-5.2 g/g for montmorillonite-based organo-clays modified with surfactants [101]. However, activated carbon has been found to outperform clay adsorbents by over an order of magnitude in terms of both adsorption capacity and costs [102]. Synthetic zeolites have also been studied in laboratory conditions for the adsorption of short-chain hydrocarbons with observed adsorption capacities as high as 1 g/g [103]. Janks & Cadena studied the removal of hydrocarbons with tailored zeolites –modified with ammonium salts– and found that removal depended largely on the type of modifying functional group. The tailored zeolites removed as little as 9.4% (monoethanolamine) of the total BTEX and as much as 85.2% (ethylenediamine). However, the expense of zeolites as an adsorbent have prevented further exploration in industrial set-ups. On the other hand, there is also a variety of plant-based materials that can be used as adsorbents. These adsorbents are attractive for several reasons, chief amongst them their affordability, which allows for them to be easily replaced. Walnut shell media is a classical adsorption media for oil contaminants, Srinivasan et al. found that oil viscosity affected the adsorption rate and total capacity, with adsorption capacities around 0.3-0.8 g/g. Additionally, simple compression is an economic and practical method used for oil recovery from spent adsorbent [104].

The use of synthetic polymeric adsorbents is another option for TOC and COD remediation in oily wastewaters. Like in the case of GAC, organoclays and zeolites, there is not an abundance of literature that directly uses industrial oily wastewaters, but there are a number of studies on the adsorption of independent hydrocarbons like BTEX and PAH [105–107], phenols [108,109], and organic acids [110]. This does not mean that adsorbents are not in use by the industry, merely that as a relatively-well established technology, rather than not many industrial piloting experiments have been published on the subject. In 1992, the Nalco Chemical Company patented the process of removing organics from produced water in the production of

crude oil by polymeric adsorbents, which were later regenerated using an organic solvent [111]. In 2002, Carvalho et al. evaluated several methacrylate (MA) and divinylbenzene (DVB) copolymers for produced water treatment with produced water and found that most DVB copolymers were adequate for the purpose of oil removal, yielding good quality of treated water. They also found that column efficiency was highly dependent on initial oil content, and that a combination of polymeric sorbent materials in the same column yielded improved results, and managed to deliver as little as 5.6 ppm of final TPH [112]. In 2018, another study was carried out on the removal of organic components from refinery wastewaters with ion-exchange resins. Their experiments indicated good removal efficiency, as the amount of TOC in treated wastewater was as good as has been reported in the literature for activated carbon, and regeneration efficiency of the spent resin ranged from 57 to 94%. Some recalcitrant organics showed low or no tendency to be retained in the column, while others showed great resistance to desorption. The service life of the resin was estimated up to be seven times higher than that of GAC when the latter is not regenerated. However, the adsorption capacity of the best resin tested, still showed an adsorptive capacity that was 55% lower than that of activated carbon [113]. This is offset by the fact that some polymeric adsorbents can maintain an excellent effluent quality at much higher flowrates than activated carbon [114].

Given the fouling of most adsorbents are prone to form insoluble oil -which includes emulsified oil- the most successful approach has been to remove as much of emulsified hydrocarbons from wastewater before treatment with an adsorbent, be it GAC or polymeric adsorbents. Frequently, this translates in the use of an hybrid system using both a filter coalescer and an adsorbent. A U.S. Patent from 1999 by Darlington & Yuchs describes the process of adsorption of water-immiscible and partially soluble oil components in produced water with an acid-activated clay modified with ammonium salts, followed by treatment with a macroreticular adsorbent resin [115]. In 2008, Zhou et al. performed a successful two-step treatment of a synthetic oil-in-water emulsion using a hybrid system of modified resin and activated carbon, which was capable of removing most of the oil from oily wastewater, resulting in higher than 90% reduction of oil content in the treated effluent [116]. Furthermore in 2017, Carmona et al. studied the effect of pre-treatment of petrochemical wastewater with oleophilic resin DuPont™ AmberLite™ ROC110 Oil-Coalescing Media, followed by treatment or residual TOC with macroporous polymeric adsorbent DuPont™ AmberSorb™ L493 Polymeric Adsorbent [49]. This preliminary study of combined resin technologies for oil removal showed that when both resins are used individually, only Ambersorb™ L493 was capable of achieving complete hydrocarbon removal, as well as the removal of the bulk of dissolved organics. However, they proposed that treating the wastewaters first with AmberLite™ ROC110 could eliminate a sizeable fraction of total hydrocarbon content, extending the loading cycle of AmberSorb™ L493.

Table 1-1. Various studies reporting oil removal through biological treatment.

Year	Scale	Process Technology	Feed Source & Characteristics	Oil Removal & Effluent Quality	Hydraulic Residence Time (HRT)	Ref.
2001	Bench	AS (Sequencing Batch Reactor)	Produced Water: 450 mg/L TOC, 2000 mg/L COD, 100 g/L O&G, 2.7 mg/L phenol, 52100 mg/L TDS, pH 7.2.	Removal is < 58% COD, and 77% phenol. An increase in salinity resulted in decreased removal (down to 40-48% COD).	22h, Settling Time for SS of 1.5h	[67]
2007	Bench	MBR (submerged flat sheet of chlorinated PE)	Wastewater from a petrochemical Complex (China): 720-1590 mg/L COD, 14-20 mg/L O&G, pH 7.6-8.2	Quality of MBR effluent met the requirements for discharge: 38-78 mg/L as COD and 1-4 mg/L of O&G.	13 – 19 h	[117]
2007	Bench	BAF (ceramic carriers)	Refinery wastewater (China): 20-140 mg/L COD, 1-10 mg/L TPH, 70-160 mg/L TDS	Removal is 84% COD and 94% TPH. The air-water ratio must be > 5:1, otherwise aerobic digestion is inefficient.	0.5-3h, optimal HRT was 1.0h	[68]
2008	Pilot	AS	Refinery WW (Iran), 200-800 mg/L COD, 13-43 mg/L TPH, mainly n-alkanes, aromatic VOC and PAH.	90-150 mg/L COD and 5-15 mg/L TPH in effluent. Maximum 80-89% removal, with fluctuations ranging 59-80% due to dynamic changes.	-	[66]
2009	Pilot	Anoxic hydrolysis–aerobic treatment (uses plastic fiber carriers)	Produced Water from an Oil Production Plant (China): 46530 mg/L TDS, 84 mg/L TOC, 345 mg/L TOC, pH 5.8, T = 52ºC.	65% COD removal after 60 days (~120 mg/L effluent COD). Requires adding nutrients to the system, and direct sunlight avoided to avoid the growth of competing cyanobacteria. TPH removal is 30-50%.	32 h	[74]
2009	Bench	AS (open oxidation pond)	Synthetic: Saline solution mixed with surfactant and crude oil, 400-500 µL/L O&G and 1050-1350 mg/L COD.	Effluent in the effluent were < 250 mg/L COD (min. removal of 76%) and < 70 mg/L O&G (removal was > 85%).	6 days (8 days with evaporation)	[118]
2010	Bench	AS (Sequencing Batch Reactor)	Synthetic: 35-250 g/L TDS, 175-350 mg/L O&G (crude oil), 1125-4500 mg/L COD, pH 7. Produced water: 1240 mg/L COD, 15 mg/L O&G, 540 mg/L TOC, 16400 mg/L TDS, pH 8.2.	91-98% COD removal. Highest removal achieved at higher inlet concentrations after 20 days of operation. Removal decreased with increased salinity. Real produced water had 81% COD removal.	21h	[119]
2012	Pilot	MBR (UF, PVDF, Hollow Fiber Support)	Refinery wastewater: 200-700 mg/L COD, 400-700 mg/L TN	45-100 mg/L COD in the permeate due to recalcitrant components.	2.1 – 8.6 h	[120]
2013	Bench	AS	Refinery wastewater (Portugal): 14-291 mg/L O&G, 109-373 mg/L COD, 0.09-0.64 mg/L phenols, pH 6-7	Removal of 95% COD and 87% TOC with biomass recycle, and 94% COD and 85% TOC without.	> 20h for high removal rates..	[121]
2013	Bench	MBR (immersed flat sheet MF, PE)	Synthetic produced water: 312-936 mg/L crude oil, 600-1800 mg/L COD, 115-346 mg/L O&G.	83.2-83.6% COD and 89.2-95.5% O&G removal in steady state	48h (Sludge HRT of 80 days)	[122]
2015	Pilot	Anaerobic digestion	Petrochemical & industrial wastewater mixture of different origin: 348-529 mg/L COD, 30-35 mg/L TN, 380-552 mg/L sulfate, pH 7.5.	Removal is 72-79% COD (97-109 mg/L COD in the effluent). Benzene, ketone, ethanol, esters, amides, nitriles and phenols are completely eliminated in the effluent.	20h (Sludge HRT of 30 days)	[123]
2015	Pilot	MBR (Immersed UF, PP Hollow Fiber Support)	Wastewater from a refinery water treatment plant: 580 mg/L COD, 2100 mg/L TDS, pH 7.6.	Removal is 77-81% COD (100 mg/L COD in the effluent).	25 – 36 h	[70]
2016	Pilot	BAF (Volcanic Rock carrier)	Industrial wastewater: 60 to 120 mg/L COD, 13.6 mg/L TN, pH 6.9-7.8, 27ºC.	Median removal is 29.35% COD (maximum removal is 40% COD). Removal of various sVOC is 30-63%.	Constant at 3h	[69]
2016	Pilot	MBR (UF, Hollow Fiber Support)	Synthetic: 20 g/L NaCl, 20 mg/L TPH (diesel fuel C10-C30), 350 mg/L COD.	Average removal is ~90% COD, and 88% TPH. Removal worsens at higher salinity. Rapid Fouling and degradation of the membrane	Constant at 16h	[124]
2017	Bench	BAF (GAC carrier)	Produced water & fracturing flowback: 770-6360 mg/L COD, pH 6-7, 10 – 15 g/L TDS	Removal is 79.9-94.3% COD. Aeration and high feed concentrations improve performance.	40-70h.	[125]
2019	Bench	Anaerobic reactor	Wastewater form a storage tank in an oil recovery facility: 36 g/L COD diluted to 10-20 g/L COD with tap water	COD removal was 60-80%. Higher removal for short-chain (<C12) aliphatic hydrocarbons (50-74%) and some small ring (<C10) aromatics.	> 30 days	[126]
2019	Bench	MBR (Commercial UF, flat sheet PVDF)	Refinery wastewater, API effluent: 195-520 mg/L COD, 3-15 mg/L NH_3, pH 6-8	Removal was 94-97% COD (36 mg/l COD in the effluent) with HRT = 24h, at HRT = 12h removal was only 74% COD.	16-24 h	[71]

Table 1-2. Various studies reporting oil removal by membrane separation technologies.

Year	Scale	Membrane Type & Material	Feed Source & Characteristics	Oil Rejection & Effluent Quality	Stabilized Flux	Transmembrane Pressure (TMP)	Fouling	Ref.
1991	Pilot	Crossflow MF, Ceramic (0.2 and 0.5 µm pores)	PW: 150,000-200,000 mg/L TDS, 27-283 mg/L O&G, pH 6-7	2 – 8.8 mg/L O&G	500-1200 l/(m^2·h)	Stable operation at 0.8 bar approx.	Stable operation with pre-treatment only (0.5 µm)	[127]
1996	Pilot	Tubular UF, PVDF (inside diameter 12.5 mm and 6mm)	North Sea PW: 50 mg/L TPH, 60ºC	Rejection of 96%TPH (2 mg/l in permeate). BTEX reduced by 54%.	150-598 l/(m^2·h)	6-10 bar	Less fouling favored at high crossflow velocity	[87]
2006	Bench	Tubular UF, PVDF modified with nano-sized alumina particles	Daqing Oilfield WW: 637 mg/L COD, 214 mg/L TOC, 15.5 mg/L TPH	Rejection of 90.14 % COD, 98.73% TOC, 98.04% TPH	150-170 l/(m^2·h)	1 bar	Flux decline of 11% in 4h,	[128]
2008	Bench	Flatsheet NF / RO, commercial Polyamide	Colorado PW: pH 8.5, 722-2000 mg/L TDS, 47.7-136.4 mg/LTOC	Removal of 28-34% TOC (NF) and 66% TOC (RO).	2 – 5 l/(m^2·h) (RO) 20 – 80 l/(m^2·h) (NF)	1.4 to 7 bar	Not reported	[85]
2010	Bench	Flatsheet MF / UF, commercial PSU & PAN	Synthetic: 100 mg/L TPH Ind. WW: 78 mg/L TPH	66.3-95.0% (MF) 97.2-99.7% (UF)	50 – 150 l/(m^2·h)	3 bar	50-80% Flux Decline (6h),	[86]
2015	Bench & Pilot	Tubular UF, Ceramic (Zirconia oxide)	Synthetic: 100 mg/L oil, 90-113 mg/L TOC, pH 6-7	< 1 mg/L oil in permeate	217 l/(m^2·h) (stabilized)	2 bar	BW every 30 min. Low irreversible fouling (17% flow loss)	[129]
2016	Pilot	Tubular UF, Ceramic + Crossflow NF, Polyamide	Refinery wastewater: 2000 mg/L COD, 310-470 mg/L O&G, pH 9.5	100% removal of non-polar oil, 30-60% removal of polar oil in UF.	175-240 l/(m^2·h) depending on feed sample	1-3 bar	50% decrease in flux the first 6h, before values stabilized.	[88]
2016	Bench	Tubular MF / UF, Ceramic (SiC & TiO_2)	Arabian Gulf PW after DAF: 37-56 mg/L O&G	73-86% as O&G	180 l/(m^2·h),	0.2 to 0.6 bar	40-64% Flux Decline (6h),	[130]
2017	Bench	Flatsheet MF, Ceramic	Synthetic: 100-250 mg/L TPH	75.12-95.47% as TPH	36 l/(m^2·h),	1.37 to 3.44 bar	50-70% Flux Decline (40min),	[131]
2017	Bench	Flatsheet UF, PSU	Synthetic:100-400 mg/L oil, pH 8, 10-30 mg/L TDS	79-97.25% as TPH	15 l/(m^2·h),	1 to 4 bar	25-40% Flux Decline (30min),	[132]
2018	Pilot	Submerged UF, PVDF + RO, Polyamide	Flowback produced water: 530 mg/L, 18,900 mg/LS TDS, pH 7.6, 49.8 NTU.	Removal of COD is 8.8%, and turbidity is 99.6% by UF. COD in the RO effluent 10.9 mg/L.	20-35 l/(m^2·h), operation >35 l/(m^2·h) was not stable	up to 0.7 bar	UF fouling is low at 20-35 l/(m^2·h), rapid TMP increase >50 l/(m^2·h)	[89]
2018	Pilot	Tubular MF, Ceramic / Spiral UF, PVC + Hollow fiber UF, PAN / Spiral RO, polyamide	Petrochemical wastewater, API effluent: 26-199 mg/L O&G, 124-436 mg/L COD, 81-292 mg/L TOC	Rejection of TOC 70-95.7% (MF), 5.2-32% (UF, PVC), 16.7-50.7% (TOC), 88.2-93.7% (RO)	462 l/(m^2·h) (MF) 165 l/(m^2·h) (UF, PVC), 111 l/(m^2·h) UF (PAN), 66.9 l/(m^2·h) (RO)	2.5 bar (MF) 2 bar (UF) 15 bar (RO)	Long-term steady flux of MF was only 48% of initial value after 24h.	[133]
2019	Pilot	Tubular MF, Ceramic (alumina with 0.1, 0.2 and 0.4 µm pores)	Synthetic: 650-1000 mg/l commercial vegetable oil.	Rejection of 84.3-95.5%, higher at low flow rates, smaller pore diameter and higher feed concentration.	429 lmh (650 ppm), 406 lmh (800 ppm), 378 lmh (1000 ppm) with 0.4 µm pores	2 bar	Decrease in flux at high oncentrations of oil and small pore diameters.	[134]

Table 1-3. Summary of technologies used in oily wastewater remediation.

Stage	Technology	Removal mechanism	Oil droplet size (μm)	Average effluent concentration (mg/L)	Advantages	Disadvantages	Ref.
Primary Treatment	API Separator	Gravity	>150	50 – 200	(1) Simple and robust technology (2) Low energy requirements (3) Effective bulk oil and TSS removal	(1) Inefficient emulsified oil treatment (2) Very large footprint (3) Large residence times (45-60 min)	[19–21]
	Corrugated Plate Interceptor (CPI)	Gravity, Coalescence	40 – 150	25 – 100	(1) Simple and robust technology (2) Low energy requirements (3) Effective bulk oil and TSS removal (4) Lower footprint than API separator	(1) Inefficient with fine oil droplets (2) Very large footprint (3) Large residence times (30 min)	[21]
Secondary Treatment	Induced Air Flotation (IAF)	Flotation	25 – 100	10 – 40	(1) Efficient removal of small droplets (2) Low retention time (< 5min) (3) Compact: low footprint (4) Low capital costs	(1) High maintenance costs (2) Large requirement of air (3) Generation of an air waste stream (4) Requires use of chemicals	[25–27]
	Dissolved Air Flotation (DAF)	Flotation	25 – 100	10 – 30	(1) Efficient removal of small droplets (2) Robust technology, no moving parts (3) Low maintenance costs	(1) Higher residence time (5-15 min) (2) Large footprint and capital costs (2) Large requirement of air (3) Generation of an air waste stream	
	Centrifuges	Centrifugal force	> 2	5 – 25	(1) Efficient removal of small droplets (2) Lower retention time	(1) High energy requirements (2) High maintenance costs	[39,40]
	Hydrocyclones	Centrifugal force	> 10 – 15	20 – 30	(1) Efficient removal of small droplets (2) Lower retention time (3) Low footprint	(1) High energy requirements (2) No separation of solids (3) High maintenance costs	
	Coagulation/ Flocculation	Alteration of inter-particle repulsions	3 – 5	depends on influent (95 – 99% removal)	(1) Greater removal is achieved (2) Breaking of stable emulsions (3) Low retention times (4) Partial removal of dissolved oil	(1) High chemical consumption (2) Costly (3) Downstream effects and secondary pollution of effluent	[28–31]
	Electrocoagulation	Alteration of inter-particle repulsions	3 – 5	1 – 5	(1) Removal of emulsified oil and dissolved oil. (2) Simple equipment. (3) Easy automation. (4) Very short retention times (2-5 min)	(1) Costly operation (2) High energy consumption (3) Costly equipment	[33–38]
	Filter Coalescers	Coalescence	> 5	5 – 10	(1) Cost-effective (2) No pre-treatment required (3) Low sensitivity to bed depth	(1) SS loading and clogging (2) Variable efficiency depending on influent water	[41–50]

Table 1-3. Summary of technologies used in oily wastewater remediation (continuation).

Tertiary Treatment	Air Stripping	Air-liquid mass transfer	-	0.1 – 0.2 (VOCs) (84 – 99% removal)	(1) Efficient removal of VOCs. (2) Cost-effective (3) Recovery of hydrocarbons	(1) No removal of non-volatile species (2) Sensitive to TSS, requires pre-treatment	[51–53]
	Conventional chemical oxidation	Chemical oxidation	-	Depends on type of oxidant used	(1) Low capital costs (2) No pretreatment required (3) Removal of non-biodegradable compounds	(1) Cost of operation can be high (2) Use of hazardous chemicals (3) Incomplete organic removal, high effluent COD	[54,55]
	Catalytic Wet-Air Oxidation (CWAO)	Chemical oxidation	-	1-50 mg/L COD	(1) Complete oxidation to CO_2. (2) Removal of recalcitrant compounds.	(1) High Energy Costs (2) Harsh Operating Conditions.	[56–58]
	Photo-catalytic oxidation	Chemical oxidation	-	> 20 – 100	(1) Very high removal rates (2) Very low residual organics	(1) High capital costs (2) High energy consumption (3) Cost of reagents	[59,60]
	Activated Sludge System (ASS)	Biological treatment	~ 2	1 – 15	(1) Can deal with the soluble oil fraction (2) Environmentally friendly	(1) Large footprint (3) Deals poorly with process upsets (3) Finding a compatible microbial strain (4) Cannot deal with high organic loads	[63–66]
	Biological Aerated Filters (BAF)	Biological treatment	~ 2	< 1 mg/L TPH and 10-80 mg/L TOC	(1) Can deal with the soluble oil fraction (2) Environmentally friendly (3) Smaller footprint	(1) COD removal is limited (2) Deals poorly with process upsets (3) Cannot deal with high organic loads	[68,69]
	Membrane Bio-reactor (MBR)	Biological treatment	~ 2	1 – 4	(1) Can deal with the soluble oil fraction (2) Environmentally friendly (3) High COD removal	(1) Large footprint (2) Deals poorly with process upsets (3) Cannot deal with high organic loads	[70,117]
	Solvent Extraction	Extraction	-	Depends on solvent and initial composition	(1) Capable of removing soluble oil (2) Low energy requirements (3) Simple operation/design	(1) Handling of hazardous solvents (2) Solvent regeneration is energy-intensive	[75–79]
	C-Tour	Extraction	-	10 – 14 mg/L (70% removal)	(1) High energy demands. (2) Allows oil recycling into the process.	(1) Poor removal of volatile fraction. (2) Poor removal of dissolved organics.	[80,81]
	MPPE	Extraction	0.1-10	0.1 – 8	(1) Recovery of hydrocarbons (2) In-situ regeneration (3) Can be fully automated	(1) Not efficient with heavy oil fractions (2) Requires regeneration (3) Requires specific pre-treatment	[82,83]
	Media Adsorption	Adsorption	0 - 2	0.1 – 10	(1) Small footprint (2) Cost-effective (3) Efficient removal of emulsified, and dissolved oil (4) High water recovery (~100%)	(1) High retention times (2) Rapidly saturated at high feed concentrations (3) Waste disposal for media or regeneration of spent media is necessary.	[96–98,111–113]
	Ultrafiltration	Membrane filtration	> 1 (> 0.01)	10	(1) Compact module design (2) Removal of low molecular organics in dissolved oil / trace oil	(1) High energy requirements (2) Membrane fouling (3) Chemicals required for cleaning	[86,87,128]

Chapter 2

Study of the chemical composition of hydrocarbon-contaminated industrial wastewaters

The Author of this document, Maria dels Àngels Tejero, is fully responsible for the information included in it. Even though part or the whole work here presented might have been completed in one of the DuPont de Nemours Company ("hereinafter "DuPont") facilities, the content of this document is based on the opinion of the Author. Nothing stated herein is DuPont's opinion and DuPont has not offered to take responsibility for it.

1. Review of the composition of oily wastewaters

The composition of oily wastewater is very complex. In an industrial context, the oil present in oily water –excluding the food industry– refers to petroleum-based hydrocarbons. This is a very broad definition that can include a wide variety of substances such as crude oil, gasoline, diesel fuel, motor oil, lubricating and hydraulic oil. As petroleum and petroleum-derived products are complex mixtures of hydrocarbons, their composition varies considerably depending on the source of the petroleum and the refining process.

Water that has been in contact with crude or refined oil will carry significant amounts of petroleum hydrocarbons. Depending on the characteristics of the mixture of oil-in-water, these oily substances will appear as *free*, *emulsified* or *dissolved* oil. What is known as free oil presents as large oil droplets of over 150 μm, and emulsified –also named dispersed– oil appears as small droplets in the range of 0.5-150 μm suspended inside the aqueous phase. Dissolved oil is comprised of polar constituents of oil that have dissolved into water within their limits of solubility. As not all hydrocarbons show equal affinity to water, some will be found in significant amounts and some only in trace quantities. Dissolved oil is usually comprised of smaller hydrocarbons that usually include benzene, toluene, ethylbenzene and xylene (BTEX), small polycyclic aromatic hydrocarbons (PAHs) and phenols [135]. It is generally accepted that oily waters will have simultaneously important quantities of emulsified and dissolved oil, and any given sample of oily wastewater may contain more than a hundred different organic species.

1.1 Standard industrial characterization

The incredible chemical complexity of oil makes it very difficult to measure the presence of non-polar organics in water on a case-by-case basis for routine analysis. The prevalent practice in the industrial sector is to characterize oily waters by quantifying their organic content in the form of Oil & Grease (O&G). Oil & Grease measurements have been named –for reasons that will soon become evident– as “the most method-defined of all method-defined parameters” [136]. This is because, although it is relatively easy to gain an acceptable intuitive understanding of what is meant by “oil and grease”, it is hard to come up with a solid scientific definition.

Additionally, there is some confusion about the terminology used to refer to O&G measurements, which changes according to the industry sector and the specific method used. In oil-drilling platforms and the wider petrochemical industry, these measurements are known as TOG (Total Oil and Grease), whereas in water treatment plants or the food industry the preferred term is FOG (Fats, Oil and Grease). The caveat is that TOG and FOG measurements will account not only for organic compounds originating from petroleum but also polar organics of animal and vegetable origin. If polar organics have been removed from the sample through the use of silica gel, the measurement is then known as TPH (Total Petroleum Hydrocarbons). In the case of waters originating from the petroleum industry, TOG and TPH can generally be considered equivalent measurements as the presence of fatty acids of biological origin is rare. In another twist, the method defined by the US EPA (Method 1664-B) uses its own terminology and refers to TOG as HEM (N-Hexane Extractable Material) and non-polar material as HEM-SGT (Silica Gel Treated N-Hexane Extractable Material) [137].

As a general overview, the determination of O&G is carried out in two steps: sample preparation and analysis. Sample preparation is achieved by extracting the organic compounds –ideally just oil and grease, but in practice anything that has an affinity for the extracting medium– from an acidified aliquot of the sample stream. The analysis is carried out with an appropriate technique, usually gravimetry, Infrared Spectroscopy (IR) or Gas Chromatography with Flame Ionization Detector (GC-FID). However, it is important to remember, O&G measurements only provide a one-number gross value of non-polar organic compounds susceptible to be extracted from the sample, without identification of its individual constituents. The

information obtained by this type of measurements is pretty non-specific and will be highly dependent on the analytical method used, of which there are more than a few (Table 2-1).

Even though such methods are often used for routine control and screening purposes, they can turn out to be inadequate even for that task. It is important to acknowledge their inbuilt weaknesses. TOG and TPH measurement have the tendency to produce false negatives and severely underestimating the extent of petroleum hydrocarbons present in a water sample, producing generally misleading data. High values of O&G will reliably indicate the presence of hydrocarbons in a sample, but low or undetectable values do not indicate that hydrocarbon contamination is not present. This is mainly because, as a purely empirical measurement, it is highly dependent on sample medium and adequate calibration. Medium interference can be caused by the presence of compounds in the sample that block the extraction of petroleum hydrocarbons by another hydrocarbon, such as sulfur and phthalate compounds. The problem of inadequate calibration is more insidious and far-reaching. If the nature of the calibration standards and the hydrocarbon sample are very different, the results obtained will not be an accurate reflection of hydrocarbon content. Usually, the specific nature of the hydrocarbons present in a sample is unknown. Adequate standards are difficult to select, and it becomes easy to obtain erroneous data that is difficult to validate. In the end, the method used to measure TOG and TPH is only as good as the calibration standard used [138].

There are also other considerations in O&G measurements that are more specifically method-related. Some crude oils will contain material that is not soluble in a specific solvent, leading to artificially low recoveries because the method will detect only a fraction of the petroleum organics present. Gravimetric methods are particularly inadequate for the measurement of light hydrocarbons (hydrocarbons that volatilize at $T < 70^{o}C$), and therefore inadequate to evaluate contamination caused by gasoline and fuel oil. IR Spectroscopy-based methods do not share this deficiency and have been proved adequate to the detection of contamination by gasoline fractions. Before 1990, most methods for O&G determination with IR Spectroscopy used 1,1,2-trichloro-1,2,2-trifluoroethane as extraction solvent (also known as trichlorotrifluoroethane, fluorocarbon 113, Freon 113, FC-113 or CFC-113). It was a particularly convenient solvent for this purpose as it presents no C-H bonds, so it does not interfere with readings of the CH_3-and -CH_2- bands that are used for quantification purposes. However, the Montreal Protocol of 1995 banned the production/import/export of hydrochlorofluorocarbons as "Class II" ozone-depleting substances (ODS) starting in 2003. This prompted the gradual withdrawal of methods using fluorocarbon 113 by standards organizations such as the US EPA (EPA Method 413.1, 413.2 and 418.1) and the ASTM (ASTM D3921-96). Currently, the only method approved for testing oil and grease in wastewater in the US is US EPA Method 1664B, that uses n-hexane as the extraction solvent. However, as it is a gravimetric method, it presents all the disadvantages typical of such methods. When it is desirable to measure n-hexane or other components with a boiling range near or below the boiling point of n-hexane, the US EPA recommends the use of ASTM International Method D7066-04, which uses a dimer/trimer of chlorotrifluoroethylene (S-316) as extracting solvent. Since then, methods have been developed that carry out analysis through GC-FID, mainly ISO 9377-2:2000 and OSPAR 2005-15. However, these methods are incapable of providing a true "total petroleum hydrocarbon" value, as inevitably the fractions that are too volatile and too non-volatile will be lost at the beginning and the end of the chromatograph, falling outside the integration borders established by the standard [139].

Table 2-1 Summary of Test Methods for Determination of Oil & Grease in water samples.

Method	Analyte	Range	Preparation Method	Analytical Method	Year	Status	Ref.
EPA Method 413.1	TOG	5-1000 mg/L	LLE (with fluorocarbon 113)	Gravimetric	1978	Withdrawn (2007)	[140]
EPA Method 413.2	TOG	0.2-1000 mg/L	LLE (with fluorocarbon 113)	IR Spectroscopy	1978	Withdrawn (2007)	[141]
EPA Method 418.1	TPH	>1 mg/L	LLE (with fluorocarbon 113) and treatment with silica gel	IR Spectroscopy	1978	Withdrawn (2007)	[142]
ASTM D3921-96	TOG	0.5-100 mg/L	LLE (with fluorocarbon 113)	IR Spectroscopy	1980	Withdrawn (2013)	[143]
EPA Method 1664B	HEM SGT-HEM	5-1000 mg/L	LLE (with n-hexane) and treatment with silica gel	Gravimetric	1999	Current	[137]
Standard Method 5520B	TOG	> 1.4 mg/L	LLE (with n-hexane)	Gravimetric	1999	Current	[144]
Standard Method 5520C	TOG	> 0.2 mg/L	LLE (with fluorocarbon 113)	IR Spectroscopy	1999	Current	
Standard Method 5520D	TOG	> 0.2 mg/L	Soxhlet Extraction (with n-hexane)	Gravimetric	1999	Current	
Standard Method 5520F	TPH	1.4-1000 mg/L	LLE (as in 5520B or 5520C) and treatment with silica gel	Gravimetric or IR Spectroscopy	1999	Current	
ISO 9377-2:2000	Hydrocarbon Oil Index	0.1-100 mg/L	LLE (hydrocarbon solvent, boiling Point between 36ºC and 69ºC) and treatment with Florisil	GC-FID	2000	Current	[145]
ASTM D7066-04	TOG TPH	5-100 mg/L	LLE (with S-316, a dimer/trimer of chlorotrifluoroethylene) and treatment with silica gel	IR Spectroscopy	2004	Current	[146]
OSPAR 2005-15	Hydrocarbon Oil Index	0.1-100 mg/L	LLE (with n-pentane)	GC-FID	2005	Current	[147]
ASTM D7575-11	TOG	5-200 mg/L	SPE (with a membrane disc)	IR Spectroscopy	2010	Current	[148]
ASTM D7678-17	TOG TPH	0.1-1000 mg/L	LLE (with cyclohexane or cyclopentane) and treatment with Florisil	Mid-IR Laser Spectroscopy	2011	Current	[149]

Considering all of the above, it is very common to supplement measurements of O&G with other analytical techniques for the quantification of organic material in water as a general indicator of water quality. Usually, this is done by carrying out measurements of TOC and COD. TOC (Total Organic Carbon) analysis, which is determined by the quantity of carbon dioxide generated by the oxidation of organic matter can be used to determine the general presence of organic compounds. This is also the case of Chemical Oxygen Demand (COD), which is a measurement of the oxygen required to oxidize soluble and particulate organic matter in water. These measurements are more reliable when it comes to calibration and method bias. However, they are even more non-specific than O&G measurements and will measure petroleum-based hydrocarbons alongside not only other non-polar compounds but NOM (Natural Organic Matter) [150].

O&G, TOC and COD measurements yield a gross bulk index value, which is useful for routine monitoring, but oftentimes insufficient in cases where differentiating between organic species is desired. In the context of wastewater treatment, it is the inability to differentiate even within broad families of organics that presents the biggest hurdle for the development of oil-removal technologies.

1.2 Speciation of oily water

1.2.1 Produced water

The abundance of literature concerning the species present in oily wastewater changes greatly depending on the wastewater source. The best-characterized form of oily wastewater is *produced water*. During the decade of 1990, the focus of legislators changed from a regulation based mainly on dispersed oil measurements only, to a more risk-based regulation aimed at reducing the discharge environmentally harmful waste. This is particularly true of the regulations governing the discharge of produced water in the North Sea, particularly Norway. Therefore, important efforts have been made in the characterization of *produced water* in the last 20 years.

Produced water is largely a naturally-occurring form of oily water, but its chemical properties can show very large variations depending on the geological age and geochemistry of the deposit rock formations, as well as the chemical composition of the oil and gas phases of the reservoir. It will also be impacted by production chemicals –specialty additives– introduced in order to aid recovery, protect the system from corrosion, prevent bacterial growth and inhibit scale formation [151]. However, cross-examination of existing studies shows that overall patterns of the composition are very similar from oil-field to oil-field and that the most significant differences are quantitative. As a relevant example, the TOC of produced water can range from less than 0.1 to more than 11,000 mg/L, although typical values will more often oscillate between 67-600 mg/L [4,152].

In produced water, the contribution of dispersed oil to O&G, TOC, and COD measurements is very large. The amounts of dispersed oil will vary depending on several factors that include the density of oil, the shear history of oil droplets and the interfacial tension of water and oil. In cases where the oil density is not significantly different from water, there will be little driving force for the coalescence of oil droplets and significant emulsion will be present. Shear forces, high velocity or pressure, will result in small-sized oil droplets easily stabilized by low interfacial tensions. The addition of surfactants can also result in large amounts of dispersed oil in produced water.

However, even though large amounts of TOC in produced water are often due to the presence of dispersed oil, most of the environmental impact is caused by its dissolved components. The dissolved oil fraction is dominated by aromatic hydrocarbons [153]. Although saturated aliphatic hydrocarbons are majority components of free and dispersed oil, they are only a minuscule fraction of soluble oil. Because of their high molecular weight and low solubility they are always present in very low concentrations in produced water [151]. Røe-Utvik and Rytter-Hasle identified several groups of organics –based on physicochemical and

biological properties– that are representative of the main organic contaminants of produced water: BTEX (benzene, toluene, ethylbenzene and xylene), NPD (naphthalenes, phenanthrenes and dibenzothiophenes), PAH (Polycyclic Aromatic Hydrocarbons), aliphatic hydrocarbons, alkylated phenols and organic acids [154,155]. Table 2-2 shows the concentration range of each group according to different studies.

Table 2-2. Concentration ranges (mg/L) of naturally-occurring organic chemicals in produced water.

Dispersed Oil	BTEX	NPD	PAH	Phenols	Organic Acids	Ref.
3 - 30	20 - 40	n.a.	n.a.	2	900-1000	[4]
n.a.	1.70 - 35.65	0.13 - 1.18	0.007 - 0.108	0.1 - 21.5	n.a.	[153]
n.a.	2.4 - 9.0	0.93 - 1.60	0.13 - 0.52	0.1 - 42.5	688 - 1135	[154]
10 - 40	1 - 40	0.9 - 10	0.01 - 0.13	0.37 - 18.1	55 - 760	[155]
17 - 30	0.068 - 578	n.a.	0.04 - 3.0	0.4 - 23	0.001 – 10.000	[156]
17.3 - 24.9	8.35 - 8.90	1.02 - 1.03	1.12 - 1.15	3.65 - 4.21	n.a.	[157]
n.a.	2.4 - 27.5	0 - 2.3	0 - 0.127	n.a.	n.a.	[158]

n.a. = no data available

The most abundant form of hydrocarbons in produced water are the low-molecular-weight, high-volatility, semi-soluble one-ring aromatic hydrocarbons: benzene, toluene, ethylbenzene and xylenes (BTEX). The extreme volatility of BTEX can cause these components to quickly reduce in concentration over time, and they are susceptible to bio-degradation if properly aerated. Nonetheless, depending on the conditions of underwater discharge, they can remain in solution for a long time and be transported rather long distances, having a great impact on aquatic environments [156]. Benzene is normally the most abundant of all BTEX components. With increasing alkylation, concentrations decrease due to decreasing solubility in water [159]. In addition to showing the highest concentration, benzene –a human carcinogen– is the compound that persists for longer in the environment. If we look at permissible levels for chemical contaminants in drinking water in public water systems as supplied by the US EPA –the Maximum Contaminant Levels or MCLs– more than 91% concentrations reported by oil-well operators exceed drinking water maximum levels for BTEX, usually benzene and toluene [158]. MCL values are currently 0.005 mg/L for benzene, 1 mg/L for toluene, 0.7 for ethylbenzene and 10 mg/L for xylenes [160].

Polycyclic Aromatic Hydrocarbons (PAH) are semi-volatile hydrocarbons containing two or more fused aromatic rings. These compounds are of the highest environmental concern because of their toxicity and persistence in marine environments. PAHs are a major component found in O&G measurements, however, the majority are present mainly in dispersed droplets. Only 5-10% of PAH in produced water pertains to the dissolved fraction. Like BTEX, the most abundant species are typically the more water-soluble species with and 2-3 rings: naphthalene, fluorene, phenanthrene, and their alkylated derivatives. The compounds that fall under the label of NPDs (naphthalene, phenanthrene, and dibenzothiophenes) are the smallest forms of PAH, and are usually grouped together for reporting convenience. PAH concentrations are orders of magnitude lower than BTEX, usually in the parts per billion range (μg/L). Concentrations of total PAHs typically range between 0.04 and 3 mg/L, while the drinking water MCLs establish the limit at 0.2 μg/L of total PAH [156].

Other families of organics –phenols and organic acids– are often ignored by standard industrial analysis practices. Not typically classed as hydrocarbons, these organics contribute to TOC and DQO measurements, but not always to O&G measurements. This is problematic because they can also have a large environmental impact, particularly phenols.

Table 2-3. Concentrations, and physicochemical properties of common produced water contaminants.

Family	Compound	Chemical Formula	MW (g/mol)	Solubility in water @ 25ºC (mg/L) [159]	Concentration in Produced Water (µg/L)	Reference
BTEX	Benzene	C_6H_6	78.12	1,785	440 – 4500	[154,156,161]
	Toluene	C_7H_8	92.15	553	340 – 3500	
	Ethylbenzene	C_8H_{10}	106.18	179	26 – 600	
	Xylenes	C_6H_{10}	106.18	146	160 – 720	
PAH	Naphthalene	$C_{10}H_8$	128.17	31.65	5.3 – 2300	[156,158,161]
	Acenaphthene	$C_{12}H_{10}$	154.21	3.70	0.1 – 29	
	Fluorene	$C_{13}H_{10}$	166.22	1.97	0.06 – 510	
	Anthracene	$C_{14}H_{10}$	178.23	0.07	n.d. – 29	
	Phenanthrene	$C_{14}H_{10}$	178.23	1.08	0.11 – 1200	
	Fluoranthene	$C_{16}H_{10}$	202.26	0.26	0.01 – 35	
Phenols	Phenol	C_6H_6O	94.11	84,050	0.58 – 20,228	[155,162]
	C_1-alkylphenols	C_7H_8O	108.1	15,360 – 32,440	0.06 – 13,740	
	C_2-alkylphenols	$C_8H_{10}O$	122.17	2,849 – 8,796	0.41 – 1,098	
	C_3-alkylphenols	$C_9H_{12}O$	136.20	666.2 – 2,315	0.06 - 221.3	
	C_4-alkylphenols	$C_{10}H_{14}O$	150.22	399.9 – 1,250	0.02 – 60.72	
	C_5-alkylphenols	$C_{11}H_{16}O$	164.25	99.90 – 416.0	n.d. – 17.38	
	C_6-alkylphenols	$C_{12}H_{18}O$	178.28	25.0 - 160.0	n.d. – 4.11	
Organic Acids	Formic acid	CH_2O_2	46.03	Very soluble	n.d. – 584	[155,163]
	Acetic acid	$C_2H_4O_2$	60.02	Very soluble	8.5 – 5735	
	Propanoic Acid	$C_3H_6O_2$	74.08	Soluble	7.39 - 4400	
	Butanoic Acid	$C_4H_8O_2$	88.11	Soluble	n.d. – 46.0	
	Pentanoic Acid	$C_5H_{10}O_2$	102.13	37.76	n.d. – 33.0	
	Malonic Acid	$C_3H_4O_4$	104.06	Soluble	n.d. – 108.0	
	Benzoic Acid	$C_7H_6O_2$	122.12	3.38	n.d. – 2540	

n.d. = not detected

Phenols and alkylphenols are major components of produced water, ranging in concentration from 0.1 to 40 mg/L, but usually less than 20 mg/L [154,156]. The most abundant species are phenol, methylphenols, and dimethylphenols. The abundance of alkylphenols decreases logarithmically with increasing alkylation numbers. The C_0 to C_3 alkylphenols are found often as part of the dissolved fraction, mainly due to their very large solubility in the aqueous phase, sometimes appearing in large concentrations [157]. However, the toxicity of long-chained alkylphenols (C_7 to C_9) must be taken into consideration in spite of the very low concentrations found in produced water (0.001 to 0.187 µg/L), because they act as endocrine disruptors in marine organisms [162].

Organic acids are also found in produced water in large quantities [155]. The abundance of organic acids in produced water is due to the natural decomposition of long hydrocarbon chains at elevated temperatures in the presence of water [164]. In fact, a very large fraction of the TOC in produced water is due to low-molecular-weight carboxylic acids like formic, acetic propanoic, butanoic, pentanoic and hexanoic acids. Acetic, propanoic and butanoic account for 80%, 15% and 3% of the TOC respectively, and another 2% is made up of other straight and branched chain acids like heptanoic acid, benzoic acids and its derivatives [4].

In the case of acids, concentrations detected in produced water also decreased considerably with increasing molecular weight, as the alkyl chains are non-polar and greater length decreases their solubility in water (Table 2-3). However, in spite of their proven abundance, organic acids with less than 5 carbon atoms are rarely adequately quantified by TOG and TPH measurements because of their low solubility in organic solvents [156].

1.2.2 Petrochemical and refinery wastewater

There is much less information available about oil-contaminated industrial wastewaters in the petrochemical sector. Doubtlessly, environmental impact studies have been carried out, but they are much less likely to be released to the public. This severely limits available information on oily industrial wastewaters. What literature is available indicates that basic components of refinery wastewater are largely the same as in produced water. However, the process and subsequent wastewater treatment can have an important effect on the abundance of specific compounds.

As a general rule refinery wastewater will present high amounts of COD (3600-5300 mg/L), phenols (160-185 mg/L), dissolved alkanes (1.8-1.85 mg/L) and TPH (50-100 mg/L) [165,166]. In 2002-2003, the Al-Ruwais refinery in the UAE carried out an extensive bulk-based and component-based analysis for the identification and characterization of major process streams. Analysis of the oily wastewater previous to primary treatment showed an average of 420 mg/L of COD, and an average of 242 mg/L of COD after primary treatment with a corrugated-plate interceptor. This is still higher than the international standard for marine discharge in refineries that is 120 mg/L for a hydroskimming refinery and 150 mg/L for a complex refinery, as well as the limits imposed for marine discharge by the UAE Federal Environmental Agency at 100 mg/L of COD. Existing treatment systems managed to reduce TPH values by 90%. However, the effluent stream still contained more than the permissible amount of TPH for discharge in the Persian Gulf (15 mg/L), and values for acceptable discharge were only achieved through heavy dilution. The refinery monitored its PAHs content, detecting consistently high levels of naphthalene in their wastewater previous to treatment (30 to 70 mg/L). Generally, phenol concentrations in process waste streams were low (around 2-4 mg/L), but high concentrations of phenol > 20 mg/L were detected in the caustic streams originating from catalyst regeneration. The existing system can only remove 23% of phenols, and low concentrations for discharge were again achieved through dilution. Unlike in produced water, other organic compounds alien to crude oil were also detected such as polychlorinated biphenyls, used as coolants, insulating and hydraulic fluids [167].

Regarding petrochemical wastewater, generalizations become more difficult, as contaminants can become very specific to a single site. Analysis petrochemical wastewater from the China National Offshore Oil Corporation Zhongjie Petrochemical Co. Ltd. found TPH levels around 500 mg/L with COD of 745 mg/L. An important part of the COD originated from settleable particles (54.85%), presumably because oil paraffin adsorbed upon suspended solids. A detailed analysis of the composition and biodegradability of the samples reveals that the most common pollutants in wastewater samples included linear and branched alkanes, benzene, toluene, ammonia and some plasticizers [168]. Extensive GC-MS screening of petrochemical wastewaters discharged into the river in North Rhine-Westphalia was carried out by Botalova et. al. in 2009. They identified non-specific contaminants typical of petrochemical wastewater that included naphthalene alkylated benzenes and phenols, aromatic and aliphatic carboxylic acids, aniline, benzothiazole, acetophenone, thioanisole, and alkylated pyridines, pyrimidines, and pyrazines. The abundance of alkylated pyridines, originates in the production of oil from coal tar, while alkyl pyrimidines and pyrazines are intermediates in the production of pharmaceuticals and flavor additives [169].

2. Objectives

The inability to differentiate within broad families of organics in the typical routine characterization of industrial wastewater presents the biggest hurdle for the development of reliable oil-removal technologies. In the context of wastewater treatment, TOC and TPH measurements indicate whether or not contaminant removal is taking place to some degree, but cannot identify which organics are being removed, and which are resilient to treatment. The general aim of this chapter has been to:

1. To identify the most prevalent organic compounds in oily water samples from the petrochemical industry
2. To identify key compound of oil water based on criteria such as prevalence, abundance, toxicity and environmental impact.
3. To identify adequate analytical methods for the routine analysis of key components of oily water.

3. Methodology

3.1. Feedwater source and sampling

This chapter focuses on the characterization of oily industrial water samples. The samples used for oily water characterization were taken from two different sources: Site 1, and Site 2.

In the case of Site 1, samples were taken from a complex section that treats process utility water used in the refining of lighter petroleum fractions and has chronic problems with oil contamination. Typically, poor separation in the drum separators leads to the presence of oily compounds in the strippers and severe fouling in the heat exchangers downstream. A process map has been represented in Figure 2-1, and within it, several sampling points used during the project. The sampling points had been identified as points of interest for future piloting. There have been four sampling points included in the sampling plan. **Sampling Point 1** (SP1) was located upstream of the process. **Sampling Point 2** (SP2) was located at the outlet of the first set of drum separators. Typical conditions of process water at this point are 60-70 ºC, 4 bar and pH 9. **Sampling Point 3** (SP3) was located on the outlet of the stripper. Typical conditions of process water at this point are 120 ºC, 14.5 bar and pH 9. **Sampling Point 4** (SP4) was located at the outlet of the second set of drum separators. Typical conditions of process water at this point are 35 ºC, atmospheric pressure and pH 9.

Samples originating from Site 2 were taken from site groundwater extraction wells, equipped with an oil skimmer to remove oil layers that are formed on top due to groundwater contamination. The sampling points considered in this project were two wells in different sectors of the site: **Sampling Point 5** (SP5) and **Sampling Point 6** (SP6).

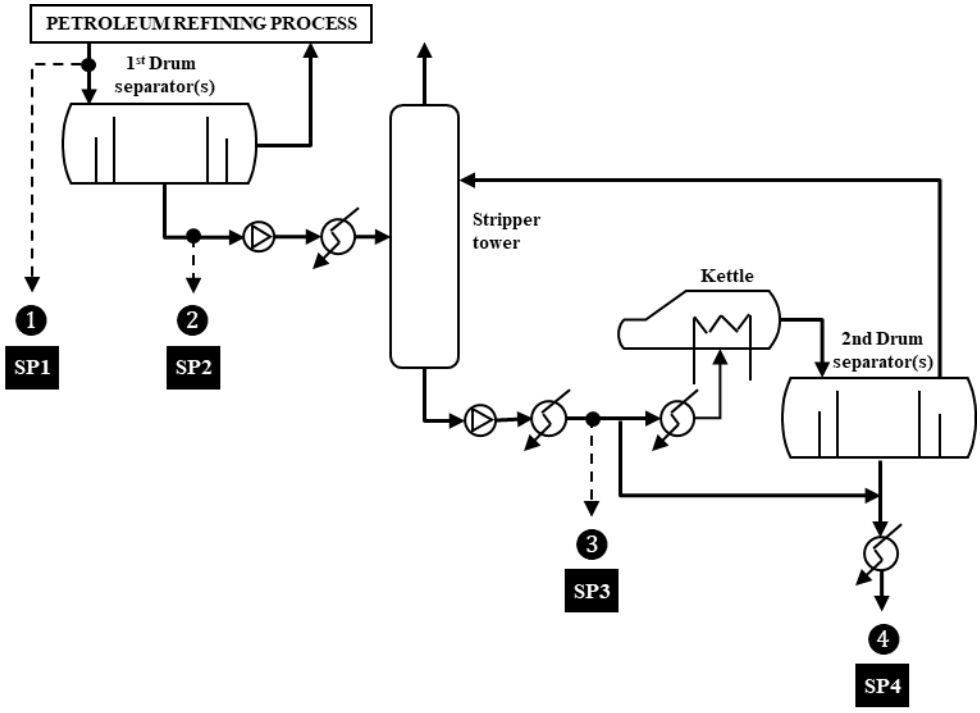

Figure 2-1. Location of Sampling Point 1-4 at Site 1.

to groundwater contamination. The sampling points considered in this project were two wells in different sectors of the site: **Sampling Point 5** (SP5) and **Sampling Point 6** (SP6).

3.2. Analytical Methods

Samples were screened for organic compounds with a combination of analytical methods available. The analytical tests performed were chosen based on existing literature, which has been previously discussed. As analysis have been carried in collaboration with the various sample sites, analysis technique has been adapted to take advantage of the analytical facilities and know-how available at each site. The methods used in sample analysis have been detailed in Table 2-4.

Table 2-4. Analytical Techniques used in sample characterization.

Target Analyte	Analytical Technique	Standard Method	SITE 1				SITE 2	
			SP 1	SP 2	SP 3	SP 4	SP 5	SP 6
TOC	Catalytic Oxidation-IR	ASTM D7573-09	X	X	X	X	X	X
TPH	LLE-IR	ASTM D-7066-4 / EPA 5520-C	X	X	X	X	X	X
GRO	LLE-GC-FID	ASTM UOP 774 / UOP 725	X	X	X	X	X	X
VOC	HS-GC-MS	ASTM D5790 / EPA 8260C	X	X	X	X	X	X
Phenol Index	UV-VIS Spectroscopy	ISO 6439:1990	X	X	X	X		
Organic Acids	IC	ASTM D4327-17	X	X	X	X		
NOC	LC-UV-MS	-	X	X	X	X		

3.1.1. Total organic Carbon (TOC)

The analysis of Total Organic Carbon (TOC) was carried out with analyzer TOC-L CSH/CSN from Shimadzu following standard method based on catalytic oxidation combustion (680ºC) coupled with infrared analysis (ASTM D7573-09, 2017).

3.1.2. Total Petroleum Hydrocarbons (TPH)

The analysis method used for the evaluation of Total Petroleum Hydrocarbons (TPH) in water samples has been based on liquid-liquid extraction followed by infrared spectroscopy (LLE-IR) following standard methods ASTM D7066-4 and EPA5520-C [49]. Water samples are pre-treated through liquid-liquid extraction (LLE) with tetrachloroethylene as extracting solvent. An aqueous sample of 250 mL is extracted with three 15 mL aliquots of tetrachloroethylene. The organic phase is collected in a 100 ml flask and filled until the mark with tetrachloroethylene. The extracted sample is placed in a 50 mm quartz cuvette and placed in the FTIR spectrometer. The FTIR analysis method considers two different regions of the spectrum for quantification: the aliphatic region (at 2930 cm-1 for –CH2 and 2960-2965 cm-1 for –CH3) and the aromatic region (at 3030 cm-1). The method shows a linear relationship between the area of the selected regions of an IR spectrum and the total hydrocarbon concentration. Calibration of the analysis method was carried out with isooctane, n-hexadecane, phenol and xylene. A stock solution of 2000 mg/l TPH (500 mg/l of each standard) was prepared, and from these five standard solutions between 0.96-80 mg/l (R^2 = 0.9996).

3.1.3. LLE-GC-FID

Liquid-Liquid Extraction and Gas Chromatography with Flame Ionization Detector (LLE-GC-FID) was carried out with the aim of identifying the individual solvent-extractable (non-polar) organic compounds (VOCs) present in water samples. A liquid-liquid extraction (LLE) was performed in order to transfer organic compounds to an organic phase for injection in GC-MS. A water sample of 250 mL was extracted with 4

aliquots of 25mL of n-hexane (C_6H_{14}). Samples were injected through direct injection into a GC capillary column equipped with a Flame Ionization Detector (FIID). The analytical procedure followed corresponds with ASTM UOP Method 744 (Aromatic Hydrocarbons up to C10 in pyrolysis gasoline) and ASTM UOP Method 725 (Determination of C4 and C5 in pyrolysis gasoline). The quantification limit of the method is 0.03% and 0.02% in weight respectively.

Table 2-5. Instrument Control Parameters for GC-FID (ASTM UOP Method 744 and 725).

Method	ASTM UOP Method 744	ASTM UOP Method 725
Column:	Capillary, fused silica covered with cross-linked polyethylene glycol-TPA (50 m x 0.2 mm x 0.3 µm)	Capillary, fused silica covered with cross-linked methyl silicone (50 m x 0.2 mm x 0.5 µm)
Inlet Temperature:	250ºC	250ºC
Injection Mode:	Split (Split ratio 1:100)	Split (Split ratio 1:80)
Injection Volume:	10 µL	5 µL
Carrier Gas Flow:	He (constant flow at 26.5 psi)	He (constant flow at 29.5 psi)
Oven Program:	180°C as initial temperature (10 min), temperature progression of 2.5ºC/min, 180°C (12 min) as final temperature	30°C (6 min) to 220 °C (25 min) at 4°C/min for a total run time of 78.5 min.

3.1.4. HS-GC-MS

Headspace Gas Chromatography with Mass Spectrometry Detection (HS-GC-MS) was used for the analysis and quantification of volatile organic components (VOCs). Headspace sampling (HS) is a technique in which volatile material is separated from a heavier sample matrix, such as water samples, and injected into a gas chromatograph for analysis. A sample is put into sealed vial and heated to a moderate temperature for a period of time, so volatile species pass to gas phase, and are then injected into the GC Column. This kind of analysis is recommended for the quantification of volatile organic components (VOCs) present in water samples. The procedure involved adding 2 g of NaCl to a 5mL sample volume, then the sample was transferred to a 20 mL head-space vial that is sealed with a crimp-cap. A dose of 10 µL of the internal standard (Toluene-d_8, 6 mg/ml) was added to the vial. A capillary column was used as GC column, operated in scan mode. Analysis conditions are included in Table 2-6.

Table 2-6. Instrument Control Parameters for HS-GC-MS.

Column	J&W 122-5533 DB5 (25 m x 0.25 mm x 1 µm)
Inlet Temperature	75ºC
Transfer Line Temperature	105ºC
Injection Mode	Split (Split ratio 0.3:1)
Injection Volume	1 uL
Carrier Gas Flow	He at 42 cm/sec (constant flow)
Oven Program	50°C (0.5 min) to 280 °C at 15°C/min for a total run time of 20 min.

3.1.5. Ion Chromatography (IC)

Ion Chromatography (IC) is a chromatographic technique that separates ions and polar molecules based on their affinity to the ion exchanger. It can be used to analyze almost any charged molecule. In this case, IC has been used for the determination of organic acids. Samples were diluted with mineralized water, then the solution was filtered and the filtrate was analyzed by IC. Quantification was carried out with external standards. The analysis was carried out with a Dionex Ion Chromatograph (ICS-5000), equipped with a

Quaternary Gradient Pump, Conductivity Detector, Eluent Generator, an ICS-5000 DC-MB Oven and AS-AP autosampler. The limit of detection was estimated < 1 mg/kg. The IC conditions are specified in Table 2-7.

Table 2-7. Instrument Control Parameters for IC.

Column	IonPac AS15-HC
Sample Loop Volume	12.5 uL
Eluent flow rate	0.25 mL/min.
Oven temperature	30ºC
Suppressor SRS current	38 mA
Eluent source	ICS-5000 EGC III (KOH)

3.1.6. Total Phenol index

The analysis of phenols was carried out with testing cuvettes LCK 345 from Hach-Lange, for a range of 0.05-5.0 mg/L of equivalent phenol. Concentrated samples were diluted before analysis. The analysis method is based on the reaction of phenols with 4-nitroaniline to form a yellow-colored complex, which is then measured through spectrophotometry. This method will measure substituted alkyl-phenols (like cresol), as they will also react and contribute to the Total.

3.1.7. LC-UV and LC-MS

Liquid chromatography is a technique used to separate a sample into its individual parts for analysis. This involves a mobile phase –a liquid sample– flowing through a stationary phase –usually a solid– carrying the mixture components with it. Sample components that display stronger interactions with the stationary phase will move more slowly through the column than components with weaker interactions. This difference in rates cause the separation of various components. This technique is especially useful for mixtures with components that do not vaporize well. The procedure used pre-treated samples for analysis by passing them through a 0.45 µm filter. Gradient elution was performed using an Agilent 1260 LC setup consisting of an autosampler unit, a thermostated column compartment at 40°C and a DAD (Diode Array Detector) operated at 190-400nm. Component elution was established at 1 ml/min on a Poroshell 120 EC-C18 Column (4.6x50mm 2.7µm) running a gradient from 10 to 100% methanol. A solution of 1% ammonium acetate in methanol was added post column at 0.1 mL/min as modifier for analysis. Identification was performed using an Agilent 6520 Q-ToF tuned, calibrated and operated in positive and negative APCI and electrospray mode. Stable spray conditions were obtained at 10 l/min gas flow at a nebulizer pressure of 50psi (Table 2-8).

Table 2-8. Instrument Control Parameters for LC-UV-MS.

Column	Poroshell 120 EC-C18 (4.6x50mm 2.7µm)					
Elution Solvent Gradient	Time (min)	0	0.5	5.5	10	10.10
	Solv Ratio of MeOH (%)	10	10	100	100	10
Elution Flowrate	1 ml/min					
Electrospray Gas Temperature	350 ºC					
Electrospray Gas Flow	10 L/min					
Electrospray Nebulizer Pressure	50 psig					

3.3. Resin treatment and effluent water composition

Water samples from each sampling point were treated with resins AmberLite™ ROC110 and AmberSorb™ L493 in a laboratory set-up. The samples were treated following the procedures previously established by Carmona *et al* [49] and Tejero *et al* [114]. The experiments were conducted in two glass columns of 4.35 cm diameter and a depth of 20 cm packing 300 mL of resin AmberLite™ ROC110 and AmberSorb™ L493 respectively. A peristaltic pump was used to introduce the feed solution into the column at a rate of 15 ml/min (30 BV/h). The set-up is fully manual, and experiments were carried out in batch mode at ambient temperature (18-22ºC) and atmospheric pressure.

4. Results and Discussion

4.1. Conventional characterization

The initial characterization of samples is carried out through TOC and TPH measurements. These measurements are sufficient to obtain a general idea of the gross amount of organic content present in oily water samples. Repeated analysis showed great differences between samples taken at the same sampling points over time. This is not entirely surprising, as petrochemical wastewater has been known to present highly variable amounts of hydrocarbons over time [49]. This usually responds to fluctuations in the process and variations in base petroleum composition. Table 2-9 shows the range of values observed at different sampling points.

Table 2-9. TOC and TPH range values for different sampling points.

Analyte		SITE 1			SITE 2		
		SP1	SP2	SP3	SP4	SP5	SP6
TOC	[mg/L]	266.7 – 330.4	273.2 – 457.2	231.8 – 326.8	637 – 1,110	115	229
TPH	[mg/L]	15.6 – 316	13.2 – 284	n.d. – 5.2	n.d. – 1.2	n.d.	n.d.

The samples analyzed show both high amounts of TOC and different amounts of TPH. However, the study of TOC and TPH values shows that the relative amounts of TPH and TOC can be very different depending on the wastewater source and sampling point. Looking at Sampling Points 1 to 4, it can be seen that the ratio of TOC to TPH evolves downstream. Sampling Point 1 –upstream of the main separation train– showed both lower concentrations of TOC and higher amounts of TPH. Some days, almost all organic content quantified as TOC could be directly related to the presence of hydrocarbons as TPH in samples taken from Sampling Point 1. However, in every sampling point further downstream, higher amounts of TOC were observed while TPH became lower. TPH concentrations were up to 50 times higher in Sampling Point 1 than Sampling Point 4, while TOC at Sampling Point 4 tripled the initial values found in Sampling Point 1. This trend can be tentatively explained by two factors: (1) the progressive application of different oil-water separation technologies (drum separators, stripper, etc.) has a visible removal effect on TPH values; (2) the accumulation of the more polar organics and the progressive degradation of hydrocarbons over time will cause a build-up of organics –as TOC– downstream. Sampling Points 3-4 presented very low amounts of TPH, but still considerably large amounts of TOC.

Samples taken from Site 2 also show that oil-related contamination does not necessarily lead to high TPH measurements while still exhibiting high TOC values. Considering that oil layers are routinely formed at Sampling Point 5 and 6, it simply appears that oil settling is wholly successful and the remaining organic contamination is a matter of hydrocarbon solubility and of the weathering of the hydrocarbon species after prolonged contact with water.

The collected data suggests that large amounts of organics not typically included under the "hydrocarbon" umbrella can be present in oily wastewater. Such compounds are more polar than typical hydrocarbons, and not solvent extractable. Thus, they do not appear as part of TPH. However, such organics still present a risk of downstream fouling, and should ideally be removed. Therefore, their identification is still a matter of interest.

4.2. Screening for organics in oily water

4.1.1. The Solvent-Extractable Organic Fraction

The solvent-extractable organic fraction of oily wastewater is that typically considered as "hydrocarbons". Therefore, the methods used for the study of this fraction –ASTM UOP 744 and 725– are typically destined for the analysis of gasoline-range organics in gasoline (GRO). Water samples from Sample Points 1 to 4 (Site 1) were extracted with n-hexane (C_6H_{14}), and the extracts examined with GC-FID. This allowed us a broad characterization of the solvent-extractable organic fraction present in oil-contaminated process waters. However, this method is not a method designed for trace compound analysis. The limit of detection of this method is of the 0.02-0.03% in mass (19 ppm), and only major organic components are detectable. As this analysis method is used to analyze gasoline directly, not hexane extracts, the matrix of the sample is different, and concentrations are going to be merely indicative so exact composition value cannot be expected.

Nonetheless, interesting results have been obtained in this manner. The main hydrocarbon contaminants detected in process wastewater were **benzene**, **toluene**, **xylene**, **styrene** and **indene**. This indicates that the main components of the solvent-extractable organic phase are monocyclic and bicyclic aromatic compounds, usually comprised within the volatile organic fraction (VOC). Results also showed that although these compounds were always detectable in the upstream Sample Points 1 and 2, they were present in small enough concentration downstream to remain undetected (Sample Points 3 & 4). These results are consistent with previous TPH results and literature sources concerning produced water. Considering that Sample points 3 & 4 are located downstream of the process stripper, it is to be expected that TPH values are low if hydrocarbon content is mainly due to highly volatile species. Indene, both heavier and less volatile was the only component detected to persist downstream to Sampling Points 3 & 4.

Similar analysis of Site 2 samples found that oil contamination was caused by the presence of highly aromatic oil. Results reported a number of known components which were accountable for 50-60% of the total composition. Specifically, the more abundant components detected were **toluene**, **benzene**, **xylene**, **styrene**, **vinyl toluene**, **dicyclopentadiene**, **indene** and **naphthalene**. The remaining 40-50% were unidentified isomers and other unknown components with similar physical properties.

Further analysis was carried out by HS-GC-MS. The analysis was run in scan mode, because the purpose was to identify all the volatile organic components present instead of specific target hydrocarbons. The compounds detected have been listed in Table 2-10. The concentrations presented are only indicative. This is because accurate quantification would require individual calibration of each component, which at the outset were unknown. Instead an internal standard was used (toluene-d8). These results obtained by this method confirm that the bulk of volatile hydrocarbons was composed of aromatics. Detected compounds include **BTEX** (benzene, toluene, ethylbenzene and xylene), **styrene**, **cumene**, other alkylated **benzene derivatives**, and some smaller polycyclic aromatic hydrocarbons such as **indene** and **naphthalene**. On top of this, there were also noticeable amounts of **phenol** and **alkylated phenols**. Such compounds are not typically analyzed through Headspace GC-MS due to their low volatility, therefore the estimated concentrations in the sample are especially inaccurate in this case, but it is a clear indicative that this type of compounds might be present in relatively high concentration.

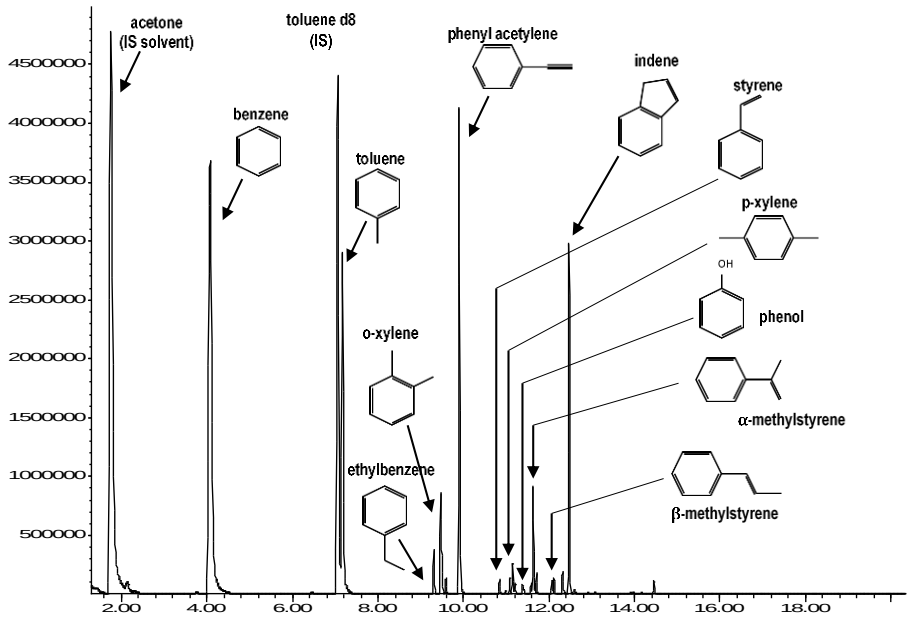

Figure 2-2. Sample HS-GC-MS chromatogram from Sampling Point 2.

Table 2-10. Concentration of individual species found in hexane extracts.

Analyte			SITE 1				SITE 2	
			SP 1	SP 2	SP 3	SP 4	SP 5	SP 6
Benzene	C_6H_6	[mg/L]	132	16.4 – 95.0	n.d.	n.d.	n.d.	0.20
Toluene	C_7H_8	[mg/L]	6.30 – 38.0	19.0	n.d.	n.d.	0.04	0.30
ethylbenzene	C_8H_{10}	[mg/L]	0.71	0.56	n.d.	n.d.	0.67	0.19
m/p-xilene	C_8H_{10}	[mg/L]	2.0 – 19.0	1.62	0.27	0.01	1.05	n.d.
o-xilene	C_8H_{10}	[mg/L]	1.0 – 19.0	n.d.	n.d.	n.d.	1.13	0.13
m-ethyl toluene	C_9H_{12}	[mg/L]	0.35	n.d.	0.01	n.d.	n.d.	n.d.
1,2,3-trimethyl benzene	C_9H_{12}	[mg/L]	n.d.	n.d.	0.07	n.d.	n.d.	n.d.
styrene	C_8H_8	[mg/L]	7.35 – 19.0	7.12 – 19.0	n.d.	0.1	1.93	0.35
α-methyl styrene	C_9H_{10}	[mg/L]	2.54	1.49	0.28	n.d.	2.23	n.d.
β-methyl styrene	C_9H_{10}	[mg/L]	0.33	0.22	n.d.	n.d.	n.d.	n.d.
4-vynil toluene	C_9H_{10}	[mg/L]	n.d.	n.d.	n.d.	n.d.	9.75	n.d.
cumene	C_9H_{12}	[mg/L]	n.d.	n.d.	n.d.	n.d.	n.d.	0.03
phenyl acetylene	C_8H_6	[mg/L]	n.d.	0.22	n.d.	n.d.	n.d.	n.d.
dicyclopentadiene	$C_{10}H_{12}$	[mg/L]	n.d.	n.d.	n.d.	n.d.	1.55	0.03
indene	C_9H_8	[mg/L]	4.80 – 38.0	4.06 – 189	0.32	0.06	17.8	n.d.
phenol	C_6H_6O	[mg/L]	0.44	0.39	0.17	0.22	n.d.	n.d.
2-methyl phenol	C_7H_8O	[mg/L]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-methyl phenol	C_7H_8O	[mg/L]	n.d.	n.d.	n.d.	0.02	n.d.	n.d.
4-methyl phenol	C_7H_8O	[mg/L]	n.d.	n.d.	n.d.	0.02	n.d.	n.d.
naphtalene	$C_{10}H_8$	[mg/L]	n.d.	n.d.	n.d.	n.d.	14.35	0.22
methyl naphthalene	$C_{11}H_{10}$	[mg/L]	n.d.	n.d.	n.d.	n.d.	3.2	n.d.

Most species identified are supported by pre-existing literature. Notably several the hydrocarbon contaminants found in industrial oily water are light aromatic hydrocarbons: BTEX, BTEX derivatives and naphthalene. This is seen across all types of hydrocarbon contaminated wastewaters. Other species identified are more process specific, such as styrene and styrene derivatives, and dicyclopentadiene, all important and valuable by-products of Ethylene Cracking Processes using naphtha feedstocks.

4.1.2. The Polar Fraction

Because the sometimes-sizable differences observed between TOC and TPH measurements, additional analytical techniques were used for the screening and identification of non-extractable contaminants of oily waters. Based on their tentative identification in previous analysis with Headspace GC-MS, the Total Phenol Index was determined through spectrophotometry for quantification of phenol-type species. Ion Chromatography (IC) was used in order to screen for organic acid species. As organic acids at pH levels typical of process samples (pH 9) will be present in the form of its conjugated base, they are far more hydrophilic than other organics and cannot be extracted alongside the rest of the organic matrix in most non-polar solvents such as n-hexane or tetrachloroethylene.

The analytical results revealed both an abundance of phenol compounds and short-chain organic acids, especially acetate (Table 2-11). Concentration of phenols in process water samples from Site 1 found concentrations of the order of 100 mg/L, which indicates that phenolic contaminants are an important contributor to dissolved oil. Concentration of phenols decreased slightly downstream, presumably because they were removed alongside oil layers. On the other hand, concentration of organic acids upstream were comparatively low, but increased significantly downstream of the process. This increase can be justified because organic acids –particularly acetate– are the end products of hydrocarbon degradation in water medium. Furthermore, organic acids become hard to remove and tend to accumulate downstream of the process owed to their high hydrophilicity and low volatility, reaching values in excess of 250 mg/l.

Samples were also analyzed with LC-UV-MS, but no peaks were observed that could be reliably identified with the UV detection system. Upon analysis with MS detection there was a peak that was tentatively assigned to the presence of triethylene glycol (TEG). TEG is a transparent, colorless, moderately-viscous, water-soluble liquid. Under normal conditions, it has no detectable odor. It is non-flammable, mildly toxic, and considered non-hazardous. It is produced mainly from the hydration of ethylene oxide. TEG is both used as a plasticizer, and –in the oil and gas industry– for natural gas dehydration [170]. Given all the above, its positive identification in oily wastewater streams from an ethylene cracking facility seems plausible, but quantification was not possible.

Table 2-11. Concentration of phenols and organic acid species in water samples.

Analyte			**SITE 1**			**SITE 2**		
			SP 1	**SP 2**	**SP 3**	**SP 4**	**SP 5**	**SP 6**
Phenol	C_6H_6O	[mg/L]	116	113	96	89	n.a.	n.a.
Formate	CHO_2^-	[mg/L]	n.d.	n.d.	n.d.	6.5	n.a.	n.a.
Acetate	$C_2H_3O_2^-$	[mg/L]	19	19	24	251	n.a.	n.a.
Propionate	$C_3H_5O_2^-$	[mg/L]	2.6	2.5	3	36	n.a.	n.a.
Oxalate	$C_2O_4^-$	[mg/L]	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.

4.2.3. Identification of key species for oil removal with resin technologies

The samples were treated with resins AmberLite™ ROC110 and AmberSorb™ L493. Treated water samples were also analyzed by HS-GC-MS, LC-UV-MS, IC and for Total Phenol Index. The results –shown in Table 2-12– indicate that treatment with AmberLite™ ROC110 can reduce significantly the concentrations of volatile hydrocarbons. However, it has little impact on the total amounts of non-extractable species. Treatment with AmberSorb™ L493 showed complete removal of remaining extractable species, significant removal of phenol species and little to no effect on the removal of organic acids.

Table 2-12. Characterization of samples treated with AmberLite™ ROC110 and AmberSorb™ L493.

Analyte		Feed Sample				Sample after AmberLite™ ROC110				Sample after AmberSorb™ L493			
		SP 1	SP 2	SP 3	SP 4	SP 1	SP 2	SP 3	SP 4	SP 1	SP 2	SP 3	SP 4
TOC	[mg/L]	266.7	273.2	231.8	637.5	226.9	247.1	209.1	669.5	78.1	84.6	73.6	253.2
TPH	[mg/L]	15.6	13.2	n.d.	n.d.	5.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzene	[mg/L]	n.d.	16.40	n.d.	0.80	n.d.	4.45	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Toluene	[mg/L]	6.30	n.d.	n.d.	n.d.	1.03	0.96	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ethylbenzene	[mg/L]	0.71	0.56	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
m/p-xilene	[mg/L]	2.00	1.62	0.27	0.01	0.05	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
o-xilene	[mg/L]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
m-ethyl toluene	[mg/L]	0.35	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1,2,3-trimethyl benzene	[mg/L]	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Styrene	[mg/L]	7.35	7.12	n.d.	0.10	0.28	0.29	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
α-methyl styrene	[mg/L]	2.54	1.49	0.28	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
β-methyl styrene	[mg/L]	0.33	0.22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
phenyl acetylene	[mg/L]	n.d.	0.22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Indene	[mg/L]	4.80	4.06	0.32	0.06	0.14	0.18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Phenol	[mg/L]	116	113	96	89	83	76	75	82	0.21	0.27	3.6	1.08
Formate	[mg/L]	n.d.	n.d.	n.d.	6.5	n.d.	n.d.	n.d.	6.5	n.d.	n.d.	n.d.	4.3
Acetate	[mg/L]	19	19	24	251	20	20	24	251	22	30	14	232
Propionate	[mg/L]	2.6	2.5	3	36	2.6	2.6	3	35	1.9	2.4	n.d.	28
Oxalate	[mg/L]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detected

In Figure 2-3 the chromatograms showing the volatile hydrocarbon species present in the sample are shown, where the removal effect upon the non-polar hydrocarbon fraction can be observed. The results verify that treatment with a coalescer resin (AmberLite™ ROC110), followed by an adsorption resin (AmberSorb™ L493) is an effective strategy for removal of the non-polar organic fraction.

The removal of hydrophilic fraction of dissolved oil is more complex. Phenols, which are not significantly removed by the coalescence process, are present in very high concentrations.

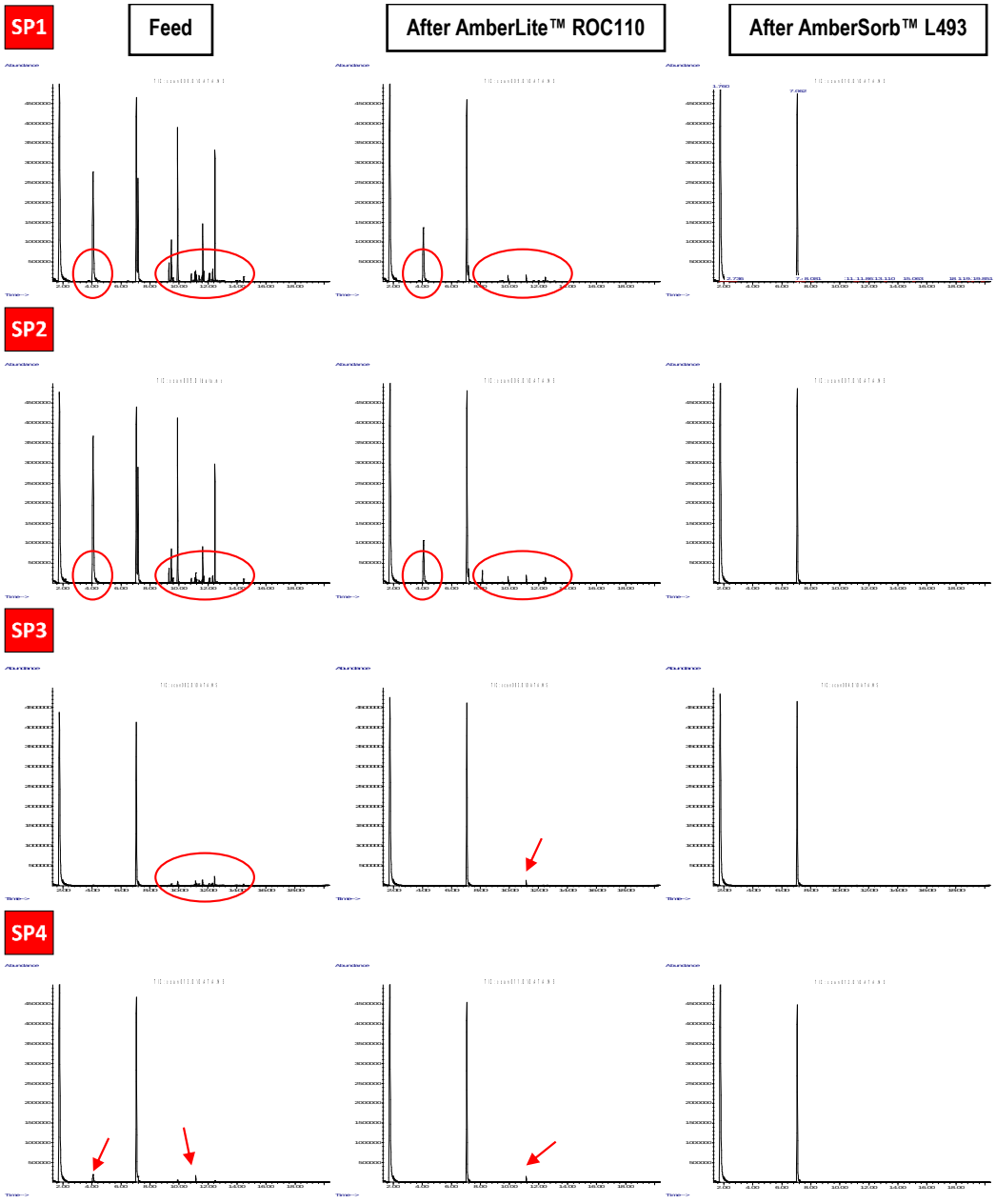

Figure 2-3. HS-GC-MS Chromatograms showing the removal of volatile species.

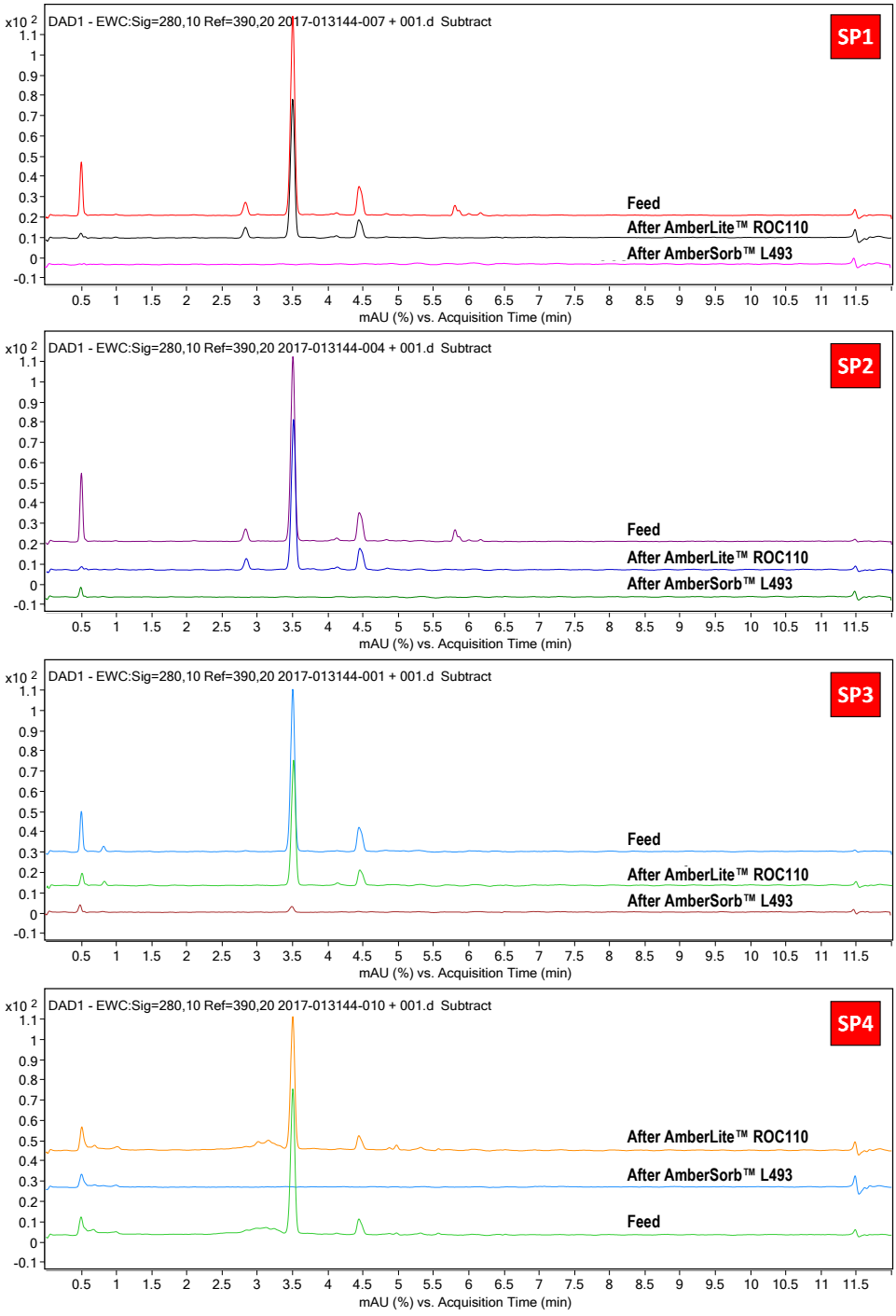

Figure 2-4. LC-UV Chromatogram showing the removal of non-volatile species (λ=280nm).

Removal after treatment with AmberLite™ ROC110 was small (8-29%). Phenols are extremely toxic, and widely regulated in the frame of industrial wastewater discharge. They have been listed by the United States Environmental Protection Agency (USEPA) and the European Union (EU) as a pollutants of priority concern. Discharge limits worldwide are as low as 0.2 mg/l (China), 0.3 mg/l (Mexico, France), 0.5 mg/l (Brazil), 1 mg/l (India, Italy) and 5 mg/l (Japan) [171]. Because the amounts of phenol usually exceed the acceptable levels for safe discharge it is necessary for them to be treated. Testing indicates that removal of phenol in samples treated with AmberSorb™ L493 is pretty good showing significant removal in the range of 95.2-99.7%.

On the other hand, short-chain organic acids –particularly acetate– are not toxic and therefore pose no problem for direct discharge. However, they are extremely bio-degradable and a readily bio-assimilable source of nutrients for bacteria. They are an important promoter of *fouling* and pose a problem for industrial reuse. Treatment with AmberLite™ ROC110 and AmberSorb™ L493 technology failed to remove organic acids.

Samples were also analyzed by LC-UV-MS. Figure 2-4 shows the UV-chromatograms obtained for both process samples and treated samples. In all cases, the overall peak intensities decrease with further treatment: feed samples show higher intensity that those treated with AmberLite™ ROC110, and those higher than those treated with AmberSorb™ L493. Although the species for each peak are not identified, these tests confirm that organic species are being removed with IER treatment.

4.3. Identifying Analytical Methods for Oily Water Analysis

The characterization of oily wastewater samples identified the more common and abundant contaminants in oily water. They were found to be both benzene derivatives, small species of polycyclic aromatic hydrocarbons, phenols and short-chain organic acids. Accordingly, appropriate analytical methods for each type of contaminants were developed and implemented for routine sample analysis.

TOC measurements –as bulk measure of total organic content- have been considered necessary for routine process sample analysis. These should be supplemented with TPH measurements. Ideally TPH should be measured with IR techniques to avoid the loss of lighter gasoline fractions, if they are present in the samples. The method for TPH measurement described in section 2.1.2 was considered appropriate. It has been modified to allow the semi-automation of the sample preparation process by substituting Liquid-Liquid Extraction (LLE) for Solid-Phase Extraction (SPE). Extraction was carried out in a SPE DEX-500 extraction unit with 47 mm Pacific® Oil & Grease Premium Disks (Biotage). The method successively elutes 6 ml of tetrachloroethylene and 25 mL of ultrapure water for disc conditioning. This is followed by the elution of a volume of sample: 250 ml if concentrations are > 8 mg/L, 1L if concentrations are < 8 mg/L. The discs were eluted three times with 9 mL of tetrachloroethylene, dried and brought to a fixed volume of 50mL. IR analysis

Table 2-13. Analytical techniques implemented for oily water characterization.

Measurement	Analytical Technique	Standard Method	Target Analytes
TOC	Catalytic Oxidation-IR	ASTM D7573-09	Total sum of covalently bonded carbon oxidizes under test conditions.
TPH	SPE-IR	ASTM D-7066-4 / EPA 5520-C	Total sum of hydrocarbons that are solvent-extractable under test conditions.
BTEX-N	SPE-GC-MS	EPA 525.2	Benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, napththalene
Organic Acids	IC	ASTM D4327-17	Acetate
Phenol Index	UV-VIS Spectroscopy	ISO 6439:1990	Phenol and substituted phenolic compounds which react with 4-aminoantipyrine under test conditions.

was carried out as previously described. The analysis method was validated with a synthetic mixture of stearic acid and n-hexadecane at 1 ppm, 5 ppm and 50 ppm. Method error is ±8%, with a limit of detection (LOD) of 1ppm.

The determination of Phenol Index has remained as described in Section 2.1.6. A method was implemented for the analysis of BTEX and Napthtalene by SPE-GC-MS. Although the preferred method for the analysis of volatile components in water is HS-GC-MS, the quantification of this components by SPE has been found to be acceptable (80-100%) with relatively high concentrations (concentrations greater than 1 mg/L). The current method uses a SPE DEX-500 extraction unit with 47 mm C18 disks. The method elutes 6 ml of methanol (≥99.9%, VWR Chemicals) and 25 mL of ultrapure water for disc conditioning. This is followed by the elution of a 50 mL sample. The discs were eluted three times with 9 mL of dichloromethane, dried and brought to a fixed volume of 50 mL (Full method is described in Chapter 5). Additionally, method for acetate –as the more common of organic acid species– analysis has been developed by IC (Full method is described in Chapter 5).

5. Conclusions

A study of the composition of petrochemical oily wastewater obtained satisfactory results and reached the conclusion that the most prevalent organic compounds are relatively soluble and in most cases light-weight hydrocarbons. These types of compounds can be broadly grouped into several compound families. Elements within a family can usually be analyzed together and follow mostly the same trends in their behavior toward oil-removal technologies. These compound families are:

- **Monocyclic Aromatic Hydrocarbons** such as benzene and its alkylated derivatives, particularly the smaller and more soluble hydrocarbons (benzene, toluene, ethylbenzene and xylene or BTEX). The proposed method for analysis of this contaminants would be HS-GC-MS, or in its stead LLE-GC-MS or SPE-GC-MS.
- **Polycyclic Aromatic Hydrocarbons** or PAHs, which are not extremely abundant due to their low solubility in water but are extremely toxic and can have a devastating impact in the environment due to their persistence. Smaller two-ring PAH components such as naphthalene or indene can reach relatively high concentrations. The proposed method for analysis is LLE-GC-MS or SPE-GC-MS.
- **Phenols** and its alkylated derivatives (mostly cresols) are also a major component of this type of wastewaters. The recommended method for analysis in wastewaters would be their derivatization and analysis through spectrophotometry as a general Total Phenol Index or HPLC.
- **Organic Acids** and the conjugated bases, particularly those with small alkyl chains are are an abundant species in process water (formate, acetate and propionate). The most appropriate method of analysis would be IC.

Chapter 3

Characterization of polymeric resins

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1. Introduction to polymeric resins properties

Ion exchange, adsorption and coalescence are different and distinct processes with very different mechanisms, but they are all surface-based processes where molecules, ions or atoms attach to the surface of a solid material. Having a large and extensive surface where molecules and ions can attach is essential. Polymeric resins –which include ion exchange resins, polymeric adsorbents and coalescer resins– are essentially spherical beads of a functionalized synthetic polymer matrix with a large surface area in a small volume and well-defined pore structure. Resin structure and functionalization are determined by the synthesis process. It informs many intrinsic resin properties such as capacity, selectivity, swelling and stability (chemical, thermal and mechanical). Other properties such as particle size are also determined by a resin synthesis process.

Polymeric resins always consist of an insoluble polymer matrix, and the functional groups that are anchored in it. The polymer matrix is made of long hydrocarbon chains structured by means of a cross-linking agent, which gives the matrix a stable tridimensional structure. Polystyrene, polyacrylic and phenolic matrixes are very common. Copolymers of styrene-divinylbenzene (PS-DVB) are widely used in the manufacturing of both ion-exchange and adsorbent resins. Figure 3-1 (a) shows the structure of a PS-DVB resin where divinylbenzene acts as the crosslinking agent [172]. These resins are obtained by polymerization of styrene and the subsequent addition of small amounts of divinylbenzene (typically 0.5 to 25 wt%). The degree of crosslinking –the mass percentage of DVB to styrene monomer before polymerization– is directly related to a resin's pore structure. The pore structure in turn affects some bulk properties which have direct consequences on their practical application, such as density, capacity and selectivity. According to IUPAC, pores are classified by their size –micropores (size < 2nm), mesopores (2nm < size < 50nm) and macropores (size > 50nm)–, their availability –*open* pores, *dead-end* pores, *through* pores and *closed* pores– and their shape –cylindrical, slit-shaped, cone shaped, ink-bottle shaped, etc. [173–175].

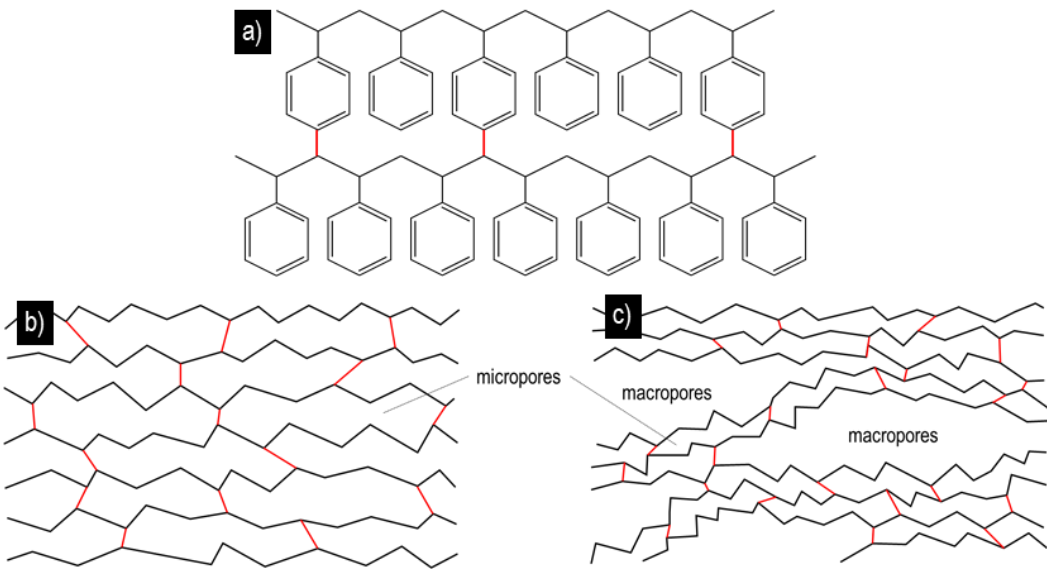

Figure 3-1.Structure of a (a) cross-linked matrix, (b) gel-type resin and (c) macroporous resin.

Resins with lower degrees of crosslinking receive the name of gel-type resins and present a pore structure composed mainly of micropores (1 to 2 nm). These are the voids between polystyrene chains, and their size is relatively constant. As a result, the matrix has a pseudo-crystalline structure and the beads are transparent. Resins with higher degrees of crosslinking lead to a structure that is more rigid and compact at the same time. Because this would severely limit the viability of intra-particle transport, a *porogen* is used during polymerization of resins with higher degrees of crosslinking (usually toluene or C4-C10 alcohols). This *porogen* does not react, but takes up space within the solid structure, and when it is removed leaves behind large permanent voids in the macropore range (20 to 100 nm). These resins are known as *macroporous* resins, which show double porosity: the micropores of the polymer matrix and the permanent macropores that facilitate intra-particle transport. Macroporous resins are usually opaque, have larger amount of surface area per volume and display greater chemical and mechanical strength. They are also more brittle [172]. In addition to the traditional gel-type and macroporous resins, a third type of polymeric resins called *hypercrosslinked* copolymers. These copolymers are obtained through the post-synthesis crosslinking of linear polystyrene by Friedel-Crafts-type reaction, leading to a degree of crosslinking up to 40% or higher. This produces highly homogeneous copolymer beads with a very high inner surface area, and very high mechanical strength. Usually, these *hypercrosslinked* polymers are superb adsorbents, with an adsorption capacity for organic compounds that far exceeds the capacity PS-DVB based macroporous polymeric adsorbents [176–178].

The functionalization of ion exchange resins will render them either anionic (usually amine or ammonia groups) or cationic (generally sulfonic or carboxylic groups). Usually polymeric adsorbents can have cation- or anion-exchange groups or no ion-exchange groups at all, in which case they are inert. In order of decreasing polarity there are ionized adsorbents, phenolic adsorbents and inert adsorbents. Weakly ionized adsorbents –usually strongly basic- are used as organic scavengers for color removal. Phenolic adsorbents with weakly basic amine groups are used to remove color impurities in food-processing streams. Inert adsorbents are highly cross-linked non-functionalized macroporous PS-DVB copolymers with a very high surface-to-volume ratio. These last are typically used to remove non-ionic organic species like phenols and chlorinated solvents from aqueous solutions [172].

The structure of a resin informs the stability of its structure in front of different types of stress. The mechanical stability –defined by resistance to compression and breaking– of macroporous resins is usually better. They are usually both harder and more resistant, because the larger amount of crosslinking in the structure offers better support. A resin's chemical stability –its ability to work in highly oxidizing conditions without experiencing changes in the polymeric matrix– is also improved by a higher degree of crosslinking. Thermal stability –which allows a resin to withstand high temperatures– is informed by both resin structure and its functional groups. In the case of sulfonic resins, thermal degradation happens by elimination of sulfonic groups.

Particle size is a variable that is usually defined during the polymerization process of PS-DVB resins. Particle size is a very important parameter in ion exchange resins, adsorbents and other granular materials that are usually packed inside a column, as it defines system hydraulics in commercial set-ups (bulk density, void fraction and pressure drop). Particle size usually follows a Gaussian distribution. As a general rule, fine resins have fast adsorption kinetics, but high pressure drop. Coarse resins have slower kinetics –owing to lesser resistance for internal mass transfer– and low pressure drops. This is a trade-off, so for the most part, commercial resins usually have a particle diameter between 210 and 1120 μm. Particle size measurement is a key performance indicator for commercial resins: customers require products with predictable mean particle sizes, and that do not contain excessive amounts of material significantly different from the mean for consistent behavior. Historically, characterization of particle size distribution of a commercial resin was carried out by sieving a resin sample into different fractions with successively smaller mesh sizes [172].

Currently, the method most favored by the industry is HIAC, which stands for High Accuracy Particle Counting [179].

For commercial purposes, an adequate estimation of pressure drop across a resin bed is necessary for the dimensioning of the mechanical equipment such as pumps, nozzle plates, etc. Particle size has an important effect upon pressure drop, alongside other parameters such as fluid viscosity, linear flow rate, resin bed depth, void fraction and resin elasticity. The most important parameters to consider in pressure drop (dP) modeling are:

- Viscosity (η): the viscosity of the flowing liquid is depended on both temperature and composition. The pressure drop is approximately proportional to the viscosity of the liquid.
- Density (η): the density of the flowing liquid is also depended on both temperature and composition. This variable is important in turbulent flow conditions.
- Linear velocity (u_0): fluid velocity is directly related to dP through a resin bed.
- Bed Depth (L): dP is directly proportional to resin bed depth.
- Particle size (d_p): dP is inversely proportional to the square of the particle diameter. Most resins with a non-uniform particle size distribution must calculate an average. Usually, por classified beds, the harmonic mean size ($d_{HMS,v}$) it the value of choice for dP calculations.
- Void Volume Fraction (ε): this parameter describes the amount of void spaces -interstitial spaces- between the particles of a packed bed. The effect of ε on pressure drop is very important. For many regular geometries, the void volume can be either calculated or estimated. For hard and perfectly smooth spheres of identical diameter, the arrangement of particles can range from the tightest packing provided by the hexagonal arrangement (ε = 25.9%) to the loosest packing provided by the cubic arrangement (ε = 47.6%). However, it is very difficult to predict the actual arrangement of spheres in a bed, and therefore the theoretical estimation of ε usually contains a lot of unsubstantiated suppositions. Real resins are not actually totally smooth. They are also a little elastic, which means that after some time of operation – particularly in downflow mode– the resin beads tend to slide past each other towards a tighter packing leading to the compression of the bed. Finally, resin beads have a particle size distribution –they are not the same size– and smaller beads can sit between larger beads. Bed classification through backwashing and settling can help reduce pressure drop as bigger beads sit at the bottom of the column and finer beads on top.
- Suspended solids: the presence of suspended solids in the feed stream can add considerably to the pressure drop of the system, particularly if they get lodged in the interstitial spaces of the column.

In the field of fluid dynamics, the equations normally used to calculate the pressure drop of a fluid flowing through a packed bed of solids are the Kozeny-Carman equation and the Ergun equation. The Kozeny-Carman equation (Eq. *3-1*) is derived from the Hagen Poiseuille equation, and is valid for laminar flow conditions through a randomly packed bed of monosized spheres.

$$\frac{dP}{L} = 180 \cdot \frac{\eta \cdot u_0}{\left(\Phi_p \cdot d_p\right)^2} \cdot \frac{(1-\varepsilon)^2}{\varepsilon^3} \qquad 3\text{-}1$$

The Ergun equation (Eq. *3-2*) -which is an empirical equation- is more general, and considered valid for all flow conditions, both laminar and turbulent. In laminar flow conditions, the equation essentially is reduced to the Kozeny-Carman equation, with a slight variation of the constant due to small variations in the experimental data sets with which the correlations were originally developed.

$$\frac{dP}{L} = 150 \cdot \frac{\eta \cdot u_0}{\left(\Phi_p \cdot d_p\right)^2} \cdot \frac{(1-\varepsilon)^2}{\varepsilon^3} + 1.75 \frac{\rho_F \cdot {u_0}^2}{\Phi_p \cdot d_p} \cdot \frac{(1-\varepsilon)}{\varepsilon^3} \qquad 3\text{-}2$$

where dP is pressure drop, η is the dynamic viscosity, ρ_F is the density of the fluid, u_0 is the linear velocity, ε is the void volume fraction, d_p is the average particle diameter and Φ_p is particle sphericity (which in polymeric resins is usually ~1).

2. Objectives

The aim of this chapter has been the characterization of the resin materials used in oil removal applications: AmberLite™ ROC110 and AmberSorb™ L493. The hydraulic characterization of a resin, in particular, is extremely relevant to be able to predict its behavior consistently. Therefore, a characterization of particle size and bed porosity is necessary to be able to predict and model pressure drop. The individual objectives for this chapter have been:

1. To obtain accurate measurements of particle size distribution and void volume fraction that can be used to calculate accurate pressure drop curves.
2. To obtain pressure drop measurements with the resins used in this PhD dissertation.
3. To obtain and verify a valid model for the projection of pressure drop as a tool for project development.

3. Methodology

3.1 Polymeric Resin General Description

The resins that have been characterized in this section are AmberLite™ ROC110 and AmberSorb™ L493 manufactured by DuPont. The AmberLite™ ROC110 is a PS-DVB gel-type resin with sulfonic groups that has been grafted for a quaternary amine. This treatment makes the resin surface oleophilic, so the resin can function as a chemically enhanced particle coalescer. The AmberSorb™ L493 is a PS-DVB macroporous non-functionalized resin. It is used as a polymeric adsorbent due to its extremely high BET surface area and unusual pore size distribution where there is a very high percentage of macropores.

Table 3-1. Resin matrix properties according to the manufacturer [180,181].

Product Name	AmberLite™ ROC110	AmberSorb™ L493
Removal Mechanism	Coalescence	Adsorption
Matrix	Styrene divinylbenzene copolymer	Styrene divinylbenzene copolymer
Structure Type	Gel	Macroporous
Functional Group	$-SO_3^-$	None
Ionic Form	H^+, grafted with a quaternary amine	Non-ionic
Maximum Temperature	120ºC	120ºC
Crush Strength	Not available	> 500 g/bead
Bulk density	850 g/L	620 g/L
Particle Size	750 mm	297-841 mm
Average Pore Size	Not available	46 Å
BET Surface area	Not available	~1100 m^2/g
Chemical resistance	Not resistant to detergents.	Resistant to strong acid, strong base and insoluble in organic solvents.

3.2 Particle Size Determination

The measurement of particle size for macroscopic particles was carried out with a MacroCam® Dynamic Imaging Particle Analyzer (Fluid Imaging Technologies Inc.). The MacroCam® analyzer uses Direct Imaging Particle Analysis (DIPA) to perform direct image-based particle measurements rapidly enough to produce statistically significant amounts of particle data. A resin sample is prepared and mixed with an impeller set to 600 rpm. A peristaltic pump then feeds the sample through the MacroCam® instrument at 800 mL/min (Figure 1). The sample containing the particles streams by the optics in the flow cell, which contains a high-resolution camera, backlit by high-intensity LED light source. The camera captures thousands of particle images per second (frame rate: 22 frames per second, flash duration: 7 µs), providing an accurate analysis of particle size and shape. DIPA analysis uses digital images to measure the size and shape of sample particle. The analyzer will gather numerous measurements for a single particle (frame rate: 22 frames per second, flash duration: 7 µs), providing an accurate analysis of particle size and shape. The analysis is stopped after 20,000 particle counts. Particle size range is 15 µm to 5 mm which includes the typical range of commercial Polystyrene/DVB Copolymer resin beads (75-1600 µm). Instrument accuracy in this range is ±1.2%, and in the range of fine mesh materials (15-500 µm) is ±4.4%.

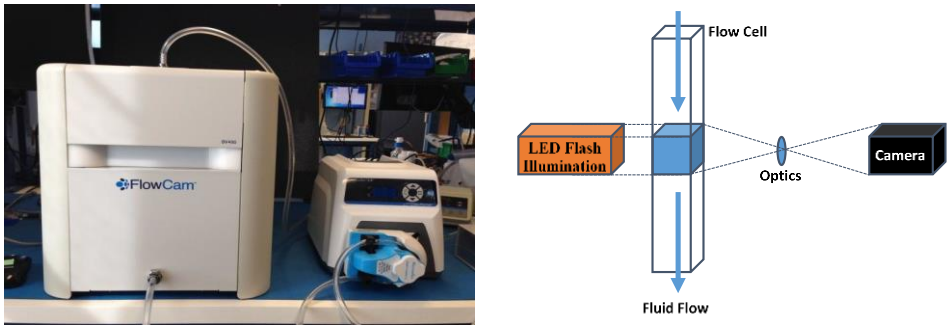

Figure 3-2. FlowCam Macro DIPA Solution for larger particles (15 µm to 5 mm).

Sample preparation for AmberSorb™ L493 was carried out by placing a sample of 0.5L of resin in a 4L beaker and with filtered demineralized water. In the case of AmberLite™ ROC110 –an oleophilic resin- the use of a surfactant was necessary in order to obtain accurate measurements. The surfactant prevents the formation of gas bubbles on the surface of resin beads, as well as the formation of resin clusters, which would distort the results. The surfactant used was CAT-FLOC 8108 PLUS (Nalco Ltd.).

3.3 Bulk density, Particle Density and Void Volume

The apparent or bulk density (ρ_B) and water retention capacity of an ion exchange resin are measured using ASTM Standard Method D2187-94 [182]. This method is called the settle-and-drain method, where resin beads are classified before performing the bed volume measurements. Bulk density is calculated using Equation *3-3*:

$$\rho_B = \frac{M}{V_B} \qquad 3\text{-}3$$

The particle density of a resin (ρ_R) can be measure following the procedures described by resin manufacturer DuPont [183]. In this method, 40 ml mater are placed in a 100 mL graduated cylinder, and the initial weight (W_i) and volume (V_i) are recorded. Wet resin –fully hydrated resin without any excess moisture– is added to the cylinder until the water level reaches around the 100 mL mark. Then the final weight (W_f) and volume (V_f) are recorded. Particle density is calculated using Equation *3-4*.

$$\rho_R = \frac{W_f - W_i}{V_f - V_i} \qquad 3\text{-}4$$

The estimation of a resin void volume fraction was also carried out following the procedures described by resin manufacturer DuPont [184]. Void volume fraction is calculated using Equation *3-5*.

$$\varepsilon = \frac{V_{VOID}}{V_{BED}} = \frac{[(M/\rho_B) - (M/\rho_R)]}{(M/\rho_B)} = \frac{\rho_R - \rho_B}{\rho_R} \qquad 3\text{-}5$$

3.4 Pressure Drop

Pressure drop measurements were carried out in a set-up consisting of a temperature-controlled glass column of 100 cm height and 5.3 cm of diameter. The feed stream is introduced to the column with a peristaltic pump from feed tank. It features a pressure indicator (PI) at the inlet and another at the outlet of the column, as well as a flow-meter at the inlet (FI). Temperature is controlled by a thermostatic bath through a closed circuit that circulates water through the column jacket (Figure 3-3). The procedure for pressure drop measurements consists of the following steps:

1. The thermostatic bath is set to a fixed temperature. Normally, the reference temperature is 25ºC.
2. The column is filled with water, and packed with resin until a bed height of approximately 0.5 m is reached.
3. The resin is backwashed bottom-to-top with distillate water. The flowrate –and linear velocity- in the column is given different values and the expansion of the bed is measured. Afterwards the resin is allowed to settle.
4. The water flow is switched to a top-to-bottom configuration. The flowrate –and linear velocity- in the column is given different values, measuring the corresponding pressure drop (dP) values.

For the testing of AmberLite™ ROC110, it was coated with a surfactant (CAT-FLOC 8108 PLUS, Nalco Ltd.). This is a special requirement of this resin because of the degassing caused by its oleophilic coating, as it tends to trap air bubbles on the surface of resin beads, forming clusters that distort dP measurements.

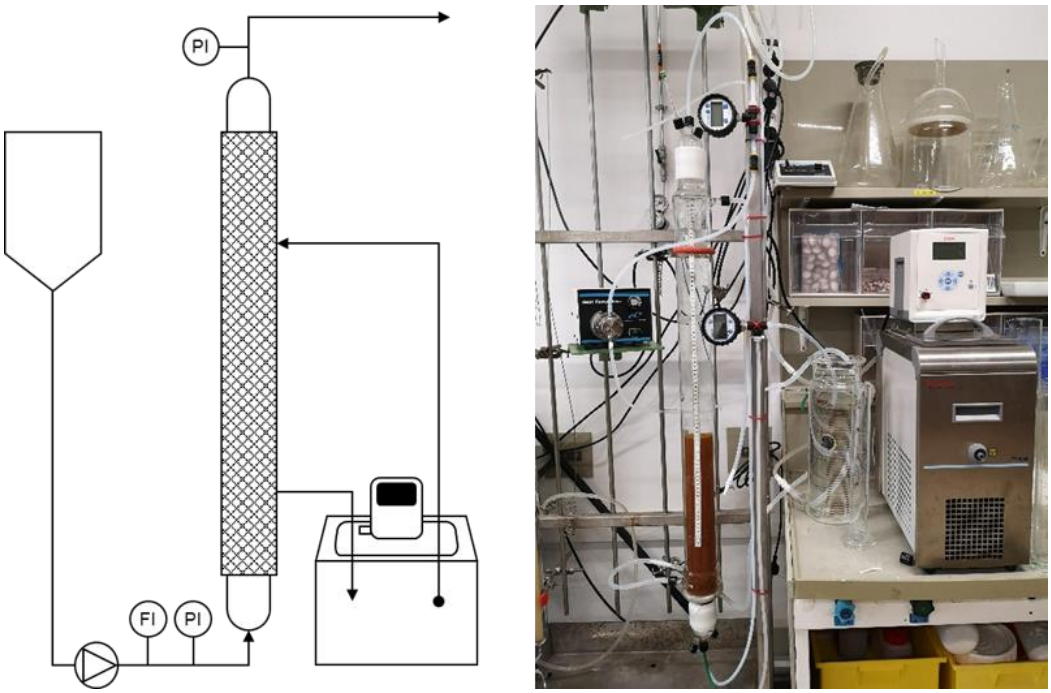

Figure 3-3. Set-up for pressure drop measurements.

4. Results and Discussion

4.1 Particle Size

The measurement of particle size through dynamic imaging generates a large amount of data in the form of particle diameter measurements (d_p). To extract information from such data, particle sorting must take place, where particles are sorted and counted in different categories comprising a range of particle diameters. From such data the frequency distribution is obtained, as well as the arithmetic mean (d_{AMS}), the harmonic mean (d_{HMS}), the median value, the mode, the uniformity coefficient, and the percentage of fines in a sample. Usually, a direct population analysis -particle size frequency ($f_{p,i}$)- is not really representative of resin properties. The volume percentage that each fraction of the particle size distribution occupies is more relevant. Therefore, the particle frequency is corrected by volume ($f_{V,i}$).

Table 3-2. Equations used for statistical particle analysis in resins.

Variable	Number-weighted Distribution	Volume-weighted Distribution
Frequency [%]	$f_{N,i} = \frac{N_i}{\sum_{i=1}^{n} N_i}$	$f_{V,i} = \frac{V_{p,i} \cdot N_i}{\sum_{i=1}^{n} V_{p,i} \cdot N_i}$
Arithmetic Mean Size [µm]	$d_{p,AMS,N} = \sum_{i=1}^{n} (f_{N,i} \cdot d_{P,i})$	$d_{p,AMS,V} = \sum_{i=1}^{n} (f_{V,i} \cdot d_{p,i})$
Harmonic Mean Size [µm]	$d_{p,HMS,N} = \frac{1}{\sum_{i=1}^{n} (f_{N,i}/d_{P,i})}$	$d_{p,HMS,V} = \frac{1}{\sum_{i=1}^{n} (f_{V,i}/d_{P,i})}$
Uniformity Coefficient [-]	$UC = \frac{d_{P,60}}{d_{P,10}}$	$UC = \frac{d_{P,60}}{d_{P,10}}$

Table 3-3. Summary Data Report of AmberLite™ ROC110 and AmberSorb™ L493.

Resin	AmberLite™ ROC110	AmberSorb™ L493
Number of Particles, N	20,000	20,000
Volume of superfines (d_p < 250µm) [%]	0.12	0.16
Particle Diameter at 10% (µm)	517.17	500.49
Particle Diameter at 60% (µm)	770.58	775.76
Particle Diameter at 90% (µm)	915.78	904.35
Uniformity Coefficient	1.49	1.55
Population Arithmetic Mean, $d_{p,AMS,N}$ (µm)	573.04	516.96
Population Median, $d_{p,MD,N}$ (µm)	581.91	532.66
Mode, Mo (µm)	710.00	710.00
Volume-Weighted Mean, $d_{p,AMS,V}$ (µm)	726.18	719.68
Volume Median Diameter, $d_{p,MD,V}$ (µm)	728.66	734.50
Harmonic Mean Size, $d_{p,HMS,V}$ (µm)	687.94	677.56

The volume-weighted particle size of a resin will usually follow a normal distribution, where the particle size directly derived from population analysis will not. Additionally, the population mean is lower than the volume weighted mean, owing to the presence of superfine particles, which represent a very small volume percentage. The population mean for AmberLite™ ROC110 is 573.6 ± 200.9 µm and for AmberSorb™ L493 is 517.5 ± 232.8 µm, whereas the volume weighted mean is 726.2 ± 153.6 µm for AmberLite™ ROC110 and 719.7 ± 153.8 µm for AmberSorb™ L493. In Figure 3-4, direct and the volume-weighted the particle size distribution have been represented, showing which illustrate this point.

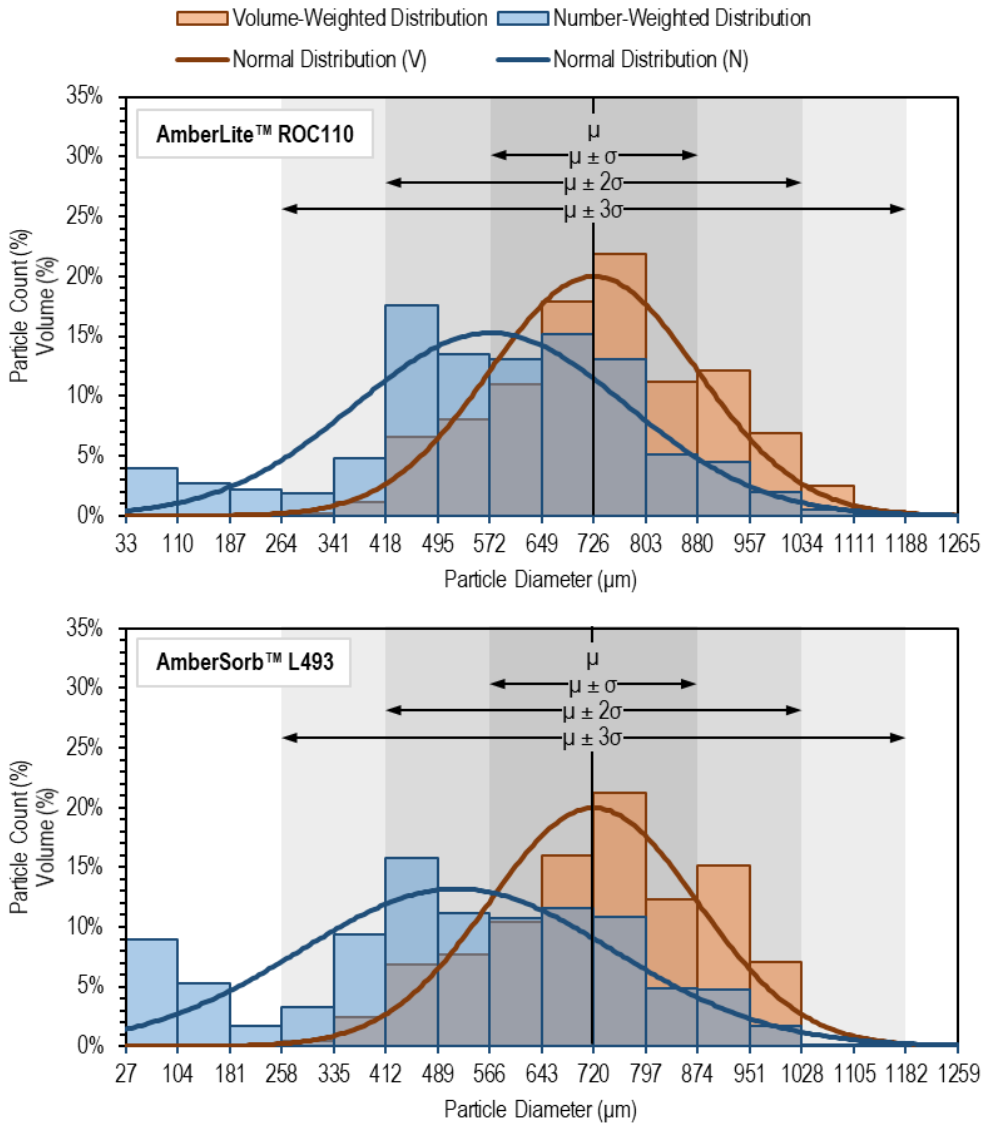

Figure 3-4. Particle size distribution of AmberLite™ ROC110 and AmberSorb™ L493.

The harmonic mean size (d_{HMS}) has been calculated, and it has been found to be somewhat smaller than the mean zise (d_{AMS}): 687.9 µm for AmberLite™ ROC110 and 677.56 µm. The Uniformity Coefficient (UC) is a numerical expression size variability in resins and is calculated as the ratio of the particle diameter at 60% and at 10% of cumulative frequency. The uniformity coefficient has been found to be 1.49 and 1.55 for AmberLite™ ROC110 and AmberSorb™ L493 respectively. This is a typical of non-uniform resins. Similarly, the percentage of superfine particles (with diameters < 250µm) has been found to be < 2% in both cases, which is within typically acceptable values for commercialization. The results obtained in particle analysis are in accordance with products specifications and –being representative of this product– can be used for future modelling purposes.

4.2 Bulk density, Particle Density and Void Volume

Although bulk density (ρ_B) and water retention are usually specified by the manufacturer, there are other characteristic parameters that affect the properties of a resin bed that are not included in published material. The values for bulk density and water retention capacity obtained empirically match reasonably well with those provided with the product documentation that have been collected in Table 3-1. Additionally, the results also include resin density (ρ_R) and void volume (ε), for which we had no reference values. In the results we see that AmberLite™ ROC110 has much higher resin density (ρ_R) than AmberSorb™ L493. The difference can be surely attributed to the fact that AmberSorb™ L493 has very high porosity compared to typical ion-exchange resins. There are also noticeable differences in the void volume that were obtained. The AmberSorb™ L493 resin has a 35% void volume, which would be consistent with a tighter packing of the resin beads, and the AmberLite™ ROC110 resin has a void volume of 40%, which would represent a looser packing. The measurements remain between the two theoretical extremes represented by the pure hexagonal packing (25.9%) and the pure cubic packing (47.6%), and like most ion exchange resins they have an ε of 34-40%. Such difference can be partially explained by the fact that AmberSorb™ L493 has a larger uniformity coefficient -meaning a higher number of particles that can be packed in interstitial spaces- lending itself to a more compact bed. Additionally, particle interactions with the fluid -water in this case- cannot be discounted. The surface treatment of AmberLite™ ROC110 that makes it highly hydrophobic, alters its interactions with water and wet surfaces as well as other fluids like air.

Table 3-4. Experimental values for bulk density, resin density, water retention and void volume.

Resin Product	Bulk Density (mg/L) WET	Bulk Density (mg/L) DRY	Water Retention [%]	Resin Density (mg/L)	Void Volume [%]
AmberLite™ ROC110	800 ± 40	510 ± 50	37 ± 3	1340 ± 60	40 ± 5
AmberSorb™ L493	620 ± 20	270 ± 40	56 ± 8	970 ± 30	35 ± 4

4.3 Pressure Drop

4.3.1 Experimental measurements

The expansion of a bed in upflow mode is an important consideration for the design of resin bed columns. This is true even when the loading phase is happening in downflow mode, as in this case regeneration phase is happening in upflow. Bed expansion (BE) is calculated by the subtraction of a packed bed's settled depth bed (Z_B) -previously classified- to the expanded bed depth (Z_{FL}) in upflow configuration for any given linear velocity.

$$\mathrm{BE}\ [\%] = (Z_{\mathrm{FL}} - Z_{\mathrm{B}}) \times 100 \qquad \text{3-6}$$

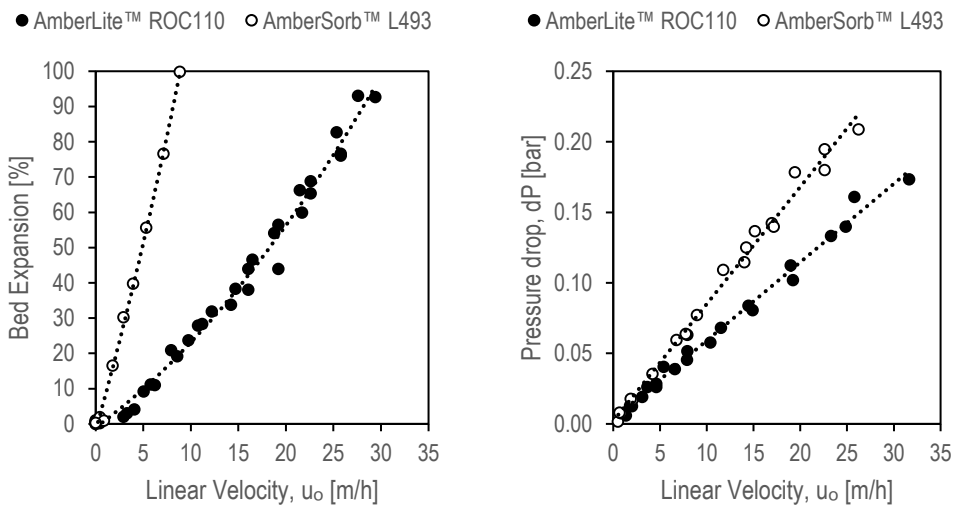

Figure 3-5. Bed expansion and bed pressure drop for AmberLite™ ROC110 and AmberSorb™ L493.

The bed expansion for a bed of AmberLite™ ROC110 and AmberSorb™ L493 is represented in Figure 3-5. Bed expansion for AmberSorb™ L493 requires lower linear velocities. It is thought that this is justified by the much lower resin density of this type of resin. In contrast, the behavior of AmberLite™ ROC110 shows that bed expansion is not very significant at lower velocities (<5 m/h). This is an important property, as this resin is designed to operate in upflow mode -coalescer mode-, and bed fluidization in not recommended.

The pressure drop has been calculated by subtracting the value of the pressure drop across the empty column to the values of the measured pressure drop (Equation *3-7*).

$$dP_{BED} = dP_{LOADED} - dP_{EMPTY} \qquad 3\text{-}7$$

The dP values obtained do not contemplate the pressure drop of the installation, including the physical column, valves and nozzle plates. The results show that the resin AmberSorb™ L493 has a larger pressure drop than the AmberLite™ ROC110. This is also consistent, given that AmberLite™ ROC110 has a slightly larger harmonic mean size and also higher void volume.

4.3.2 Pressure Drop modelling

The modelling of the pressure drop in the resin column bed was carried out with the Kozeny-Carman (Equation *3-1*) and the Ergun equation (Equation *3-2*). The equivalent particle diameter (d_p) used is the Harmonic Mean Size determined in section 3.1 ($d_{HMS,V}$). Experimental Void Volume (ε) values in section 3.2 were used. The viscosity of water was calculated using the Vogel equation. For the fluid density the DIPPR105 Equation was used. The parametric values and the calculated property values used are included in Table 3-5.

Table 3-5. Equations and values of fluid properties (Temperature in K).

Variable	Equation	Units	Parameters A	B	C	D	Value at T = 20ºC	Ref.
Viscosity	$\eta = e^{A+\frac{B}{C+T}}$	mPa·s	-3.7188	578.919	-137-546	-	1.00166	[185]
Density	$\rho_F = \frac{A}{B^{1+\left(1-\frac{T}{C}\right)^D}}$	kg/m³	0.14395	0.01120	649.727	0.05107	1002.09	[186]

The results of modelling the pressure drop have been represented in Figure 3-6. In the case of the AmberLite™ ROC110 resin, the best fit was for the Kozeny-Carman Equation. In the case of AmberSorb™ L493, the best fit was exhibited by the Ergun Equation. The differences in the equation fit cannot be attributed to regime flow. The calculation of the Reynolds Number (Re) for the particle bed shows that in the range of velocities for the experiments the system remained in a purely laminar flow (Re <10). Both equations are equally valid from a theoretical point of view, and the small differences in the data fit are likely due to the small variations in the equation constants for laminar flow.

Table 3-6. Fluid and Resin values used for the modelling of Pressure drop, with model fit statistics.

		Amberlite™ ROC110		AmberSorb™ L493	
		Ergun	Kozeny-Carman	Ergun	Kozeny-Carman
Fluid Properties	Temperature, T [ºC]	20	20	20	20
	Viscosity, η [Pa·s]	$1.0017 \cdot 10^{-3}$	$1.0017 \cdot 10^{-3}$	$1.0017 \cdot 10^{-3}$	$1.0017 \cdot 10^{-3}$
	Density, ρ_F [kg/m³]	1002.09	1002.09	1002.09	1002.09
Resin properties	Particle Size, d_p [µ]	687.94	687.94	677.56	677.56
	Void Volume, ε [-]	0.353	0.353	0.404	0.404
	Sphericity, Φ_p [-]	1	1	1	1
Model Fit	Mean Square error, e^2	$1.67 \cdot 10^{-2}$	$6.77 \cdot 10^{-3}$	$1.78 \cdot 10^{-3}$	$1.49 \cdot 10^{-2}$
	Determination coefficient, R^2	0.80	0.93	0.98	0.90

These small differences however, are not entirely significant. The estimation of dP for polymeric resins is inherently imprecise. The precision with which dP values can be estimated for a resin bed is not smaller than ± 20% [187]. Small batch-to-batch variations in particle size, and consequently bulk density and void volume, are inevitable in resin production. This is not entirely trivial, as a 5% reduction in d_P may result in as much as 11% pressure drop increase. Furthermore, a mere 2% variation in ε will result in as much as 9% difference in pressure drop estimations. In the estimations that have been carried out in this chapter, there is a reasonably good fit because the resin used for the determination of the dP, d_p and ε was from the same production batch. If the uncertainty for the measurement of ε is introduced as specified in Table 3-4 (4-5%) and for d_p as per the method error specified in Section 2.2 (1.2%) the minimum and maximum estimated values for dP show differences that far exceed the differences between the values projected by the Ergun and Kozeny-Carman equations with average values. The minimum and maximum estimated values using the Kozeny-Carman equation have been represented in Figure 3-6 alongside the experimental data. We can see that both models are acceptable considering the error existing within the measurements of resin properties. From a purely pragmatic point-of-view, using the Kozeny-Carman equation for estimating dP would be more appropriate, as it tends to estimate higher values for dP. Additionally, an appropriate safety factor (SF) should be applied –ideally SF = 2 – in any future column and system designs.

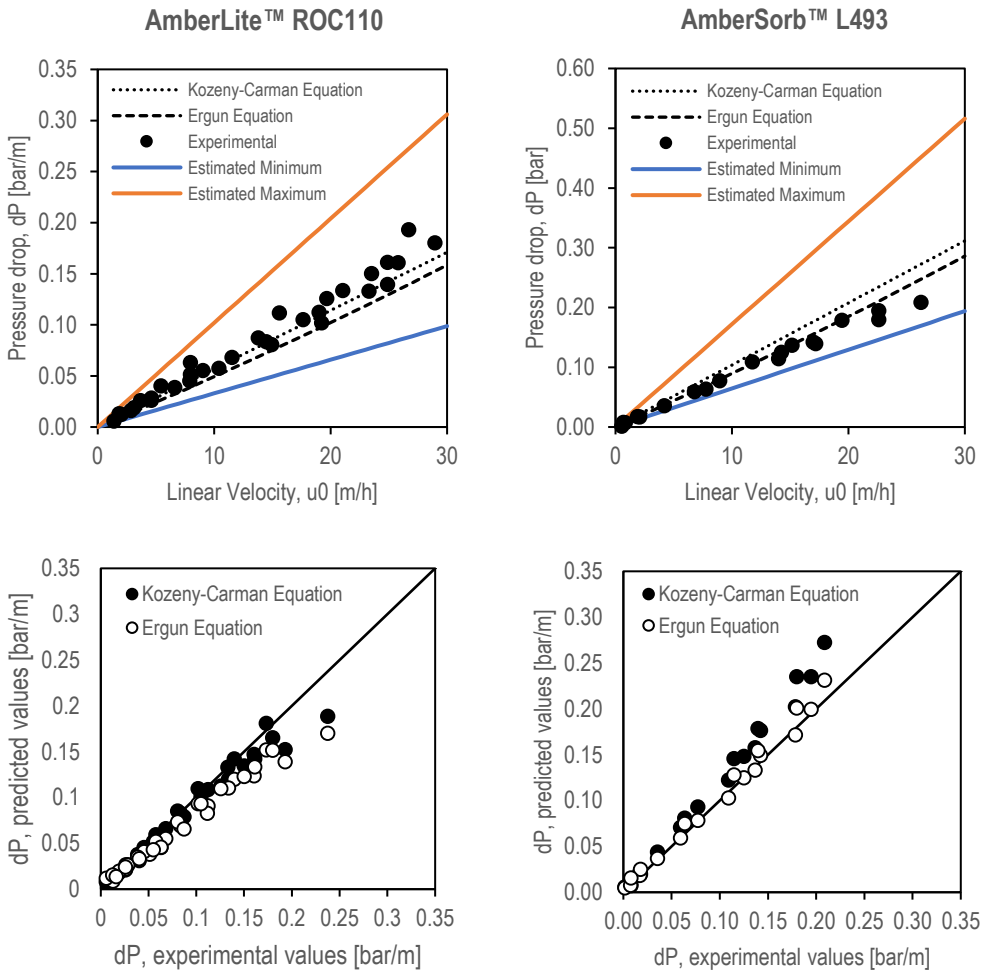

Figure 3-6. Model fit for the Kozeny-Carman and the Ergun Equation.

Because the experiments were carried out at constant temperature and, because of limitations in the testing equipment, the values of dP at different temperature would have to be estimated by extrapolation using the model. That also applies to differences in viscosity brought on by different amounts of oil in the fluid phase. Typically, the viscosity of produced water varies from 1.5 to 2 centipoise at 10°C, 0.7 to 1 centipoise at 38°C, and 0.4 to 0.6 centipoise at 65°C [188]. The projected variations of dP from the variation of temperature –in water– and viscosity –for other compositions– have been represented in Figure 3-7.

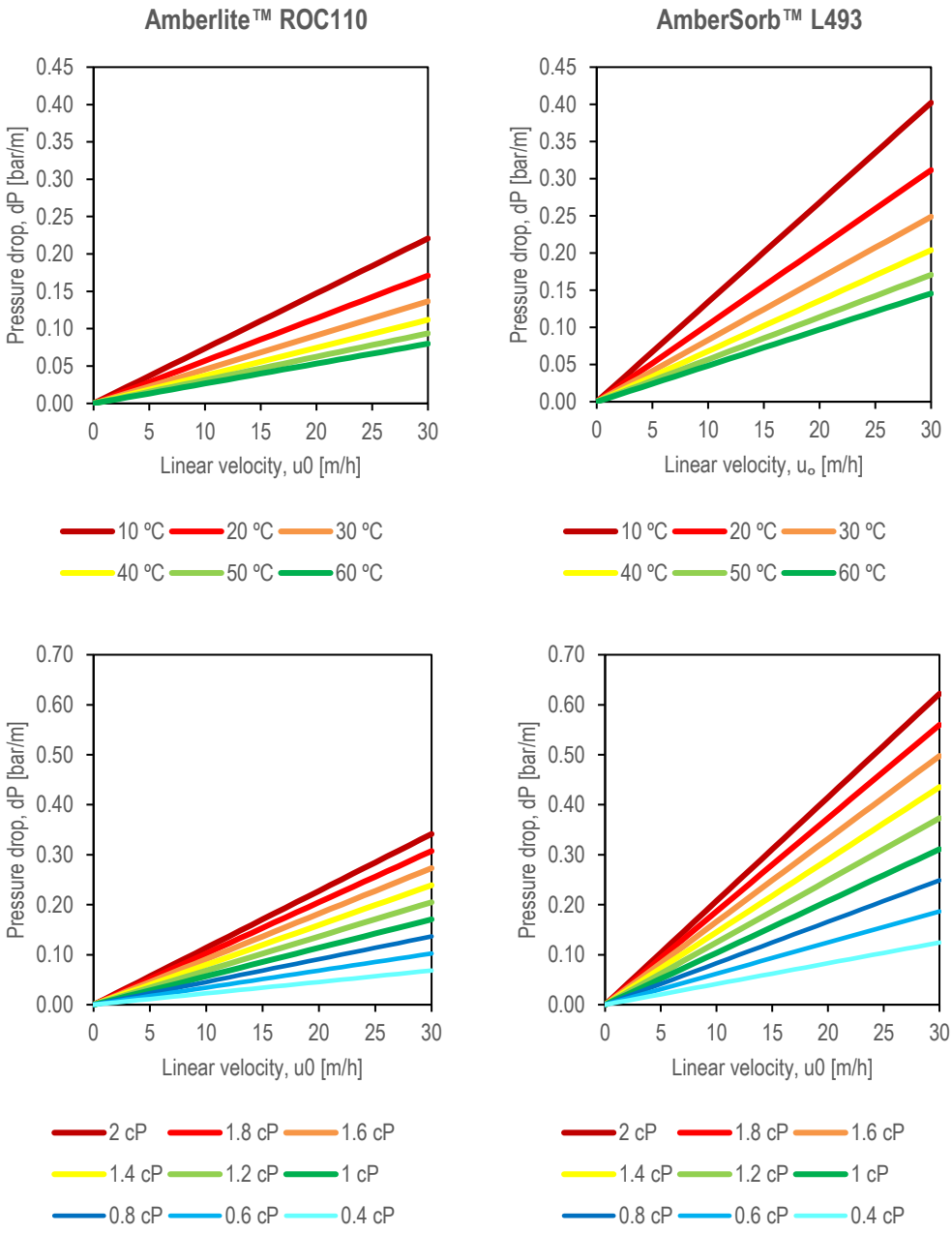

Figure 3-7. Projected dP for different temperatures and viscosities.

5. Conclusions

The characterization of AmberLite™ ROC110 and AmberSorb™ L493 has been achieved through particle size, pressure drop and void volume determination:

- Accurate measurements of particle size have been obtained for both resins using Direct Imaging Particle Analysis (DIPA), and an appropriate particle size distribution curve was developed. This distribution is representative of these resins and can be used as reference for future calculations.
- A void volume fraction was determined for a resin bed of the target resins. AmberLite™ ROC110 shows an unexpectedly high void volume fraction (ε) given is particle size and uniformity coefficient, caused by its singular functionality and hydrophobic surface. Its determination has allowed to more closely define the system, for accurate modelling.
- Accurate pressure drop (dP) measurements have been obtained that have provided accurate pressure drop curves based on experimental data.
- This chapter has verified that either the Kozeny-Carman or the Ergun equation provide an adequate tool to predict and model the pressure drop behavior of both AmberLite™ ROC110 and AmberSorb™ L493. Although the Ergun equation is generally more reliable given that it is accurate at both low and high velocities, in practice the simple Kozeny-Carman is perfectly adequate for this application given the low velocities at which coalescers and adsorption systems typically operate at.

Chapter 4

Removal of emulsified oil by coalescence through a particle bed

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Chapter 5

Removal of dissolved oil by adsorption

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Chapter 6

Case study of a de-oiling system for oil removal

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Chapter 7

Conclusions

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Our thesis has been that polymeric resin can be used to clean-up oil wastewater and other hydrocarbon contaminated waters. However, the design of resin-based oil removal systems is a complex endeavor that requires in-depth knowledge of both the technology itself and the streams to be treated.

The composition of oily water

The organic species most commonly found in oily wastewater include linear and branched alkanes, aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), phenolic compounds and organic acids. Most of these compounds are either natural components of oil or products of hydrocarbon degradation. On a case-by-case basis, oily wastewater can also contain a number of oxygenate compounds of the family of esters, ethers, aldehydes and ketones. Many of these components are oil and fuel additives and can have great effect over an oil-removal processes.

But although the type of compounds found in oily water is pretty consistent, oil water is an extremely variable type of wastewater. Variability exists over time, subject to atmospheric and process variations, and between different kinds of streams. Previous to the design of a de-oiling system, it is strongly recommended to carry out a chemical analysis of a representative sample to quantify Total Petroleum Hydrocarbons or TPH, BTEX (benzene, toluene, ethylbenzene and xylene), Polycyclic Aromatic Hydrocarbons or PAHs and phenol index. A qualitative analysis of the feed stream is also recommended to identify any potentially problematic compounds. On the adequate characterization of oily water resides our ability to correctly design adequate oil-removal systems and make adequate recommendations.

Coalescence with modified resins

The use of **resins coated with quaternary-ammonium −like AmberLite™ ROC110− can efficiently remove emulsified oil from water**. This emulsified oil is most adequately quantified as TPH or some other type of Oil & Grease measurement. It is particularly **efficient in the separation of the oil fractions with high molecular weight and low water solubility**, specifically molecules in the diesel range (C9-C25). Oily wastewater with large amounts of insoluble oil and low amounts of suspended solids is a good candidate for coalescence treatment. Coalescer resins are not suited to the treatment of hydrocarbon-bearing waters that carry large amounts of TOC, without a correspondingly high amount of TPH. AmberLite™ ROC110 will not remove soluble organics from wastewater, however its use is still recommended if oil-sensitive technologies are used downstream.

The process of coalescence with AmberLite™ ROC110 is strongly **influenced by the feed concentration and the linear velocity** of the resin bed. These two factors are the most important considerations in the design of a resin coalescer bed and help define a system's efficiency. However, there are other important factors that strongly influence removal efficiency, particular composition. **Every oily wastewater's specific make-up is unique, making it impossible to accurately predict removal efficiency** even with a detailed composition report. There is a number of species that can be present in oily water and are part of soluble oil −also typically included in the TPH index− that act as surfactants. Surfactants act as emulsion stabilizers, and as such will have a negative effect on process efficiency. The design of coalescer systems in wastewater streams carrying very large amounts of surfactants is not recommended. Bench-testing or piloting is considered the best avenue to determine viability and before full industrial design is attempted.

Additionally, **high amounts of suspended solids are a limiting factor in the implementation** of this technology. A high amount of suspended solids −over 10 mg/L of TSS− will cause an irreversible layer of fouling to grow atop the resin bed. The recommendation should be to **use an appropriate pre-treatment technology**. There are several options in this regard depending on the particularities of each stream. Coalescer

resins are a technology for secondary oil treatment and must usually be preceded by a primary oil treatment step. A vast number of them can achieve significant TSS removal by themselves, including gravity separators, decanters, clarifiers, and even Dissolved Air Flotation (DAF). Other options in instances where space is more limited, desanding hydrocyclones or multi-media filters can be used, depending on the total amount of TSS and the amount of oil.

Adsorption of oily water with synthetic adsorbents

Adsorption of oil water onto AmberSorb™ L493 is a complex phenomenon. The adsorption of the different components found in dissolved oil is influenced by their polarity and solubility. **Adsorption is favored by decreasing polarity and solubility in water**, which normally go hand-in-hand. Therefore, typical components were more strongly adsorbed in this order: **naphthalene (PAHs) > toluene (BTEX) > phenol > acetate (smaller organic acids)**. This is evident both in single-component adsorption and multi-component adsorption, with synthetic and real wastewater samples. There is an extremely high selectivity towards the adsorption of naphthalene (PAH) and toluene (BTEX), while polar charged organics are not adsorbed. It has been observed that adsorption of oily water presents a very **clear case of chromatographic peaking** during an adsorption cycle.

The adsorption of oily water is a case of **non-ideal multicomponent adsorption behavior**, where interactions between organic solutes affect the adsorption of the individual components. This means that **modelling the multicomponent adsorption of oil, based exclusively on the single-component isotherms of common oil components is not possible**. In order to develop an accurate predictive tool, further experiments would have to be carried out, that have been currently carried out. This would necessarily include adsorption experiments with different mixtures of components, in different combinations in order to determine the interaction between oil components.

Regarding the regeneration and recovery of spent adsorbents, **desorption with steam is considered the best solution** with environmental considerations in mind. The water recovery using steam regeneration is as high as 90%, with small amounts of generated waste, and does not require the use of additional costly equipment or added chemicals. Nonetheless, one must consider that there will be a loss of total adsorption capacity between 10 and 20%. On the other hand, one must consider that regeneration with steam is not possible when non-volatile species are being adsorbed. In cases where emulsified oil is removed by adsorption alongside dissolved oil, steam regeneration will only be partially effective.

Asphaltenes are a known foulant of adsorbents, where they are strongly attached and come to block the pores. Heavier components of oil will tend to accumulate, diminishing resin capacity with each cycle. Regeneration of asphaltene-contaminated resin is only possible with a water-miscible organic solvent such as methanol. However, regeneration with methanol is not usually desirable for end-users, as methanol is by itself a problematic and highly flammable waste. The recommendation is that **waste streams known to carry emulsified oil should implement appropriate pre-treatment −like AmberLite™ ROC110− so that only dissolved oil is adsorbed onto AmberSorb™ L493**. If the adsorbent should be fouled irreversibly in a period of system upset, then the methanol as sporadic solution would be encouraged.

Annex 1

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