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**Application of micellar enhanced ultrafiltration for the removal of soluble organic
compounds present in produced water**

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Application of micellar enhanced ultrafiltration for the removal of soluble organic compounds present in produced water

Master dissertation for the degree of Master in Chemical Engineering presented to the Graduate Program in Chemical Engineering at Federal University of Santa Catarina.

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RESUMO

A água produzida é atualmente o maior efluente da indústria de petróleo e gás. Alguns dos compostos presentes na água produzida são classificados como compostos orgânicos solúveis, como os ácidos naftênicos (ANs). Devido à solubilidade desses compostos em água, a ultrafiltração com o uso de surfactantes é uma técnica promissora para remoção de ANs, uma vez que as moléculas de surfactante englobam os contaminantes de modo a formar estruturas maiores, possibilitando, assim, sua retenção por membranas de ultrafiltração. O ácido ciclohexanocarboxílico foi filtrado neste estudo com membranas poliméricas fabricada em poliéster sulfona (PES) com tamanho de poro de 10 kDa. Um planejamento fatorial completo 2^2 foi elaborado para os ensaios de ultrafiltração, e os parâmetros avaliados foram a pressão através da membrana (TMP) e a concentração de surfactante adicionada à corrente de alimentação. Para correta dosagem de surfactante nos ensaios, a concentração micelar crítica (CMC) foi determinada para os surfactantes CPC, SDS e Triton X-100 na presença do ácido naftênico pelo método de tensão superficial. A concentração de AN foi determinada por FTIR. A ultrafiltração com o surfactante CPC se mostrou uma técnica satisfatória para remoção do ácido ciclohexanocarboxílico em pH ácido, alcalino e neutro. A melhor condição obtida foi com 50 vezes a CMC do surfactante e TMP de 4.0 bar, com remoção de 68 % de AN, indicando a ultrafiltração com o CPC uma alternativa promissora para remoção de ácidos naftênicos.

Palavras-chave: Ultrafiltração com surfactantes. Água produzida. Ácidos naftênicos.

RESUMO ESTENDIDO

Introdução

A água produzida é atualmente o maior efluente da indústria de petróleo e gás, sendo composta por uma emulsão complexa de fase orgânica dispersa na fase aquosa. Alguns dos compostos presentes na água produzida são classificados como compostos orgânicos solúveis, como os ácidos naftênicos (ANs). Devido à solubilidade desses compostos em água, a ultrafiltração com o uso de surfactantes é uma técnica promissora para remoção de ANs, uma vez que as moléculas de surfactante englobam os contaminantes de modo a formar estruturas maiores, possibilitando, assim, sua retenção por membranas de ultrafiltração.

Objetivos

O objetivo deste trabalho é avaliar a remoção de compostos orgânicos solúveis classificados como ácidos naftênicos através da técnica de separação de ultrafiltração com membranas e uso de surfactantes. Para a correta dosagem de surfactante nos ensaios de ultrafiltração, foi determinada a concentração micelar crítica (CMC) de cada surfactante utilizado – sendo estes cloreto de cetilpiridínio (CPC), dodecil sulfato de sódio (SDS) e Triton X-100 (TX100) – em solução aquosa de ácido ciclohexanocarboxílico. Para os ensaios de ultrafiltração, os parâmetros avaliados foram o pH, a natureza iônica do surfactante, a pressão através da membrana, a concentração de surfactante adicionada à corrente de alimentação, a remoção de ácido naftênico e o fluxo de permeado.

Metodologia

O AN utilizado como contaminante padrão neste estudo foi o ácido ciclohexanocarboxílico, selecionado devido a sua elevada solubilidade em água (2 g L^{-1}), baixa massa molar ($128,17 \text{ g mol}^{-1}$) e cadeia cíclica, características estas que podem dificultar a formação de micelas. A membrana polimérica utilizada nos testes de ultrafiltração foi fabricada em poliéster sulfona (PES) com tamanho de poro de 10 kDa. Um planejamento fatorial completo 2^2 foi elaborado para os ensaios de ultrafiltração, e os parâmetros avaliados foram a pressão através da membrana e a concentração de surfactante adicionada à corrente de alimentação. A concentração micelar crítica foi medida por tensão superficial em solução aquosa contendo 500 mg L^{-1} de ácido ciclohexanocarboxílico na presença dos surfactantes cloreto de cetilpiridínio (CPC), dodecil sulfato de sódio (SDS) e Triton X-100 (TX100), com naturezas catiônica, aniônica e não-iônica, respectivamente. A quantificação de AN foi realizada por FTIR. Para tal, as amostras aquosas de filtrado foram submetidas à extração com o solvente orgânico diclorometano, realizada através de agitação para promover a transferência do AN da fase aquosa para a orgânica. Uma vez que a passagem de monômeros de surfactante pela membrana é um fenômeno inerente à técnica de ultrafiltração com uso de surfactantes, a etapa de agitação ocasionou a formação de emulsão entre as fases aquosa e orgânica. Por este motivo, a metodologia de extração para leitura no FTIR sofreu modificações ao longo do estudo de acordo com o surfactante utilizado.

Resultados e discussões

A ultrafiltração com membranas para remoção de ácido ciclohexanocarboxílico – selecionado neste estudo como um ácido naftênico modelo – mostrou ser uma técnica bem-

sucedida para remoção de ANs com o surfactante CPC em soluções ácidas, alcalinas e neutras. Ainda que o ácido ciclohexanocarboxílico possua alta solubilidade em água, cadeia carbônica cíclica e baixo peso molecular, o planejamento experimental proposto neste trabalho atingiu uma remoção de ácido naftênico de 68 % usando 50 vezes a CMC e pressão através da membrana de 4.0 bar. Ambos os experimentos utilizando 50 CMC nas pressões de 2.0 e 4.0 bar apresentaram remoções do ácido similares (68 e 67 %, respectivamente), o que sugere que pressões maiores podem ser testadas a fim de aumentar o fluxo de permeado e manter o percentual de remoção.

O método de determinação da concentração micelar crítica por tensão superficial foi verificado de maneira satisfatória para correta dosagem de surfactante nos ensaios de ultrafiltração. Os resultados obtidos para cada surfactante em solução aquosa (somente o surfactante em água) foram semelhantes aos encontrados na literatura. Para o SDS, a CMC encontrada foi abaixo do valor reportado na literatura; entretanto, ao repetir a determinação da CMC com um SDS de maior pureza (99 %), o valor obtido foi semelhante ao encontrado na literatura. Este fato demonstra que a presença de impurezas ou outros compostos diminui a CMC, visto que estas competem com as moléculas de surfactante para saturar a interface livre. A CMC na presença de ácido ciclohexanocarboxílico foi reduzida em relação a CMC somente em água, uma vez que o ácido naftênico atua como surfactante (molécula anfifílica), com percentuais de redução de 68 %, 44 % e 58 % para os surfactantes CPC, SDS e TX100, respectivamente.

Para os testes com o Triton X-100, as remoções de AN foram muito próximas de zero de acordo com testes propostos no planejamento experimental. Além disso, na análise de tamanho de micela, foi verificado que o surfactante não apresentou um aumento do tamanho de micela na presença do ácido ciclohexanocarboxílico. O ácido valérico foi também testado em uma filtração com o TX100; porém, a remoção deste AN foi também próxima de zero e, portanto, insatisfatória.

A fim de verificar se o surfactante teria influência na resposta fornecida pelo FTIR, um teste de Tukey para o surfactante Triton X-100 revelou não haver diferença entre as absorvâncias médias com e sem surfactante nos pontos avaliados da curva de calibração. Desta forma, a curva padrão de AN foi utilizada sem a necessidade de um fator de correção devido à presença do surfactante. Já com o surfactante CPC, foi considerada uma perda de 4.75 % em termos de absorvância. Para o surfactante SDS, o tempo de filtração com 10 vezes a CMC – utilizando a membrana de 10 kDa e pressão através da membrana de 4.0 bar – foi de mais de 10 horas até a conclusão do experimento. Por este motivo, os testes de ultrafiltração não foram realizados com o surfactante SDS.

Considerações finais

O surfactante catiônico CPC demonstrou ser satisfatório para a remoção do ácido naftênico, ainda se tratando de um composto orgânico de alta solubilidade, com cadeia carbônica pequena e cíclica. Pressões de filtração mais altas combinadas a dosagens de surfactante maiores são parâmetros promissores para pesquisas futuras com o CPC para remoção de ácidos naftênicos. Além disso, diferentes surfactantes podem ser testados para formação de micelas mistas com os ANs.

Palavras-chave: Ultrafiltração com surfactantes. Água produzida. Ácidos naftênicos.

ABSTRACT

Produced water (PW) is the major effluent of O&G industry and it is composed of a complex emulsion in which the oily phase is dispersed in the aqueous phase. Some of the compounds present in PW are denominated water soluble organics (WSO), which include naphthenic acids (NAs). Due to the solubility of NAs in water, micellar enhanced ultrafiltration (MEUF) is a promising technique for the removal of WSO since surfactants trap the contaminants into larger structures to retain it in UF membranes. Cyclohexanecarboxylic acid solution was filtered in this work with polymeric membranes (PES) of 10 kDa according to a complete 2^2 factorial design varying TMP (transmembrane pressure) and surfactant concentration in the feed. For proper dosage of surfactant in MEUF experiments, the CMC of CPC, SDS and TX100 was determined in the presence of NA by surface tension method. NA concentration was determined by FTIR analysis. MEUF using CPC was satisfactory for the removal of cyclohexanecarboxylic acid in acid, alkaline and neutral pH. The optimal filtration condition was achieved with 50 times the CMC and TMP of 4.0 bar, with 68 % of NA removal indicating the surfactant as a promising alternative for the removal of naphthenic acids.

Keywords: Micellar enhanced ultrafiltration. Produced water. Naphthenic acids.

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LIST OF ABBREVIATIONS AND ACRONYMS

CMC – Critical micelle concentration

CPC – Cetylpyridinium chloride

DLS – Dynamic light scattering

FTIR – Fourier-transform infrared

MEUF – Micellar enhanced ultrafiltration

MWCO – Molecular weight cutoff

O&G – Oil and gas

PW – Produced water

SD – Standard deviation

SDS – Sodium dodecyl sulfate

SI – International system of units

TMP – Transmembrane pressure

TX100 – Triton X-100

UF – Ultrafiltration

WSO – Water soluble organics

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1 INTRODUCTION

The oil and gas industry operations are water-intensive, and therefore cost-effective water management is a major topic for most segments of the petroleum industry. The water to be treated is either co-produced with the hydrocarbons, generated as a by-product from oil and gas processing, and/or used to support on production activities. These water streams are denominated produced water (PW) (ADHAM et al., 2018). In 2009, estimated produced water brought to surface was in 21 billion barrels per year in the US and 50 billion barrels per year in the rest of the world (DICKHOUT et al., 2017). The abundant quantities of discharge associated with the complex compounds, such as water soluble organics, present in produced water have made the effluent a target of concern and research in recent years (BAKKE; KLUNGSØYR; SANNI, 2013).

Advanced treatment of produced water has been motivated for several reasons such as modifications of regulatory guidelines, regional water scarcity and operational challenges (ADHAM et al., 2018). Regulatory guidelines for the discharge of produced water are necessary since the bulk of this effluent is released into the environment causing environmental and economic impacts (ALZHRANI; MOHAMMAD, 2014). Treated PW can be reused for several purposes such as irrigation and reinjection into wells to improve oil extraction (WESCHENFELDER et al., 2015). However, produced water composition varies from well to well, raising the need to address environmental standards according to the specific region (LEE; NEFF, 2016). From an economic perspective, there is an emerging need to obtain sustainable, efficient and cost-effective technology for water purification in large scale (DE; MONDAL, 2012).

Membrane technology aiming the treatment of produced water is an attractive separation process. Membranes are able to retain particles smaller than 10 μm (nanofiltration) and stable oil droplets from PW. In addition, there is a wide range of operational parameters which can be adjusted according to the specific properties of the oil in each reservoir (DICKHOUT et al., 2017). The advantage of using membranes rather than other conventional separation processes consists in the implementation of a continuous operation mode (ROSEN, 2004). Furthermore, micellar enhanced ultrafiltration – which is based on the use of surfactant to involve the contaminants particles and increase the size of the structures – allows the use of membranes with larger pore sizes resulting in a higher permeate flux and higher contaminant retention ratio (DERISZADEH; HARDING; HUSEIN, 2009).

In this work, MEUF was proposed as an alternative treatment for the removal of a class of water soluble organics known as naphthenic acids by the use of a nonionic, a cationic and an anionic surfactant. The novel of this work is based on the use of a naphthenic acid with low molecular weight, high solubility in water and cyclic carbon chain – all characteristics which may difficult naphthenic acid removal by micellar enhanced ultrafiltration. In this context, cyclohexanecarboxylic acid was selected for filtration experiments, supposing that the success of its removal may be suitable for other naphthenic acids. NA concentrations were determined by FTIR and modifications were required during preparation of samples according to the surfactant used. The critical micelle concentration for each surfactant in the presence of cyclohexanecarboxylic acid was assessed in order to assertively dose the surfactant concentration for MEUF experiments.

1.1 OBJECTIVES

1.1.1 General objective

The general objective of this work is to evaluate the removal of water soluble organics (WSO), such as naphthenic acids, by micellar enhanced ultrafiltration (MEUF).

1.1.2 Specific objectives

In order to achieve the general objective, the following specific objectives were addressed:

- I. Determination of critical micelle concentration (CMC) in the presence of cyclohexanecarboxylic acid for the surfactants:
 - i. Cetylpyridinium chloride (CPC);
 - ii. Sodium dodecyl sulfate (SDS);
 - iii. Triton X-100 (TX100).
- II. Assessment of the influence of the operational variables:
 - i. pH;
 - ii. Surfactant feed concentration;
 - iii. Transmembrane pressure (TMP).

2 LITERATURE REVIEW

A review of the literature is presented containing the major topics of this work. The main characteristics and treatment technologies of produced water are summarized. Membrane technology, micellization and interfacial behavior of surfactants are detailed. Micellar enhanced ultrafiltration definition and its state of art on the removal of soluble organic compounds is also presented.

2.1 PRODUCED WATER

The production of oil and gas occurs by deep drilling the surface of the Earth to recover hydrocarbons and attend the global energy demand. In this processes, water streams are brought to the surface as a by-product called produced water (MUNIRASU; HAIJA; BANAT, 2016). Produced water is estimated to be the largest waste stream in the exploration and production of oil and gas. PW characteristics and volumes depend on the natural geological formation and the age of the reservoir. Over time, the fraction of oil and gas decreases and the fraction of water increases (EBRAHIMI et al., 2010). Produced water can be naturally formed in the well or it can be derived of water reinjection used to improve oil recovery and manage reservoir pressure. Though, few portions of produced water are treated for reuse and/or recycle purposes worldwide (ADHAM et al., 2018).

2.1.1 Main characteristics of produced water

PW is a complex and stable emulsion in which the oily phase is dispersed in the aqueous phase, also known as an oil-in-water emulsion. The complexity of PW is due to its many constituents, such as dispersed oil, dissolved organics, suspended solids and dissolved inorganics. (LEE; NEFF, 2016). The extraction and production of oil and gas may bring to surface PW with oil and grease fractions above 500 mg L^{-1} and salt concentrations varying from 80 to $200\,000 \text{ mg L}^{-1}$ (WESCHENFELDER et al., 2015).

Furthermore, chemical additives such as corrosion inhibitors, flow enhancers and biocides used in the production operations can also be found in PW. All those compounds act as surfactants influencing the emulsion stability (DICKHOUT et al., 2017). Produced water constituents are based on the geological formation of the reservoir and migration channels in

which it was located for millions of years. Some common compounds and parameters in PW are benzene, toluene, ethylbenzene, xylene (BTEX), polycyclic aromatic hydrocarbons (PAH), total organic carbon (TOC), total petroleum hydrocarbon (TPH), total suspended solids (TSS) and salinity (LEE; NEFF, 2016), as shown in Table 1.

Table 1 – Range and mean concentrations of the main compounds and parameters of produced water from 23 samples of offshore oil platforms in Brazil: BTEX (benzene, toluene, ethylbenzene and xylene); PAH (polycyclic aromatic hydrocarbons); TOC (total organic carbon); TPH (total petroleum hydrocarbon); TSS (total suspended solids) and salinity.

Compound/Parameter	Range concentration (mg L⁻¹)	Mean concentration (mg L⁻¹)
BTEX	1.4 – 20	4.9
PAH	0.44 – 0.61	0.53
TOC	86 – 971	307
TPH	86 – 971	10
TSS	1.9 – 106	11
Salinity	38,182 – 179,766	75,434

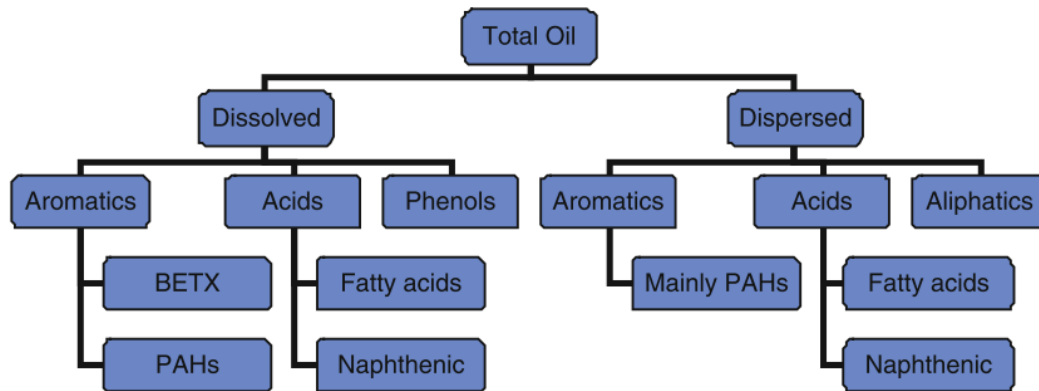
Source: LEE; NEFF, 2016.

Due to the complexity of produced water, it is challenging to evaluate the toxic effects of an individual compound. Hence, studies are usually conducted assessing a class of constituents (i.e., organic fraction, NA fraction) (LI et al., 2017). Some of the fundamental parameters that needs to be take in account on the removal of water soluble organics from PW are the physicals properties of the compounds, such as solubility and the stability and dispersion level of their oil droplets. All these factors influence the speed of the separation process and the resources required to obtain a successful removal (PINTOR et al., 2016).

2.1.1.1 Water soluble organics

The major class of compounds classified as water soluble organics (WSO) are phenols, PAH, BTEX and acids. The term “water soluble” may bring some confusion since a fraction of WSO is dissolved and a fraction may be partially dispersed in the oil phase (FAKSNESS; GRINI; DALING, 2004), as illustrated in Figure 1.

Figure 1 – Scheme of total oil in produced water.



Source: YANG, 2016.

Most environmental regulatory companies are based on total oil and grease (TOG) analysis to quantify WSO (dispersed and dissolved) for ocean discharge (NEFF; LEE; DEBLOIS, 2016). Table 2 demonstrates monthly averages and daily maximum concentrations of TOG for ocean release in some countries and regions. In Brazil, the disposal of produced water must be based on monthly average concentration of 29 mg L^{-1} , or daily maximum of 42 mg L^{-1} . (CONSELHO NACIONAL DO MEIO AMBIENTE, 2007).

Table 2 – Monthly average and daily maximum concentrations (mg L^{-1}) of TOG allowed in some countries and regions for PW released in ocean.

Country	Monthly average (mg L^{-1})	Daily maximum (mg L^{-1})
Canada	30	60
USA	29	42
OSPAR (NE Atlantic)	30	-
Mediterranean Sea	40	100
Western Australia	30	50
Nigeria	40	72

Source: NEFF; LEE; DEBLOIS, 2016.

It is of great importance to monitor oil in produced water; however, it is not well comprehended what really composes oil in PW and what the standard methods or field analyses are in fact quantifying. A good example of this is the OSPAR (Oslo-Paris Convention) standard which changed the old infrared-based method for dispersed oil quantification. The old method did not measure only dispersed oil, and the alteration caused a series of challenges to meet the standard under OSPAR (YANG, 2016).

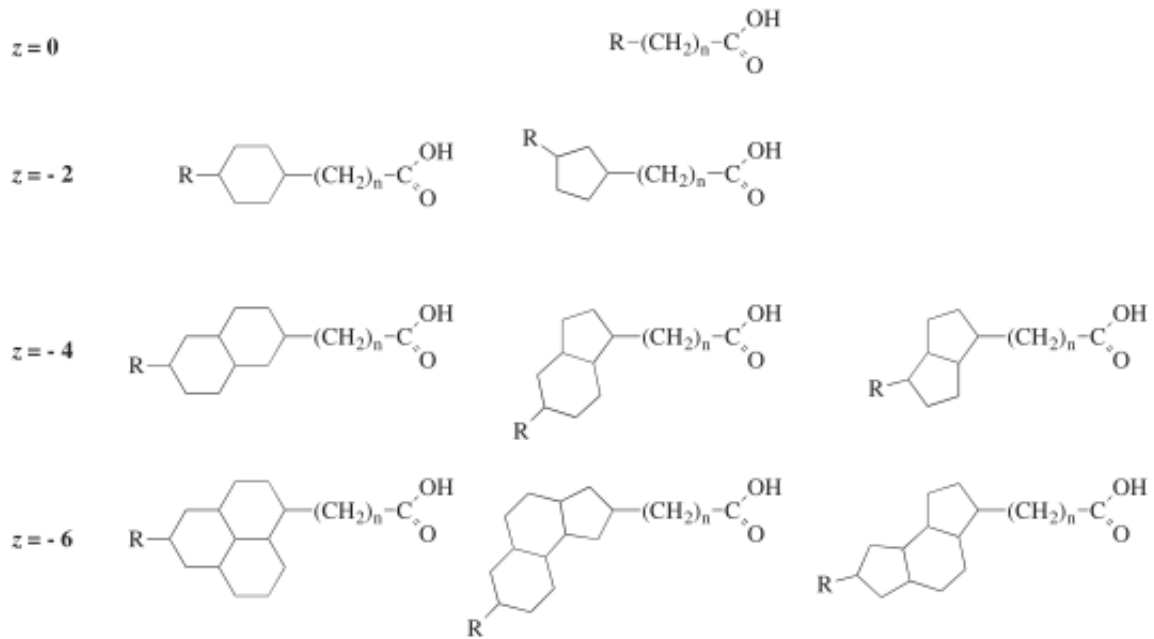
Thus, a major challenge in the O&G industry consists in determining the specific compounds present in produced water to assess its toxicity potential. In the area of research, it is fundamental to study both representative synthetic effluents, especially with NAs, as well as the full matrix of produced water constituents to bring efficient treatment alternatives (BROWN; ULRICH, 2015).

2.1.1.1.1 Naphthenic acids

Naphthenic acids (NA) are polar organic carboxylic acids which are originated essentially from partial aerobic biodegradation and incomplete catagenesis of bituminous compounds (CLEMENTE, 2005; WATSON et al., 2002). Natural occurring events, such as earthquakes and erosion, put bitumen in contact to aerobic biodegradation circumstances, which combined to high pressure and temperature conditions accelerates the catagenesis for organic matter (QUINLAN; TAM, 2015). Naphthenic acids are vast components of WSO constituents of bitumen in the oil sands deposits of northeastern Alberta, Canada (HEPLER, LOREN G; ZHU, 1989).

NAs are a complex class mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids with general chemical formula, where $C_nH_{2n+Z}O_2$, where n indicates the carbon number and Z is zero or a negative even integer that specifies a homologous series. Values of n range from 5 to 33, and molecular weights varying from 100 to 500 g L⁻¹ (CLEMENTE; YEN; FEDORAK, 2003). In other words, the Z number points to a lack of hydrogen due to ring arrangement and R represents aliphatic branchings (Figure 2). NAs are also considered weak acids with pKa ranging from 5 to 6 (QUINLAN; TAM, 2015). Some common monoacid structures are illustrated in Figure 2.

Figure 2 – General molecular structure of some classical NAs.



Source: QUINLAN; TAM, 2015.

The major concern in terms of toxicity for the environment are naphthenic acids of low molecular weight found in oil sand deposits. The major operational concern is related to corrosion towards process equipment and pipelines during O&G operations (QUINLAN; TAM, 2015). Naphthenic acids toxicity is typically related to their amphiphilic structures of hydrophilic carboxylic functional groups and the hydrophobic alicyclic ends, which classifies NAs as surfactants. The hydrophobic portion is typically composed by a saturated 5-6 carbon rings in several conformations, and the hydrophilic one by a carboxyl group separated from the ring structure by a carbon chain of at least two units in length. Acyclic NAs also occur, but the majority is composed by cyclic structures (HEADLEY; MCMARTIN, 2004).

2.1.2 Treatment of produced water

Produced water destined for ocean discharge is typically treated on the platform or at a shore facility to attend regulatory guidelines. The major aim of PW treatment on offshore platforms consists in producing stable crude oil and gas for transportation to shore facilities by pipelines and tankers (NEFF; LEE; DEBLOIS, 2016). Whether produced water is intended for ocean discharge or for reinjection into geologic formations, it is advantageous to treat the effluent on an offshore platform to lower treatment and/or transportation costs.

Most of oil and gas installations worldwide perform primary treatment by the use of separators, coalescers and hydrocyclones to remove dispersed oil and suspended solids. Advanced treatments are required for the treatment of emulsified oil, colloidal particulates, salinity, inorganics, organics, microorganisms, trace metals, and residual field chemicals (ADHAM et al., 2018). Although the separation of oil/water cases is not 100 % efficient even with the use of advanced processes, the association of mechanical and chemical treatment is successful for the removal of volatiles and dispersed oil, however inefficient for dissolved organics, ions, and metals (NEFF; LEE; DEBLOIS, 2016). Processes such as advanced oxidation, biodegradation and flocculation can take months, sometimes years, to treat the effluent to a desirable rate of dissolved components. In this context, membrane filtration technologies are a promising alternative (QUINLAN; TAM, 2015).

2.2 MEMBRANE TECHNOLOGY

Membrane filtration is a broad definition to describe an intermediate phase which separates other two phases acting like a barrier to the transport of matter between phases (ROSEN, 2004). Pioneer experiments employing membrane technology in the oil and gas industry are dated in the early 20th century, and the success of this application has led to the development for further applications (ALZAHIRANI; MOHAMMAD, 2014). Some of the advantages of membrane technology is that few chemicals are used, low energy requirements and it is of easy implementation and maintenance (PADAKI et al., 2015). It is of great importance the selection of a membrane which meets the requirements of the process. The membrane performance is highly related to its structural properties (morphology and pore size) and surface properties (charge, hydrophobicity, hydrophilicity and roughness). In fact, the membrane surface property like hydrophilicity is essential for a good performance (DICKHOUT et al., 2017). hydrophilicity and hydrophobicity

Separation processes using porous membranes rely fundamentally on adsorption, sieving and electrostatic principles. The membrane adsorption mechanism is related with solute characteristics, membrane and the synergy between both parameters. This interaction reduces the pore size and results in a more efficient retention of target components (PADAKI et al., 2015).

2.2.1 Membrane classification

Membranes processes are typically pressure-driven operations which applications are based on pore size distinctions. The usual classification of membrane processes according to the pore size consists of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (BAKER, 2004). Table 3 exhibits the classification of membranes separations processes according to the pore size as well as its main applications. However, membrane resistance in terms of permeate flux increases through the same scale as the pore size decrease. Thus, it is required a significant higher pressure when using membranes with small pore sizes (MUNIRASU; HAIJA; BANAT, 2016).

Table 3 – Classification of membranes separation processes and its main characteristics

Pore type (size range, nm)	Membrane type (pore size, nm)	Retained species	Dimensions (nm)
Macropores (> 50)	Microfiltration (50 - 500)	Yeasts & fungi	1000 – 10,000
		Bacteria	300 – 10,000
		Oil emulsion	100 – 10,000
Mesopores (2 - 50)	Ultrafiltration (2 - 50)	Colloidal solids	100 – 1000
		Viruses	30 – 300
		Protein/polysaccharides	3 – 10
		Humics/nucleic acids	< 3
Micropores (0.2 - 2)	Nano filtration (≤ 2) Reverse osmosis (0.3 - 0.6)	Common antibiotics	0.6 – 1.2
		Organic antibiotics	0.3 – 0.8
		Inorganic ions	0.2 – 0.4
		Water	0.2

Source: PADAKI et al., 2015.

2.2.2 Membrane casting

Membrane are commonly manufactured of polymeric and ceramic materials. Polymeric membranes are usually produced by the phase inversion method. It consists of the addition of a polymer in an organic solvent cast on a nonwoven polyester fabric (thickness < 50 μm), that results in a thin polymeric layer when placed in a nonsolvent (water). The membrane pore size is managed by polymer-solvent composition, concentration of additives, evaporation time, type and time in gelation bath, etc. (DE; MONDAL, 2012). Typical membrane polymers consist of polysulfone (PSf), polyethersulfone (PES), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF) and cellulose acetate (CA) (ZOUBEIK et al., 2018).

The incorporation of amphiphilic copolymers - composed of hydrophobic and hydrophilic fractions - in the polymeric matrix is advantageous to obtain the desirable properties for membrane blend. Typically, amphiphilic copolymers are derived from polymerization of monomers to obtain particular properties without altering the properties of the primary polymer. Most of the alterations on membrane chemistry target on hydrophobic materials rather than hydrophilic (PADAKI et al., 2015).

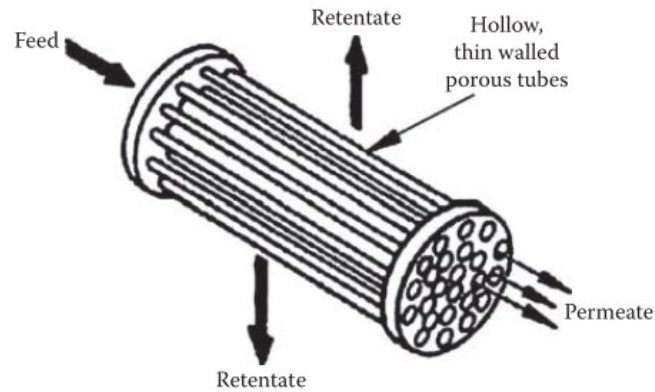
On the other hand, ceramic membranes are manufactured of inorganic compounds such as oxides of aluminum, zirconium and titanium. Some advantages of the ceramic over polymeric structures consist of higher mechanical strength, and more tolerance to different pH levels, oxidation stress and higher temperatures (ZOUBEIK et al., 2018).

2.2.3 Membrane modules

The structures in which membranes are placed are known as membrane modules. The major characteristic of these structures is presenting the highest superficial area combined with the smallest volume, allowing high permeate flux for the separation process. The typical modules are hollow fiber, plate and frame, tubular and spiral wound. Each configuration varies according to the need of the separation (ALZHRANI; MOHAMMAD, 2014). Membrane modules can be operated in cross-flow or dead-end, combined with single and multiple-pass processes (DE; MONDAL, 2012).

The plate-and-frame modules were among the primary sorts of membrane used, and its design origin is related to filter-press in which the membrane, feed spacers and product spacers are layered together between two end plates. On the other hand, hollow fiber (Figure 3) consists of a system pressurized from the shell side: the permeate flows through the fiber wall and it is carried out through the open fiber ends. This system is easily designed and it allows major large membrane areas (Figure 3), which is fundamental from an economic perspective (BAKER, 2004).

Figure 3 – Typical hollow fiber module



Source: DE; MONDAL, 2012.

2.2.4 Molecular weight cutoff

Molecular weight cutoff (MWCO) is a concept used to characterize a membrane which retains 90 % of a specific solute. The experiments are usually conducted in small-scale setups with typical solutes such as glucose, sucrose and fractions of polyethylene glycol. The measured retention is plotted as a function of the MWCO (BAKER, 2004).

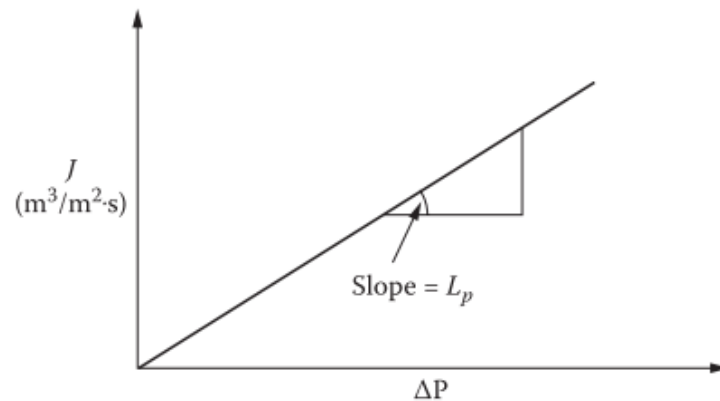
2.2.5 Membrane permeance

Membrane permeance (L_p) is a parameter which characterizes the porosity of the membrane and it is measured by distilled water runs over a series of transmembrane pressures (TMP). It is mathematically defined as:

$$L_p = \frac{J_o}{\Delta P} \quad (1)$$

where J_o is the distilled water flux and ΔP is the transmembrane pressure drop. The permeance is also given by the slope of the curve of permeate flux as a function of TMP drop (BAKER, 2004), as shown in Figure 4.

Figure 4 – A typical curve of distilled water flux as a function of TMP.

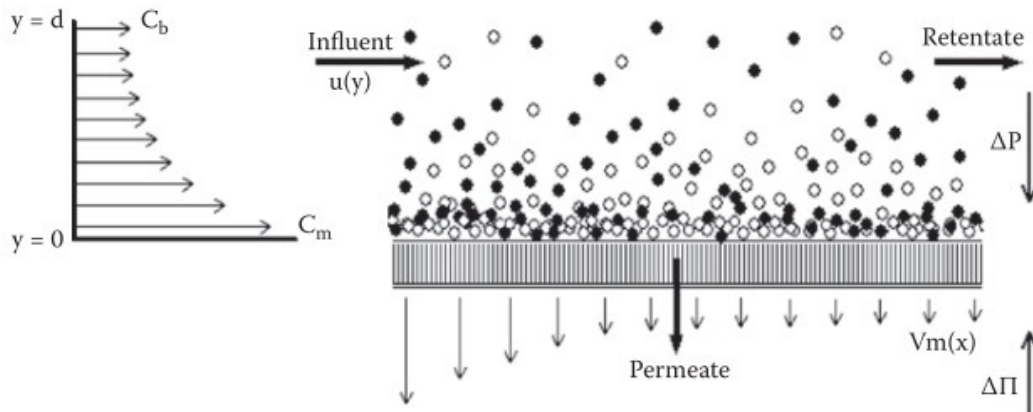


Source: DE; MONDAL, 2012.

2.2.6 Operational concerns

There are two most common operational concerns that define a good performance in MEUF: concentration polarization and membrane fouling (MUNIRASU; HAIJA; BANAT, 2016). A key factor to determine the performance of ultrafiltration membranes is concentration polarization due to macromolecules which are retained at the membrane surface. While micromolecules and the solvent permeate the membrane, macromolecules accumulate at the membrane surface forming a gel layer which results in a secondary barrier to the separation process. This layer is, in most of the cases, the major responsible for resistance in the separation process (BAKER, 2004). The resulting gradient of concentration at the membrane surface (most concentrated) to the rest of the solution (less concentrated) is demonstrated in Figure 5. This phenomenon causes: (i) reduction of the driving force; (ii) formation of a thin layer on the membrane surface; (iii) increase in concentration near the membrane which causes flux reduction.

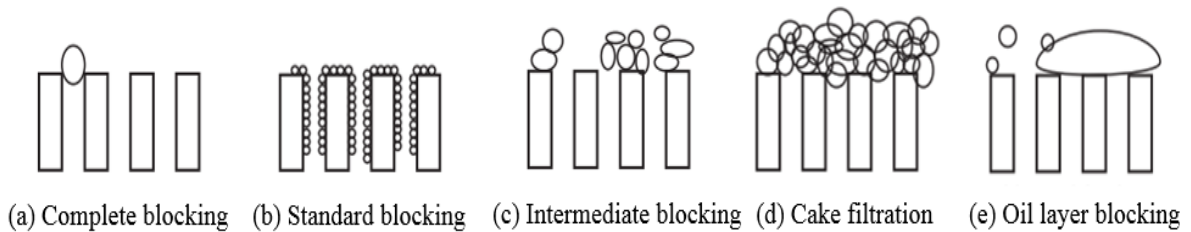
Figure 5 – Concentration polarization in a membrane channel.



Source: DE; MONDAL, 2012.

Membrane fouling is the term used to describe the deposition of oil, solids and other substances that form a layer on the membrane surface. This phenomena leads to a flux decrease, which is an indirect way to measure fouling (DICKHOUT et al., 2017). Fouling is commonly classified into four distinct mechanisms that can occur simultaneously, as shown in Figure 6.

Figure 6 – Illustrative representation of fouling mechanisms that can occur on the membrane surface.



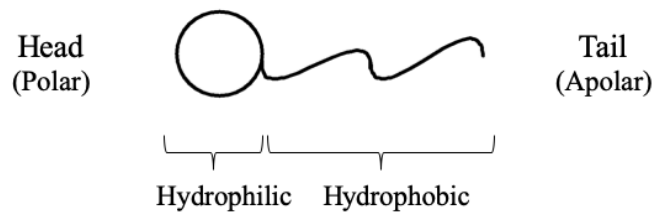
Adapted from: DICKHOUT et al., 2017.

Membrane fouling can be measured by permeate flux decline, permeate quality and the transmembrane pressure (DICKHOUT et al., 2017). Due to fouling, most membranes require cleaning, which increases operational costs when needed to use chemicals, additional energy and extra downtime for the treatment installation (ROSEN, 2004).

2.3 SURFACTANTS

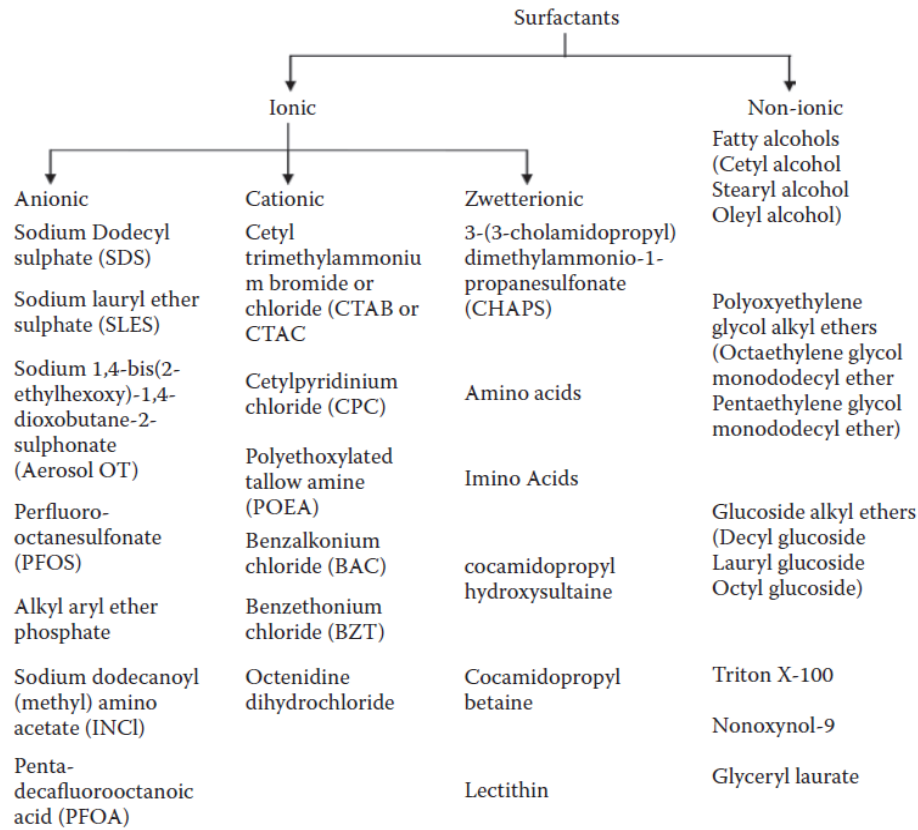
Surfactants are known as amphiphilic structures from a physico-chemical perspective due to the duality in its structure: the molecules present a hydrophobic and a hydrophilic component, as shows Figure 7. The polar group, also known as the head, contains heteroatoms such as O, S, P or N, included in functional groups such as alcohol, thiol, ether, ester, acid, sulfate, sulfonate, phosphate, amine, amide, etc. The apolar group is known as the tail and it is typically composed by a long hydrocarbon chain of the alkyl or alkylbenzene type, sometimes with halogen atoms and even a few nonionized oxygen atoms (SALAGER, 2002).

Figure 7 – Typical surfactant molecule.



Surfactant molecules are also classified as anionic (negatively charged heads), cationic (positively charged heads), nonionic (electrically neutral) and zwitterionic (cationic and anionic groups). Figure 8 demonstrates an overview of commercially known surfactants categorization according to ionic properties.

Figure 8 – Schematic representation of surfactants based on ionic properties.



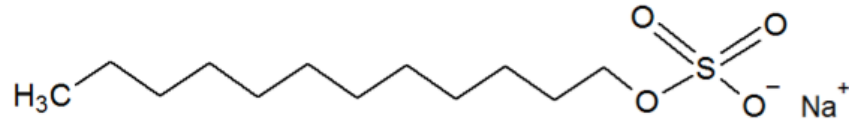
Source: DE; MONDAL, 2012.

Surfactants are also known as detergents or tensoactive agents, and the species are characterized by three main characteristics: structure formed by polar and nonpolar groups; surface activity; and the formation of self-assembled aggregates, also called micelles (DE; MONDAL, 2012).

2.3.1 Anionic surfactants

Anionic surfactants are the most typically used worldwide, accounting for approximately 60 % of the consumption in USA and Canada (ROSEN, 2004). The species include alkylbenzene sulfonates (detergents), (fatty acid) soaps, lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent) and lignosulfonates (dispersants). Anionic surfactants dissociate in water resulting in a negatively charged head (anion) and a cation, which is generally an alkaline metal (Na^+ , K^+) or a quaternary ammonium (SALAGER, 2002), as demonstrated in Figure 9.

Figure 9 – Structure of the anionic surfactant sodium dodecyl sulfate (SDS).

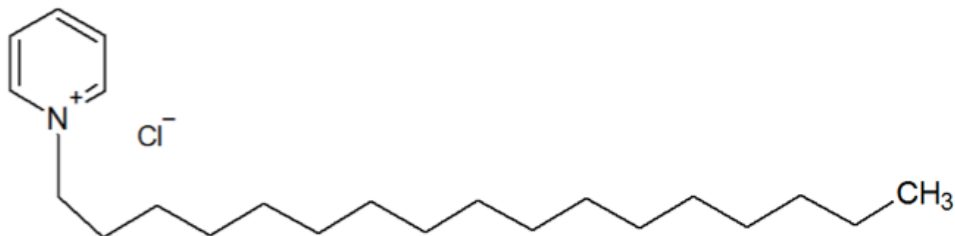


The hydrophobic chain is a linear combination of alkyl groups of 12 to 16 carbon atoms. For detergency purposes, linear chains are preferable rather than branched ones due to its effectiveness and ability to rapidly degrade (TADROS, 2005).

2.3.2 Cationic surfactants

Cationic surfactants (Figure 10) are typically more expensive when compared to anionics, due to the high pressure required for the synthesis of these compounds. They are typically used as: (i) bactericide; and (ii) to adsorb onto solid surfaces, since their positively charged head is capable of generating antistatic and hydrophobic effect. This characteristic has great importance on the development of products such as corrosion inhibitors (SALAGER, 2002). Although the cationic surfactants result in positively charged head in aqueous solutions, they are generally stable in both alkaline and acid solutions. In addition, cationic surfactants are typically compatible with inorganic ions and hard water while incompatible with metasilicates and highly condensed phosphates (TADROS, 2005).

Figure 10 – Structure of the cationic cetylpyridinium chloride (CPC).



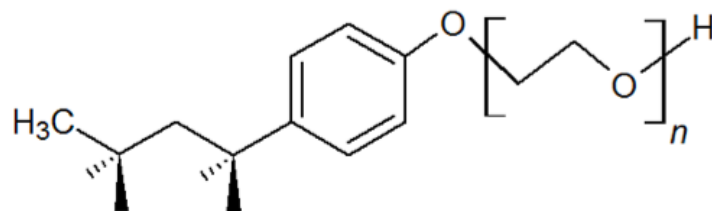
2.3.3 Zwitterionic surfactants

Zwitterionic surfactants present both anionic and cationic dissociations in aqueous solution. This class of surfactant is typically expensive, therefore its applications are for specific uses such as cosmetic industry, which requires low toxicity (SALAGER, 2002). Zwitterionic surfactants are sensitive to pH: in acidic solution ($\text{pH} < 7$), the surfactant molecules present positive charge, while in alkaline solution ($\text{pH} > 7$), they present negative charge. However, there is a particular pH at which the surfactant has both positive and negative charges, called isoelectric point (DE; MONDAL, 2012).

2.3.4 Nonionic surfactant

Nonionic surfactants (Figure 11) advantage consists in the electrically neutral property, which diminishes the interaction of the molecules in a solution with other charged components. This characteristic makes this type of surfactant suitable for all sorts of solutions (DE; MONDAL, 2012). In this context, nonionic surfactants are resistant to hard water, polyvalent metallic cations, electrolyte at high concentration and, soluble in water and organic solvents, including hydrocarbons. Commercial products are typically a mixture of a range of polyoxyethylenated chain lengths (ROSEN, 2004).

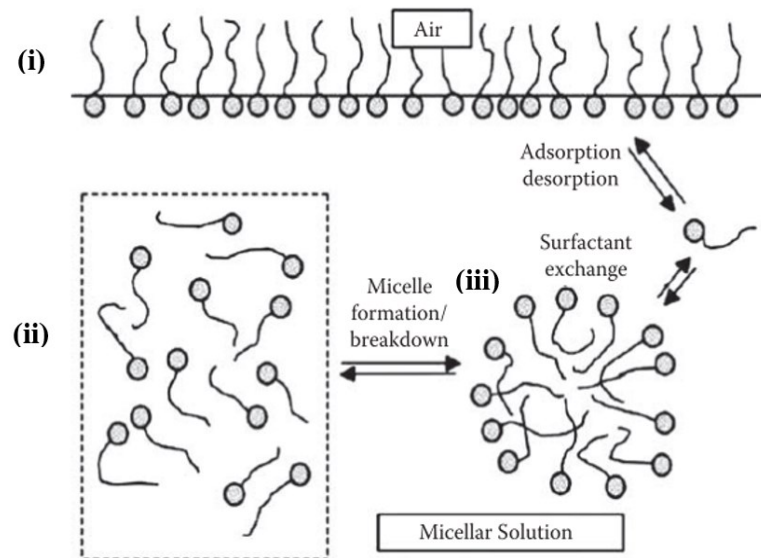
Figure 11 – Structure of the nonionic surfactant Triton X-100.



2.4 MICELLIZATION

The surfactant hydrophobic group interacts poorly with water in an aqueous solution, while the hydrophilic interacts with water molecules via dipole or ion-dipole interactions. This strong bonding is responsible for the high solubility of surfactant in water. However, the strong interaction of hydrogen bonding in water molecules tends the system to reduce contact between the hydrophobic group and the solvent, orienting the tails out of the water in the air interface. As a result, surfactant molecules are either conformed: (i) at the free interface; (ii) in the solution; (iii) within the micelle, demonstrating a dynamic equilibrium in the system, as demonstrated in Figure 12 (DE; MONDAL, 2012).

Figure 12 – Representation of the dynamics of monomers and micelles in solution: (i) monomers at the free interface; (ii) monomers in solution; (iii) formed micelles.



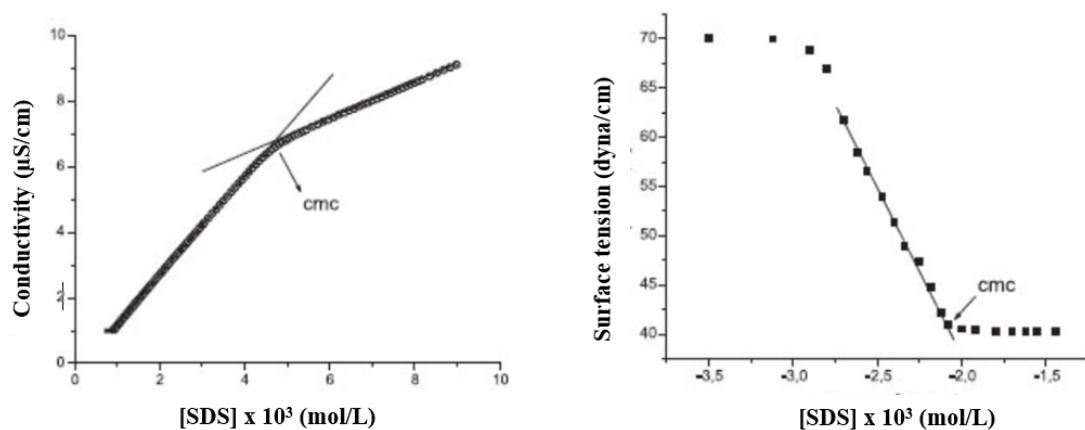
Source: DE; MONDAL, 2012.

The surface properties of the solution are modified leading to a raise in the free energy of the system, and the decrease of surface tension is one of the main implications when a surfactant is used in aqueous solutions (BURLATSKY et al., 2013). The critical micelle concentration (CMC) is referred to the concentration in which the surfactant molecules aggregate to form micelles. This parameter one of the most important ones when working with surfactants, and most research and industrial applications are based on CMC values (SHI; LUO; LI, 2011).

There are several factors which influence micelle formation, such as pH, temperature, ionic strength and the effect of the hydrophobic group. The CMC is usually expected to increase with the increase in temperature. On other hand, the CMC of a solution is lowered by the addition of an electrolyte, which decreases the repulsion between the charged groups at the surface of the micelle. In addition, the increase of the hydrophobic part (the tail) of the surfactant molecules also favors micelle formation, which is probably a result of the coiling of the long tails in the water phase (SHAW, 1992).

There are several methods to determine the CMC based on a specific property of the solution, including surface tension, conductivity, turbidity, fluorescence spectroscopy and DLS. Almost every physical property that sharply changes and relies on number or size of particles can be used to determine the CMC in all sorts of surfactants (ROSEN, 2004). Figure 13 demonstrates the determination of CMC by both conductivity and surface tension methods.

Figure 13 – Representation of the determination of critical micelle concentration from experimental data of sodium dodecyl sulphate surfactant by conductivity method and by surface tension method (logarithmic scale).



Source: RIZZATTI; ZANETTE; MELLO, 2009.

It is possible to observe that in conductivity method, the CMC is given by a change in the linear trend, while in surface tension method the CMC occurs when surface tension stabilizes.

2.4.1 Determination of CMC by surface tension

As mentioned previously, the decrease in surface tension is one of the main implications when using a surfactant in solution. Surface tension in a liquid phase can be fundamentally defined as the force acting at right angles to any line of unit length on the liquid surface (SHAW, 1992), as demonstrated in Equation 2.

$$\tau = \frac{\Delta F}{\Delta L} \quad (2)$$

where τ is the surface tension, ΔF refers to the cohesion forces of the molecules, and ΔL the length. Surface tension is given by newtons per meter (N m^{-1}) in the international system of units (SI).

The equipment used to measure surface tension is called tensiometer, and the techniques available to measure surface tension include Du Nouy ring, Wilhelmy plate, pendant drop, drop-weight and contact angle methods (ROSEN, 2004). In Table 4 is summarized the principles of some of these techniques.

Table 4 – Wilhelmy plate (static), drop-weight and pendant drop methods and principles to measure surface tension in aqueous solutions.

Method	Principles
Wilhelmy plate (static)	It measures the force required to maintain the plate at constant immersion as the surface tension alters is measured.
Drop-weight	Drops of a liquid detach themselves slowly from the tip of a vertically mounted narrow tube and its weight is measured.
Pendant drop	A pendant drop of liquid is photographed and from the several dimensions of the drop the surface tension is computed.

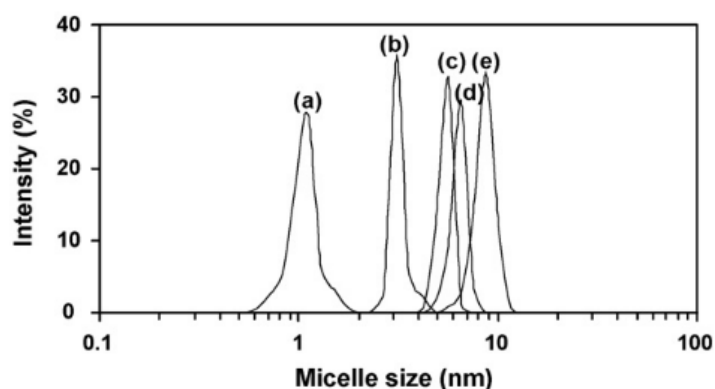
Source: SHAW, 1992.

In order to determine the critical micelle concentration, a curve can be elaborated from surface tension measurements (ordinate) as a function of the raise in concentration (abscissa). The CMC is given by the concentration in which the surface tension stabilizes (TADROS, 2005).

2.4.2 Determination of micelle size by DLS

The dynamic light scattering (DLS) method consists in analyzing the time fluctuations of the intensity of the scattered light. These fluctuations are caused by the Brownian motion of the particles (translational and rotational), which leads to a modification of the particle configuration as well as the change in the interference pattern of the scattered light (KRALCHEVSKY; DANOV; DENKOV, 2002). In micelle size context, the incident light is oriented at the solution and some of the light can be absorbed, some is scattered and some is transmitted undisturbed through the sample. Light scattering results from the electric field associated with the beam of light inducing periodic fluctuations of the electron clouds of the atoms in solution (SHAW, 1992). Deriszadeh, Harding and Husein (2009) analyzed micelle size of distinct naphthenic acids combined with the surfactant CPC by a Zetasizer equipment (Figure 14).

Figure 14 – DLS measurements of micelle size of (a) 6 mmol L⁻¹ CPC, and a mixture of 6 mmol L⁻¹ CPC and (b) 0.32 mmol L⁻¹ C₅H₁₀O₂, (c) 0.32 mmol L⁻¹ C₇H₁₄O₂, (d) 0.32 mmol L⁻¹ C₈H₁₆O₂, and (e) 0.32 mmol L⁻¹ C₁₀H₂₀O₂.



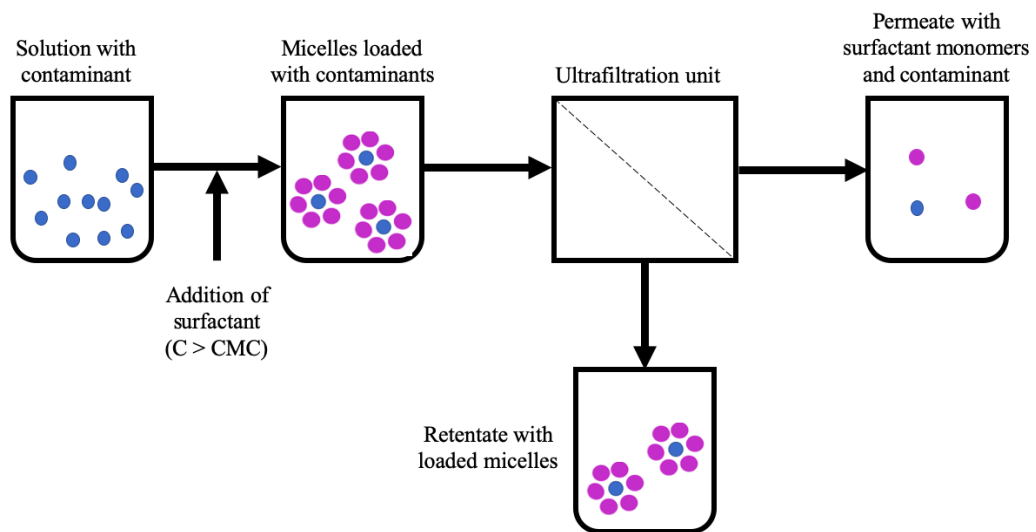
The DLS measurements were able to provide the micellar size for the micelles composed of naphthenic acids and CPC. As expected, the micelle size increased as the carbon number of the naphthenic acids increased.

2.5 MICELLAR ENHANCED ULTRAFILTRATION

Micellar enhanced ultrafiltration is the term used for physico-chemical processes designed to improve the performance of ultrafiltration membranes by the use of surfactants (ABBASI-GARRAVAND; MULLIGAN, 2014). This technology is based on adding

surfactants to the contaminated solution aiming to form micelles, which are formed above the critical micelle concentration and are able to solubilize organic and inorganic compounds. Once the micelles are formed, they result in larger structures than the pollutant molecules, allowing the treatment of aqueous solutions with the use of porous membranes (SCHWARZE et al., 2010), as shown in Figure 15.

Figure 15 – Schematic representation of micellar enhanced ultrafiltration technique.



Hence, membranes with larger pore sizes can be employed resulting in high water permeate flux and significant pollutant removal. Nonetheless, micelle formation and stability are essential parameters to be considered during the entire operation (ACERO et al., 2017). MEUF limitations are associated with membrane fouling and back contamination, which causes permeate flux reduction and surfactant molecules through the membrane, respectively (DERISZADEH; HARDING; HUSEIN, 2008).

2.5.1 State of art on the removal of soluble organic compounds

Studies have shown a coaction between naphthenic acid contaminants and the surfactant cetylpyridinium chloride (CPC), which resulted in a decrease in the CMC of the surfactant. Furthermore, this observed synergy also shows an increase of micelle dimensions and in the solubility of the organic compounds within the micellar structure. As a result, these findings have improved the permeate water flux and reduce back contamination

(DERISZADEH; HARDING; HUSEIN, 2009). Table 5 presents a state of art compilation on the removal of soluble organic compounds by micellar enhanced ultrafiltration.

Table 5 – State of art on the removal of soluble organic compounds by micellar enhanced ultrafiltration.

Author	Membrane - pore size (kDa)	Surfactant	Removal (%)	Contaminant
(DERISZADEH; HARDING; HUSEIN, 2008)	Polyacrylonitrile – 6, 13 and 50	CPC	97 - 99	p-xylene and naphthenic acid (C8)
(DERISZADEH; HARDING; HUSEIN, 2009)	Polyacrylonitrile - 13	CPC	84 - 99	Naphthenic acids (C5, C7, C8, C10)
(LEE et al., 2005)	Regenerated Cellulose - 3	CPC (Cationic) and TWEEN 80 (Non-ionic)	~ 88	Trichloroethylene
(CAÑIZARES et al., 2006)	Ceramic - 10	SDS (Anionic)	> 75	Tannic Acid
(POŹNIAK; GANCARZ; TYLUS, 2006)	Phenylene oxide - 27	CTAB (Cationic)	> 90	Herbicide 2,4-D
(VINDER; SIMONI, 2012)	PVDF (0.04 µm)	SDBS (Anionic) and Polyoxyethylene nonylphenyl (Non-ionic)	> 80	AOX
ABBASI-GARRAVAN; MULLIGAN, 2014	PVDF - 180	SDS (Anionic)	74	Effluent from olive mill
(EXALL et al., 2013)	Regenerated Cellulose - 3	CTAB (Cationic)	20 - 74	Sulfonamides
(MISRA et al., 2009)	3, 5 and 10	SDS (Anionic)	> 90	Dibutylphosphate
(VENKATAGA NESH et al., 2012)	Polyethersulfone - 10	SDS (Anionic)	94 - 98	Naphthenic acid
(ZHANG et al., 2012)	Polyethersulfone - 10	Gemini (Cationic)	~ 96	Phenol

The overall results from Table 5 demonstrate MEUF as a promising technique. MEUF combines the use of surfactants with the contaminants that already exist in the solution to

form micelles, which results in reliable, cost-effective and less energy intensive technology when compared with other separations processes, such as membrane distillation (SCHWARZE et al., 2010). Nevertheless, it is fundamental to determine the CMC for each case, considering the contaminants present in the solution and the concentration of surfactant added.

2.5.2 Determination of naphthenic acids

The authors Deriszadeh, Harding and Husein (2009) used MEUF for the removal of naphthenic acids and chromatography method was used to determine NA removals: high-performance liquid chromatography (HPLC) and gas chromatography (GC). Venkataganesh et al. (2012) also worked with MEUF for the removal of naphthenic acids; however, the authors used Fourier-transformed infrared spectroscopy (FTIR) method for NA determination. Chromatography is an analytical technique based on the separation of a mixture of chemical substances through the interaction of its components with a stationary phase (liquid or solid) and a carrier (liquid, gas or supercritical fluid) (COLLINS; BRAGA; BONATO, 2006). Fourier-transformed infrared-spectroscopy provides evidence on the presence of functional groups that have specific vibrational frequencies according to the molecule's chemical bonds. The aim of the analysis is to identify a specific compound or to investigate the chemical composition of a compound (qualitative analysis identifying the type of chemical bond or quantitative analysis measuring the concentration of the chemical bond) (CANEVAROLO JR, 2002). Table 6 demonstrates the methods and main parameters used for the determination of naphthenic acids using MEUF.

Table 6 – Methods and main parameters used to determine naphthenic acids using MEUF.

Method	Author(s)	Main parameters	Compound	Detection
HPLC	DERISZADEH; HARDING; HUSEIN, 2008.	Column: Zorbax Eclipse XDB- C18; Carrier liquid: 80:20 methanol/DI water;	Octanoic acid	Retention time: 3.6 min.
	DERISZADEH; HARDING; HUSEIN, 2009.	Injection volume: 60 L; Detection limit: 0.1 mg L ⁻¹ ; Flow rate: 1 mL min ⁻¹ .	Decanoic acid	Retention time: 5.2 min.
GC	DERISZADEH; HARDING; HUSEIN, 2009.	Column: DB-FFAP GC; Carrier gas: Helium; GC oven temperature: 100 °C for 5 min, increased to 230 °C at 10 °C/min and maintained at final temperature for 2 min; Injector and FID temperature: 150 and 250 °C, respectively.	Pentanoic acid	Retention time: 11.95 min
			Heptanoic acid	Retention time: 14.7 min.
FTIR	VENKATAGANESH et al., 2012.	The acidified samples were extracted twice with 25 mL fractions of dichloromethane as extractor solvent. The samples were analyzed by a KBr cell.	Naphthenic acid grade	The absorbances were measured at wave length 1701 cm ⁻¹ .

2.6 FINAL CONSIDERATIONS

In order to evaluate a naphthenic acid model considered hard to remove due to its high solubility in water, cyclic carbon chain and low molecular weight, this work proposed to study the removal of cyclohexanecarboxylic acid using micellar enhanced ultrafiltration. It is hoped that the success of the parameters assessed in the present study may be suitable for other naphthenic acids.

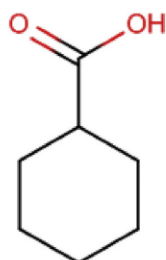
3 EXPERIMENTAL WORK

This chapter specifies the chemicals and the membranes used in this work, as well as the description of the experimental setup. A brief summary of the methodologies established and the analytical instruments employed are also presented.

3.1 CHEMICALS

The stock solution of naphthenic acid (NA) was prepared with 500 mg L⁻¹ of cyclohexanecarboxylic acid (128 g mol⁻¹, 98 wt. %, Sigma Aldrich) in distilled water with the addition of 2 g L⁻¹ of NaOH (99 wt. %, Neon) to assure total solubility of the NA. Cyclohexanecarboxylic acid was selected in this study as a model to represent the naphthenic acids contained in produced water due to its low molecular weight, high solubility in water and cyclic chain. The stock solution concentration was kept constant for all experiments. Figure 16 shows the cyclohexanecarboxylic acid molecular structure.

Figure 16 – Cyclohexanecarboxylic acid structure.



Source: API et al., 2018.

The surfactants used in this study were cetylpyridinium chloride, CPC (98 % wt. Anidrol); sodium dodecyl sulfate, SDS (95 % wt., Neon and 99 wt. %, Sigma Aldrich); and Triton X-100, TX100 (Neon), as specified in Table 7.

Table 7 – Main characteristics of CPC, SDS and TX100 surfactants.

Surfactant	Nature	Molecular weight (g mol ⁻¹)	Chemical formula
CPC	Cationic	358	C ₂₁ H ₃₈ ClN
SDS	Anionic	288	NaC ₁₂ H ₂₅ SO ₄
TX100	Nonionic	647	C ₁₄ H ₂₂ O(C ₂ H ₄ O) _n

Valeric acid (99 wt. %, Sigma Aldrich) was used as open chain naphthenic acid model. Dichloromethane (Neon, 99 % wt.) was employed as the extractor solvent for FTIR analysis and sodium chloride, NaCl (99 wt. %, Dinâmica) was added in sample preparation step. Hydrochloric acid, HCl (37 wt. %, Neon) was used for pH adjustments.

3.2 MEMBRANES

The ultrafiltration membranes used in this work present molecular weight cutoff of 4, 5 and 10 kDa, with commercial names of UH004, UP005 and UP010, respectively. The main characteristics of the membranes are shown in Table 8.

Table 8 – Main characteristics of the membranes used in this work.

Manufacturer	Nominal M.W.C.O. (kDa)	Membrane chemistry	Backing material	Thickness (µm)	Permeability (LMH bar ⁻¹)
Microdyn NADIR®	4	Hydrophilic polyethersulfone (PESH)			≥ 7
	5	Polyethersulfone (PES)	Polypropylene	210 – 250	≥ 10
	10	Polyethersulfone (PES)			≥ 50

3.3 MEUF EXPERIMENTAL SETUP

A filtration cell with perpendicular flux (Figure 17) was used to perform the filtration experiments in batch mode. The cell was manufactured in stainless steel, with an internal volume of 370 mL and a filtering area of 22.06 cm². The outside of the cell is covered by a jacket for temperature control, which was maintained by an ultra thermostatic water bath (Marconi, MA184).

Figure 17 – Filtration cell for MEUF experiments.



Pressure was the driving force for the separation process and it was implemented by commercial nitrogen gas (White Martins) and controlled by a manometer coupled to the system. The transmembrane pressure (TMP) for the permeate flux was calculated from Equation 3, where P_{in} is the pressure inside the cell (given by the manometer), and P_{out} in the atmosphere.

$$\Delta P = TMP = P_{in} - P_{out} \quad (3)$$

Membrane conditioning is a fundamental step to prepare the pores for the subsequent filtration. For all tests, the conditioning was carried out at 1.0 bar above the TMP (Table 9), and a total volume of 100 mL of distilled water was permeated through the membrane pores.

Table 9 – Transmembrane pressure (TMP) for conditioning and filtration steps.

Transmembrane pressure (TMP)	
Conditioning	Filtration
3.0	2.0
4.0	3.0
5.0	4.0

Once the stock solution of naphthenic acid was prepared, surfactant was added to the solutions to be filtered according to the concentration established in the experimental design. For each filtration batch, 2/3 of the cell internal volume (240 mL) was filled with the NA stock solution in the presence of surfactant. Four samples of 40 mL were collected by a graduated cylinder along the batches to measure permeate flux ($L\ m^{-2}\ h^{-1}$), resulting in a total sample volume of 160 mL. For each test, a flat sheet membrane (A4 size) was cut circularly in a diameter of approximately 5.3 cm (corresponding to the filtering area) to fit in the filtration cell. The membranes were not cleaned neither reused in order to maintain isonomy for all experiments. In addition, all conditioning procedures before each test presented the same permeate flux for distilled water, which also contributed to guarantee the isonomy of the experiments.

3.4 EXPERIMENTAL DESIGN

A complete 2^2 factorial design with 3 center points for each independent variable was performed for NA ultrafiltration in presence of TX100 and CPC, resulting in seven filtration experiments for each surfactant, as demonstrated in Table 10.

Table 10 – 2^2 factorial design matrix with 3 center points.

Test	Surfactant concentration (mmol L⁻¹)	TMP (bar)
1	-1	-1
2	1	-1
3	-1	1
4	1	1
5	0	0
6	0	0
7	0	0

Surfactant concentration was expressed in terms of the CMC measured for each surfactant, as shown in Table 11.

Table 11 – Experimental design levels and independent variables for experiments with TX100 and CPC.

Level	Surfactant concentration		TMP (bar)
	TX100	CPC	
Low (-1)	2 CMC	10 CMC	2.0
Center (0)	6 CMC	30 CMC	3.0
High (+1)	10 CMC	50 CMC	4.0

All filtration experiments were conducted under the temperature of 25 °C. The agitation system was not used to avoid influence on micelle stability. For TX100 experiments, pH 7.5 was selected for filtration experiments, while for CPC, filtration runs occurred at pH 8.0. The NA percent removal (% NA) was calculated by Equation 4.

$$\% NA = \left(1 - \frac{C_p}{C_f}\right) * 100 \quad (4)$$

where C_p is the concentration in the permeate and C_f in the feed solution.

3.5 INSTRUMENTS AND ANALYSIS

3.5.1 Determination of critical micelle concentration by surface tension

A tensiometer (250, Ramé-Hart Instruments) was used to determine the critical micelle concentration of each surfactant by pendant drop method. The drops were formed by a syringe coupled to the equipment and captured by its digital camera. Drops with gradual raise in surfactant concentration were read ten times by the tensiometer. For each measurement, the software provided the surface tension and the average was used to establish a plot of surface tension (ordinate) as a function of the raise in concentration (abscissa). This procedure was performed in triplicate (three distinct drops) for each solution analyzed. The CMC was read at the surfactant concentration in which the surface tension stabilized. The method validation for CMC was determined in the presence of surfactants purely in distilled water, and the

determination of CMC in the presence of cyclohexanecarboxylic acid occurred with the addition of surfactant to the stock solution.

3.5.2 Determination of micelle size by DLS

Micelle size was measured by dynamic light scattering (Nano ZS, Malvern Zetasizer), with a light scattering angle of 173° . The solutions were prepared with ten times the CMC for each surfactant to assure micelle detection in: (i) aqueous solutions, and (ii) aqueous solution in the presence of the naphthenic acid, as shown in Table 12.

Table 12 – Surfactant concentration for the determination of micelle size.

Surfactant	Concentration (mmol L ⁻¹)	
	Aqueous solution of surfactant	Aqueous solution of surfactant + NA
CPC	10.5	3.3
SDS	50	26.7
TX100	3	1.3

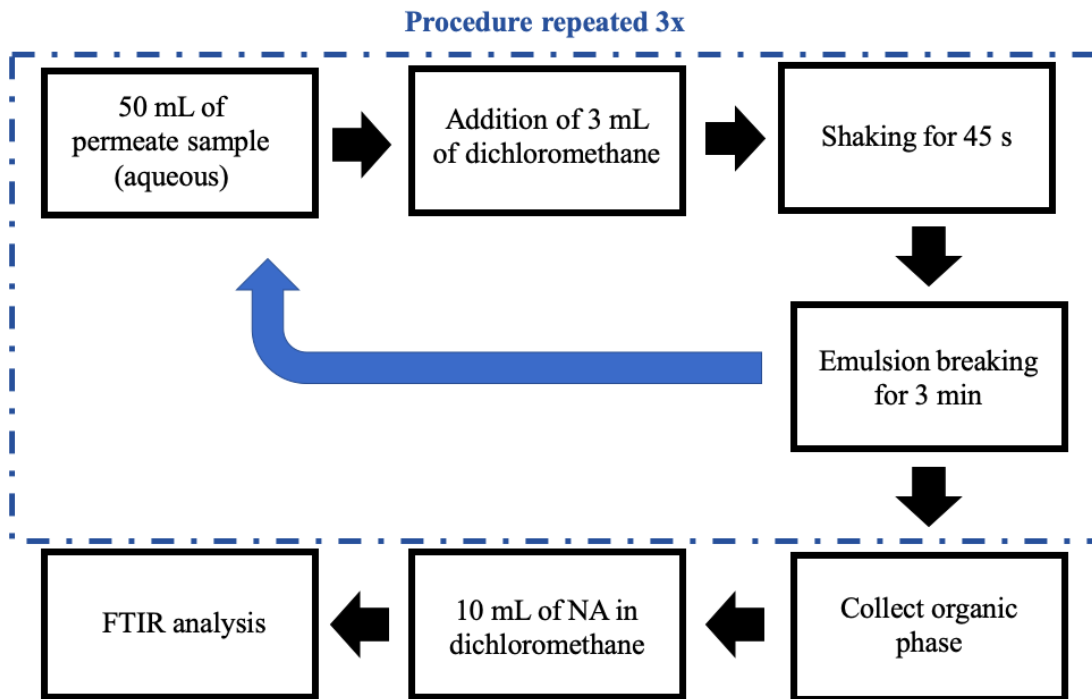
3.5.3 Determination of naphthenic acids by FTIR

The quantification of the naphthenic acids was determined by Fourier-transform infrared (FTIR) spectroscopy method (Agilent Technologies, Cary 660). A liquid-transmission cell with ZnSe window and optical length of 5 mm was used; the absorbance was read at wavelengths ranging from 1800 to 1600 cm⁻¹, region correlated to the C=O bond stretching. NAs calibration curve were constructed using the peak absorbance at 1702 and 1710 cm⁻¹ for cyclohexanecarboxylic and valeric acid, respectively. Dichloromethane was used prior to each analysis as background, and a total of 12 scans were carried out for each sample.

Each filtration sample was prepared in triplicate for FTIR analysis. A liquid-liquid extraction step was required to migrate the NA from the aqueous permeate sample to an organic solvent. Dichloromethane was used as the extractor solvent. For sample preparation, 50 mL of the solution to be analyzed had the pH adjusted to 2 with HCl. The extraction in acid solution is desirable since the NA is protonated. The sample was then transferred to a

separation funnel followed by the addition of 3 mL of dichloromethane. In the presence of the solvent, the funnel was shaken for 45 seconds under depressuring intervals each 15 seconds. The sample was then placed in the funnel support for 3 minutes for emulsion breaking. The organic phase was collected from the bottom of the funnel passing through an analytic filter containing 2 g of Na_2SO_4 to retain residual humidity. The filtered organic phase was reserved in a 10 mL volumetric flask, while the aqueous phase remained in the funnel followed by another addition of 3 mL of solvent. This procedure was repeated three times in total, as demonstrated in Figure 18. Lastly, the balloon had its volume filled until 10 mL for FTIR analysis.

Figure 18 – Schematic representation of sample preparation for FTIR analysis.

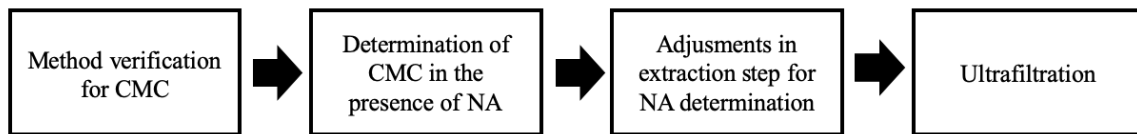


The foaming formed in the shaking step, related to surfactant monomers that did not conform in micellar structures and permeated the membrane, led to the need of modifications on extraction step according to the surfactant. The standard curve of cyclohexanecarboxylic acid for TX100 was prepared without surfactant, in duplicates, from the same stock solution. Additional samples of 200 and 400 mg L^{-1} of NA were prepared with 0.5 and 10 times the CMC of TX100, separately and also in duplicates. All the absorbances were assessed by a

Tukey's Test using the software Statistica (Statsoft Inc., USA) to verify significant differences among absorbance averages.

For CPC, the standard curve was prepared in triplicates without surfactant and with the addition of 100 g L^{-1} of NaCl in each sample before shaking step. Figure 19 summarizes in a flowchart the steps taken for the removal of naphthenic acids by MEUF.

Figure 19 – Flowchart of the steps for the removal of NA by MEUF.



Once the adjustments on extraction step were successful for NA determination, UF experiments were conducted.

4 RESULTS AND DISCUSSION

4.1 CRITICAL MICELLE CONCENTRATION

4.1.1 Method verification

The method to determine the critical micelle concentration for each surfactant was verified through the comparison between the CMC in aqueous solution reported by other authors and the CMC obtained in this work, as demonstrated in Table 13.

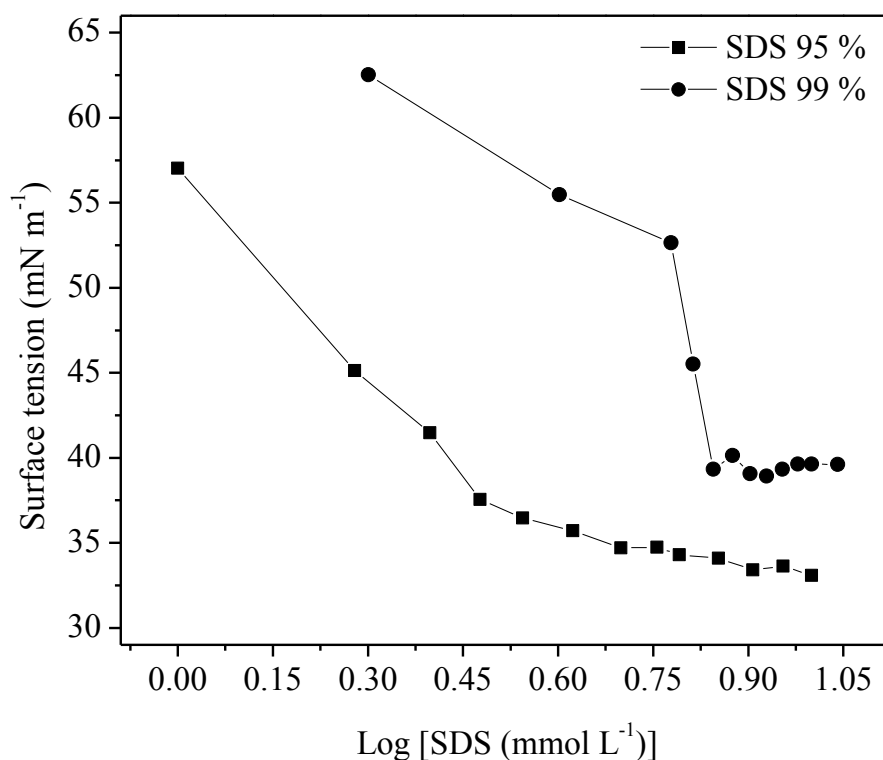
Table 13 – Comparison between the CMC reported in literature and in this work.

Surfactant	This work	Literature		
	CMC (mmol L ⁻¹)	CMC (mmol L ⁻¹)	Method	Author(s)
CPC	1.05	0.826	Surface tension	(AZUM; RUB; ASIRI, 2016a)
		0.9	Conductivity and surface tension	(MUKHIM; ISMAIL, 2012)
		0.96	Conductivity and surface tension	(ALI et al., 2016)
		0.96 - 1.03	Surface tension and microcalorimetry	(CHATTERJEE et al., 2001)
		0.9 - 1.0	Surface tension and conductivity	(SRIVASTAVA; ISMAIL, 2014)
SDS	5.00	7	Surface tension	(EL-AILA, 2009)
		8	Surface tension	(SINGH; ISMAIL, 2012)
		2.33	Surface tension	(AZUM; RUB; ASIRI, 2016b)
		8	Conductivity and surface tension	(ALAM; RAGUPATHY; MANDAL, 2016)
		7.7	Surface tension and microcalorimetry	(CHATTERJEE et al., 2001)
		8.17 - 7.78	Conductivity and microcalorimetry	(NASKAR; DEY; MOULIK, 2013)
		7.8	Surface tension	(CHAUHAN et al., 2014)
		8.2	Electrical impedance spectroscopy	(GHASEMI et al., 2014)
	8.37	Surface tension	(RAMIREZ; COLLINS, 2018)	

Surfactant	This work	Literature		
	CMC (mmol L ⁻¹)	CMC (mmol L ⁻¹)	Method	Author(s)
TX100	0.30	0.29	Surface tension	(ZHANG et al., 2010)
		0.24	Surface tension	(MACISAAC et al., 2004)
		0.167	Surface tension	(BAGHERI; ABOLHASANI, 2014)
		0.29	Surface tension	(GARCÍA-BLANCO et al., 2009)
		0.27	Surface tension	(EL-AILA, 2009)
		0.25	Surface tension	(DAS; ISMAIL, 2009)
		0.3125	Surface tension	(ALAM; SIDDIQ; MANDAL, 2015)
		0.2	Conductivity	(PAUL et al., 2013)
		0.25	Fluorescence spectroscopy	(SUN et al., 2013)
		0.28	Surface tension	(RAMIREZ; COLLINS, 2018)

The determined critical micelle concentration for CPC and TX100 was 1.05 and 0.30 mmol L⁻¹, respectively, which is very similar to the CMC reported in literature. For SDS, however, the CMC found was 5 mmol L⁻¹, which is below most of the results reported by other authors. In an attempt to assess if the reduction in CMC was due to the purity of the reagent used (95 wt. %), another experiment was carried out with a higher purity grade for SDS (99 wt. %), as demonstrated in Figure 20.

Figure 20 – Surface tension as a function of SDS concentration for 95 and 99 % purity grade.



The CMC obtained for SDS with 99 % purity grade was 7.0 mmol L⁻¹, which is in accordance to the literature. Hence, the CMC shows to be associated with reagent purity grade, suggesting that impurities compete with surfactant monomers to saturate the free interface, which results in a lower CMC (HOLMBERG et al., 2002). Once the CMC in this work is corresponding to the literature, the surface tension method was considered appropriate to determine the CMC in the presence of cyclohexanecarboxylic acid.

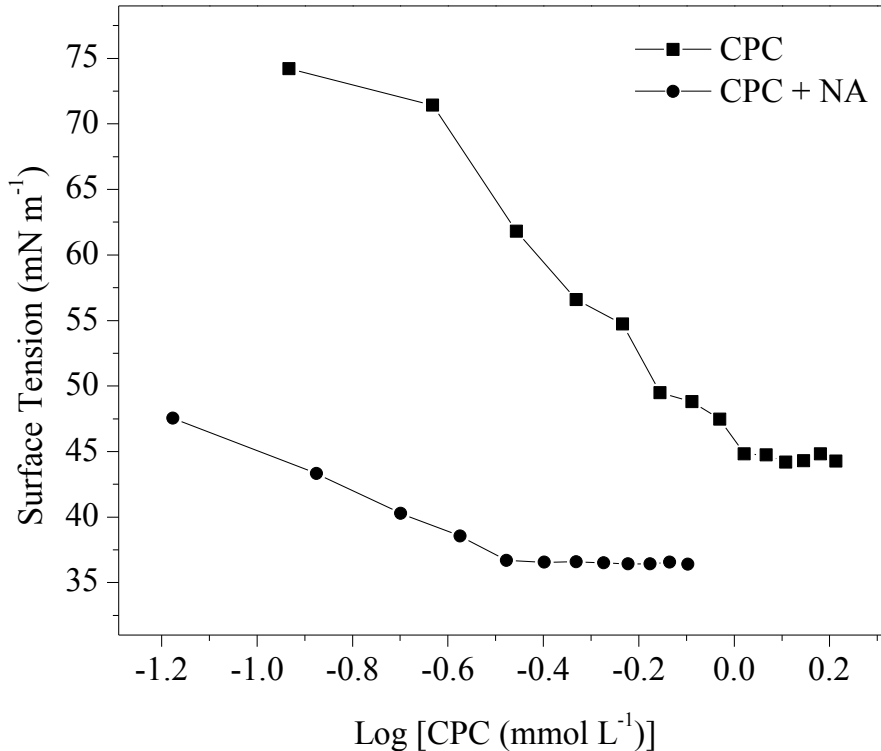
4.1.2 Determination of CMC in the presence of cyclohexanecarboxylic acid

Since the CMC is altered due to the presence of multiple components, the critical micelle concentration for each surfactant was determined in the presence of 500 mg L⁻¹ cyclohexanecarboxylic acid. Thus, it was possible to define the surfactant concentration for MEUF experiments based on the proper CMC of the naphthenic acid aqueous solution.

4.1.2.1 CPC

For the surfactant CPC, micelle formation initiated at the concentration of 0.33 mmol L^{-1} , as demonstrated in Figure 21, which represents a decrease of 68.3 % in terms of concentration when compared with the aqueous solution of surfactant.

Figure 21 – Surface tension as a function of CPC concentration.

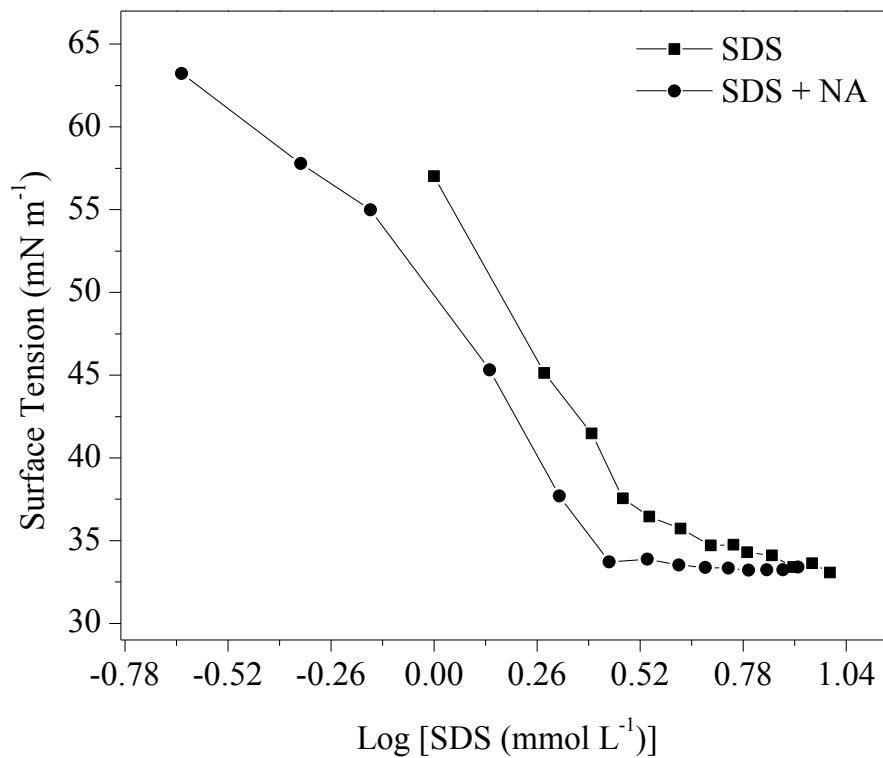


The reduction in CMC is due to the amphiphilic behavior (surfactant characteristic) of the naphthenic acids, which are driven to the air-water interface along with surfactants monomers. Thus, due to the presence of surfactant and NA, the saturation of the surface occurs at a lower surfactant concentration and, as a result, micelle formation starts (DERISZADEH; HARDING; HUSEIN, 2009).

4.1.2.2 SDS

As shown in Figure 22, the surfactant SDS started to form the micellar structure at the concentration of 2.76 mmol L^{-1} in the presence of cyclohexanecarboxylic acid. The percentage decrease in terms of concentration compared to the aqueous solution of surfactant was 44.6 %.

Figure 22 – Surface tension as a function of SDS concentration.

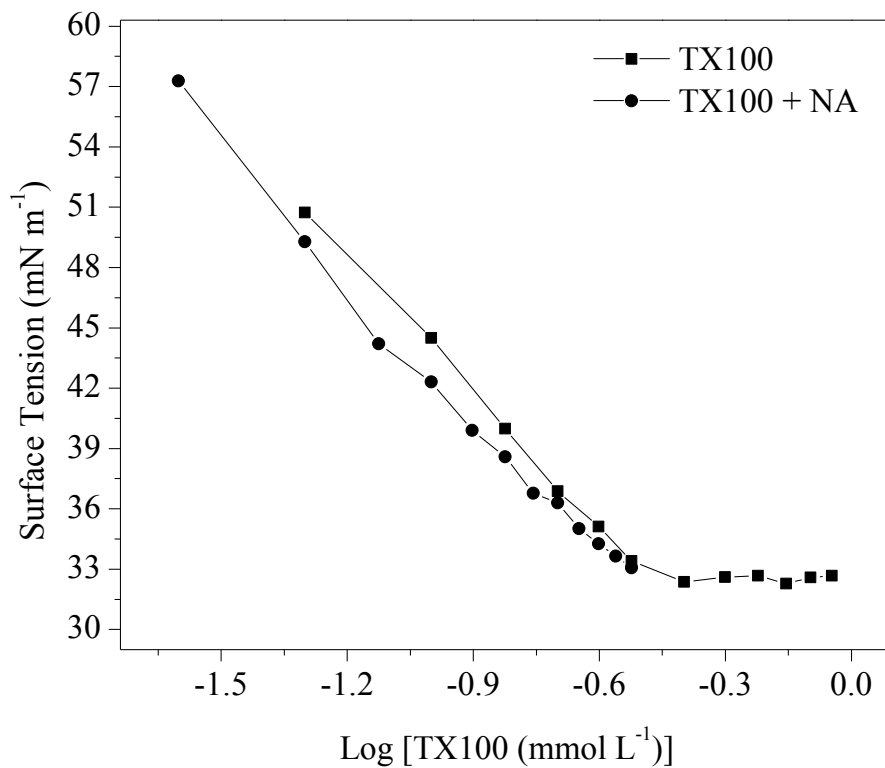


4.1.2.3 TX100

It is possible to observe in Figure 23 that TX100 exhibited a CMC of 0.12 mmol L^{-1} in the presence of the naphthenic acid, which is 58.3 % lower compared with the CMC in aqueous solution. Although Triton X-100 do not have a specific molecular weight – it's a mixture of monomers – the surfactant has the highest molecular weight (as showed in Table 7) and possibly the longest hydrophobic structure (tail) among the surfactants evaluated in this study. For this reason, surfactant molecules are closer of each other and the ability to form micelles is raised (ROSEN, 2004). In addition, Deriszadeh, Harding and Husein (2009)

assessed distinct naphthenic acids in solution with the surfactant CPC. The authors reported that the CMC decreased as the carbon number of the naphthenic acids increased, leading to the conclusion that longer chains are more effective in saturating the air-water interface. These facts may explain why TX100 presented the lowest CMC when compared with the other surfactants in this study, both in aqueous solution and in the presence of cyclohexanecarboxylic acid. However, it is not possible to ensure that the size of the chain is the only influence in micelle formation, since other properties such as the ionic strength have complex influence over the CMC.

Figure 23 – Surface tension as a function of TX100 concentration.



The surface tension in the presence of cyclohexanecarboxylic acid with TX100 did not stabilize completely, but it kept decreasing as the surfactant concentration increased. This tendency was also observed by other authors when measuring CMC by surface tension (ABBASI-GARRAVAND; MULLIGAN, 2014b; ALAM; RAGUPATHY; MANDAL, 2016; ALAM; SIDDIQ; MANDAL, 2015; CHAUHAN et al., 2014; GARCÍA-BLANCO et al., 2009; RAMIREZ; COLLINS, 2018). In this study, CMC was then read at the point in which the variation of surface tension was kept constant.

Table 14 summarizes the critical micelle concentrations in aqueous solution found: (i) for the surfactants, and (ii) for surfactants + naphthenic acid (NA), as well as the percentual reduction between both measurements.

Table 14 – Summary of the CMCs measured in this work in aqueous solution of surfactant and in aqueous solution of surfactant + NA.

Surfactant	Aqueous solution of surfactant (mmol L⁻¹)	Aqueous solution of surfactant + NA (mmol L⁻¹)	CMC reduction (%)
CPC	1.05	0.33	68
SDS	5.00	2.77	45
TX100	0.30	0.12	58

4.2 MICELLAR ENHANCED ULTRAFILTRATION

Although micellar enhanced ultrafiltration technique presents good performance in pollutant removal, surfactant monomers are expected to pass through the membrane pore sizes. During the sample preparation for FTIR analysis, the permeate samples require shaking to promote the migration of NA from the aqueous to the organic phase, as described in item 3.4.3. This process forms an emulsion which breaking point depends on the surfactant used.

4.2.1 Emulsion breaking point

The determined time necessary to break the emulsion after shaking in the presence of each surfactant is presented in Table 15.

Table 15 – Emulsion breaking point for TX100, SDS and CPC surfactants.

Surfactant	Time (min)
TX100	2
SDS	120
CPC	No emulsion breaking in 24 h

The system with the cationic surfactant CPC did not break the emulsion in aqueous solution of NA within the period of 24 hours. The system with the anionic surfactant SDS

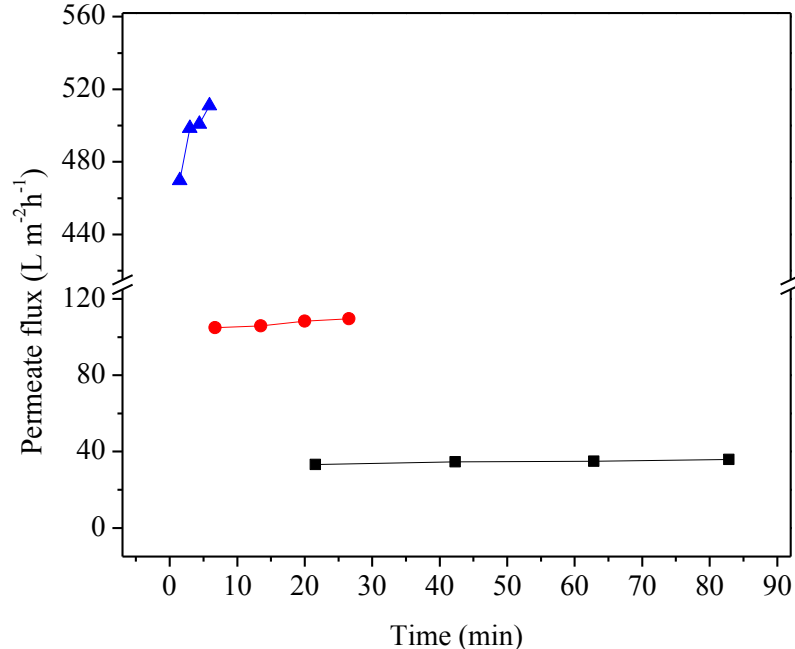
broke the emulsion; however, it was necessary 2 hours for total breaking. Since preparation sample step for extraction requires 3 shaking procedures to migrate successfully the NA to the organic phase, the surfactants CPC and SDS were not tested initially in MEUF experiments.

Triton X-100 formed the least stable emulsion. This result was expected, since nonionic surfactants are typically liquids or pastes characterized as poor foaming agents (DE; MONDAL, 2012). Thus, TX100 was first selected to initiate the micellar enhanced ultrafiltration study.

4.2.2 Membrane conditioning

The permeate flux for membranes UH004, UP005 and UP010 with distilled water is presented in Figure 24. As expected, the membrane with the highest MWCO (10 kDa) achieved the highest permeate flux during conditioning.

Figure 24 – Permeate flux with for membranes UH004 (■), UP005 (●) and UP010 (▲) with distilled.



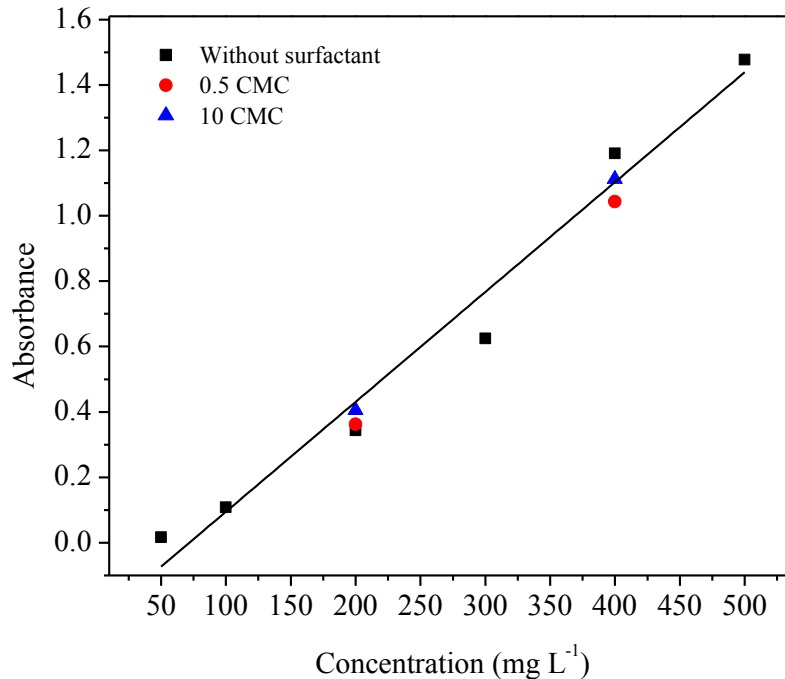
According to the manufacturer, UH004 and UP005 have the exact same primary characteristics: UH004, however, is submitted to a chemical treatment which alters the membrane material from polyethersulfone (PES) to hydrophilic polyethersulfone (PESH), and this treatment leads to a reduction in pore size. The hydrophobic membrane (5 kDa) took 26.5

minutes to permeate 100 mL of distilled water, while the hydrophilic (4 kDa) took 82.8 minutes. This result demonstrated that a smaller pore size led to a longer permeate flux, even though hydrophilic membranes are expected to facilitate the passage of water molecules.

4.2.3 MEUF using TX100

In order to verify if the presence of surfactant influences FTIR response, samples in the presence of TX100 for the concentrations of 200 and 400 mg L⁻¹ of cyclohexanecarboxylic acid were evaluated and compared with the standard curve without surfactant (Figure 25).

Figure 25 – Standard curve for cyclohexanecarboxylic acid: (■) without surfactant; (●) with 0.5 and (▲) 10 times the CMC of TX100.



The absorbance of samples at same concentration in both presence and absence of surfactant were statistically compared. The Tukey's range test demonstrated that the average absorbances measured in duplicates in the presence of 0.5 and 10 CMC did not show significant difference compared with the average absorbances without surfactant. Thereby, the standard curve for the determination of cyclohexanecarboxylic acid was used without any correction factor for the presence of surfactant TX100. The linear trend of the curve is characterized by a R² equal to 0.9743.

4.2.3.1 Selection of pH and pore size

In order to narrow the amount of filtration experiments, preliminary tests were conducted to select the pH with greater pollutant removal among an acid, a neutral and an alkaline solution of cyclohexanecarboxylic acid, as presented in Table 16. The filtrations were run with the 5 kDa membrane under the center point conditions from the experimental design with TX100 (2.0 bar and 6 CMC).

Table 16 – Filtration experiments for the selection of pH with 6 CMC of Triton X-100 and TMP of 3 bar using 10 kDa membrane.

pH	NA removal (%)
3.0	6 ± 6
7.5	15 ± 12
12.0	1 ± 5

The standard deviation (SD) does not refer to filtration experiments carried out in triplicates, but to the sample preparation step performed in triplicates. It is possible to observe that the SD for all pH is high when compared to NA removal. Nevertheless, as produced water pH is commonly neutral, the pH of 7.5 was considered the most promising and it was selected for further filtration experiments. In order to select the membrane pore size, membranes with molecular weight cutoff (MWCO) of 5 and 10 kDa were tested, as demonstrated in Table 17. The membrane with 4 kDa was not tested due to its low permeate flux (Figure 24).

Table 17 – Filtration experiments for the selection of MWCO with 6 CMC of Triton X-100 and TMP of 3 bar.

MWCO (kDa)	NA removal (%)	Filtration time (h)
5	14 ± 8	6.3
10	15 ± 12	1.8

The NA removal of 14 and 15 % suggests that the MWCO of 5 and 10 kDa did not influence the acid removal. Thereby, the subsequent filtration experiments were carried out with the 10 kDa membrane for a higher permeate flux.

4.2.3.2 Naphthenic acid removal and permeate flux

In addition to the experiments proposed by the experimental design, a filtration test without surfactant was conducted for sake of comparison, as shown in Table 18. Surfactant concentration expressed as function of its critical micelle concentration is one of the most relevant parameters when working with MEUF due to the need to assure pollutant trapping within micelles. In this context, the transmembrane pressure was also tested to evaluate micelle stability. Standard deviations refer to a single filtration run divided in triplicate samples prepared as described in item 3.5.3.

Table 18 – NA removal in MEUF assays based on the experimental design using TX100.

Surfactant concentration	TMP (bar)	NA removal (%)	Average permeate flux* (L h ⁻¹ m ²)
–	3.0	20 ± 3	273.9
2 CMC	2.0	15 ± 9	35.6
2 CMC	4.0	13 ± 8	59.2
6 CMC	3.0	21 ± 9	43.8
6 CMC	3.0	15 ± 4	46.8
6 CMC	3.0	14 ± 6	47.0
10 CMC	2.0	12 ± 11	31.6
10 CMC	4.0	18 ± 11	56.3
40 CMC	4.0	4 ± 14	31.8

*Average permeate flux of the four samples collected for each experiment.

The set of experiments proposed with Triton X-100 showed few influence of surfactant concentration on NA removal. In addition, high standard deviation was observed between the samples. A final test with 40 times the CMC was conducted to evaluate if a high surfactant dosage would increase pollutant removal; however, the filtration presented the lowest removal and the highest SD. Interestingly, the filtration test without the addition of surfactant showed a naphthenic acid removal of 20 % and SD of only 3 %. This result could be explained by the amphiphilic property of the naphthenic acid, which can cluster into micelles of its own specie.

The permeation of surfactant monomers through the membrane, even in small concentrations, always occurs when working with MEUF. The high standard deviations suggest that TX100 may influence in a disruptive way the liquid-liquid extraction of filtered samples prepared for FTIR analysis. Thus, the surfactant seems to affect the reproducibility in terms of migration of cyclohexanecarboxylic acid to the organic phase. In Table 19, the ANOVA data for the influence of critical micelle concentration (CMC) and transmembrane

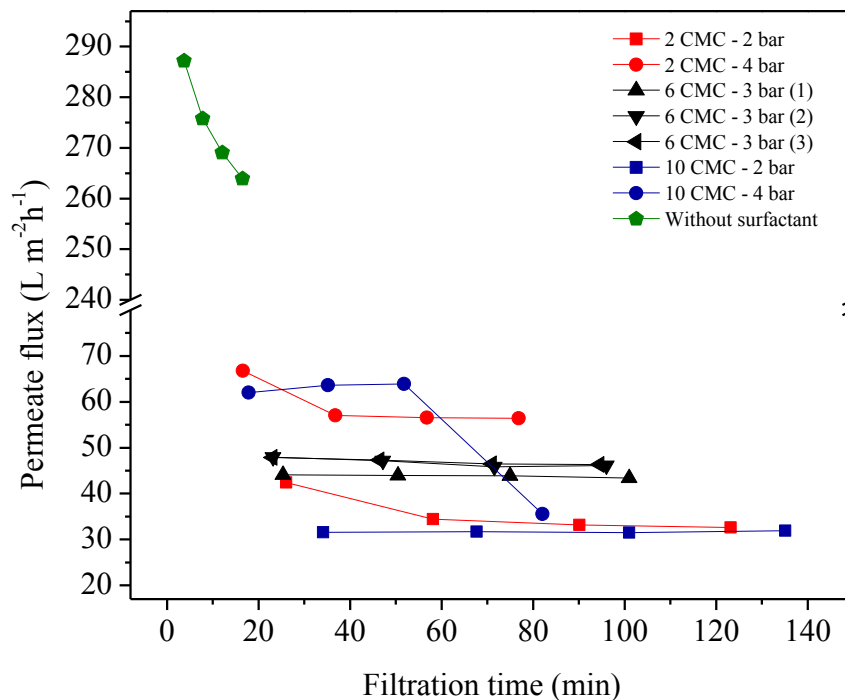
pressure (TMP) is presented. The calculated p level showed that CMC and TMP for TX100 poorly influenced on NA removal ($p < 0.05$ to assure 95 % of confidence interval).

Table 19 – ANOVA data from the experimental design for NA removal using TX100.

Factor	SS	df	MS	F	p
CMC	1.000	1	1.000	0.08	0.79
TMP (bar)	4.000	1	4.000	0.32	0.60
CMC x TMP	16.000	1	16.000	1.31	0.33
Error	36.714	3	12.238	-	-
Total SS	57.714	6			

Although the presence of surfactant in NA solution did not improve cyclohexanecarboxylic acid removal, the permeate flux for all experiments with TX100 were lower compared to the filtration without surfactant, as shown in Figure 26.

Figure 26 – Permeate flux of the experimental design with TX100 measured every 40 mL of filtered sample using 10 kDa membrane.

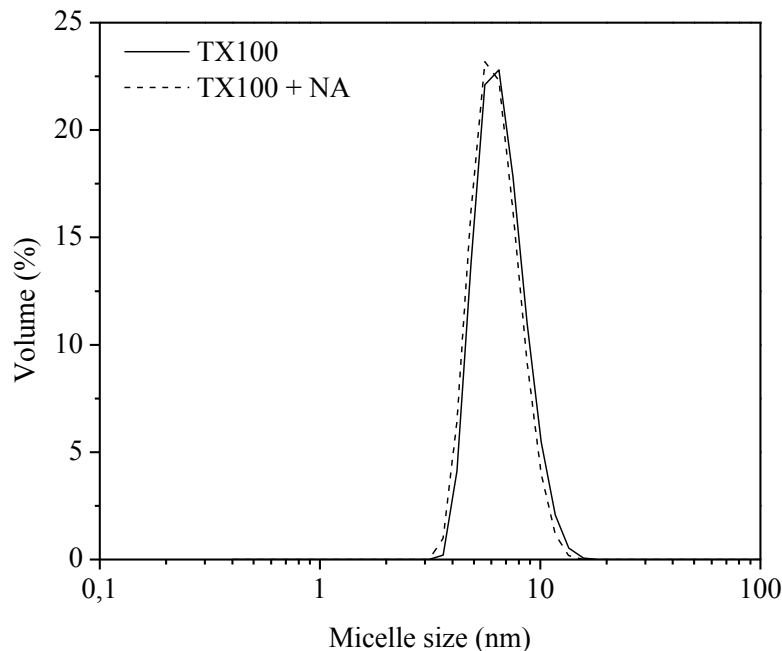


It is possible to observe that the increase in surfactant concentration did not influence permeate flux as much as the increase of transmembrane pressure. In the assays using 2 bar and TX100 concentrations of 2 CMC and 10 CMC, the permeate flux was kept approximate; however, the first 40 mL sample with 2 CMC was collected minutes before the sample with 10 CMC. This tendency was observed in the subsequent samples of both assays, which led to

a total filtration time shorter for 2 CMC compared with 10 CMC. Similarly, in the assays using 4 bar and surfactant concentration of 2 CMC and 10 CMC, the permeate flux was also approximate – with the exception of the last sample collected with 10 CMC. This last sample could have taken longer than the others due to the deposition of micelles and surfactant monomers, which could indicate that material was being retained at the membrane surface.

In MEUF, it is expected that micelles attach contaminants and raise its size to be retained by a relatively open membrane like UF (VENKATAGANESH et al., 2012). However, as it is possible to observe from Figure 27, the result of TX100 micelle size analysis shows that the structures present in solutions did not exhibit a raise in size in presence of cyclohexanecarboxylic acid. According to De and Mondal (2012), nonionic surfactants are desirable for the removal of organic contaminants due to satisfactory solubility in water and effectiveness in low concentrations. However, based on MEUF experiments and micelle size analysis, it is possible to infer that TX100 surfactant seems to be inefficient to form micelles with cyclohexanecarboxylic acid, and MEUF technique with TX100 is not suitable to remove this particular naphthenic acid.

Figure 27 – Micelle size in aqueous solution using 10 CMC of TX100: (–) TX100 surfactant only and (– –) TX100 + 500 mg L⁻¹ of naphthenic acid (NA).



4.2.3.3 Valeric acid as contaminant

In attempt to evaluate if another naphthenic acid can be removed by MEUF using TX100, a solution of 500 mg L⁻¹ of valeric acid was filtered under the center point conditions from the cyclohexanecarboxylic acid experimental design. The determination of valeric acid was also by FTIR analysis. The critical micelle concentration used as an estimative was the one determined in the presence of cyclohexanecarboxylic acid. Table 20 shows the results for valeric acid removal.

Table 20 – Filtration experiment for valeric acid removal under the center point conditions from the experimental design using TX100 (6 CMC, 3 bar, and 10 kDa membrane).

TX100 concentration	NA removal (%)
-	6 ± 4
6 CMC	6 ± 3

Besides the fact that cyclohexanecarboxylic acid has seven carbons in its structure while valeric has five, the main difference between the two proposed in this experiment is that cyclohexanecarboxylic is cyclic while valeric has an open carbon chain. Due to the removals found, it is possible to affirm that Triton X-100 is also unsatisfactory to form micelles with valeric acid and, consequently, inefficient for micellar enhanced ultrafiltration.

4.2.4 MEUF using CPC

Although CPC did not show emulsion breaking point in item 4.2.1, salt (100 g L⁻¹ of NaCl) was added to the filtered sample as an alternative to break the emulsion based on SM5520. The addition of NaCl resulted in total emulsion break, following the same methodology described in item 3.4.3. Hence, a standard curve of cyclohexanecarboxylic acid in the presence of 100 g L⁻¹ of sodium chloride was prepared.

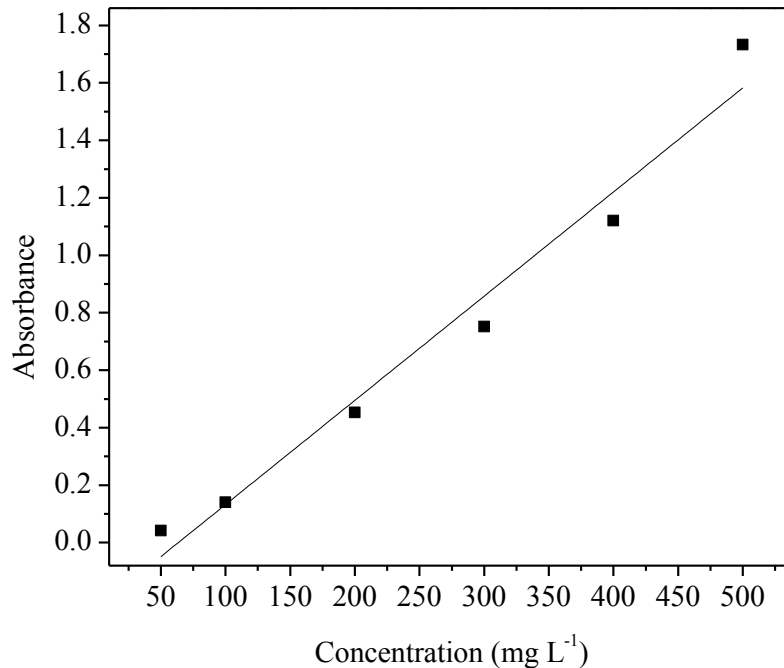
In order to evaluate if the surfactant influences FTIR response, the concentration of 0.5 times the CMC of CPC was added to the standard curve of NA and compared with NA concentrations of 200 and 400 mg L⁻¹ without CPC, as shown in Table 21.

Table 21 – Influence of 0.5 CMC of CPC surfactant in samples of 200 and 400 mg L⁻¹ of naphthenic acid.

NA concentration (mg L ⁻¹)	Average absorbance		Surfactant influence
	Without surfactant	0.5 CMC	
200	0.6094 ± 0.0574	0.5611 ± 0.0782	4.8%
400	1.5325 ± 0.2887	1.4849 ± 0.0607	4.7%

The presence of surfactant in the samples of 200 and 400 mgL⁻¹ showed a decrease of 4.8 and 4.7 % in the absorbances, respectively, which led to the conclusion that the influence of CPC is constant in this range. Thus, the percentage of 4.75 % was considered to calculate NA removal through the standard curve showed in Figure 28. The linear trend of the curve is characterized by a R² equal to 0.9739.

Figure 28 – Standard curve for cyclohexanecarboxylic acid in the presence of 100 gL⁻¹ of NaCl.



4.2.4.1 Selection of pH

In order to narrow the amount of filtration experiments, preliminary tests were conducted to select the pH with major pollutant removal among an acid, a neutral and an

alkaline solution of cyclohexanecarboxylic acid, as demonstrated in Table 22. The filtrations were run under the center point conditions from the experimental design with CPC (2.0 bar and 30 CMC).

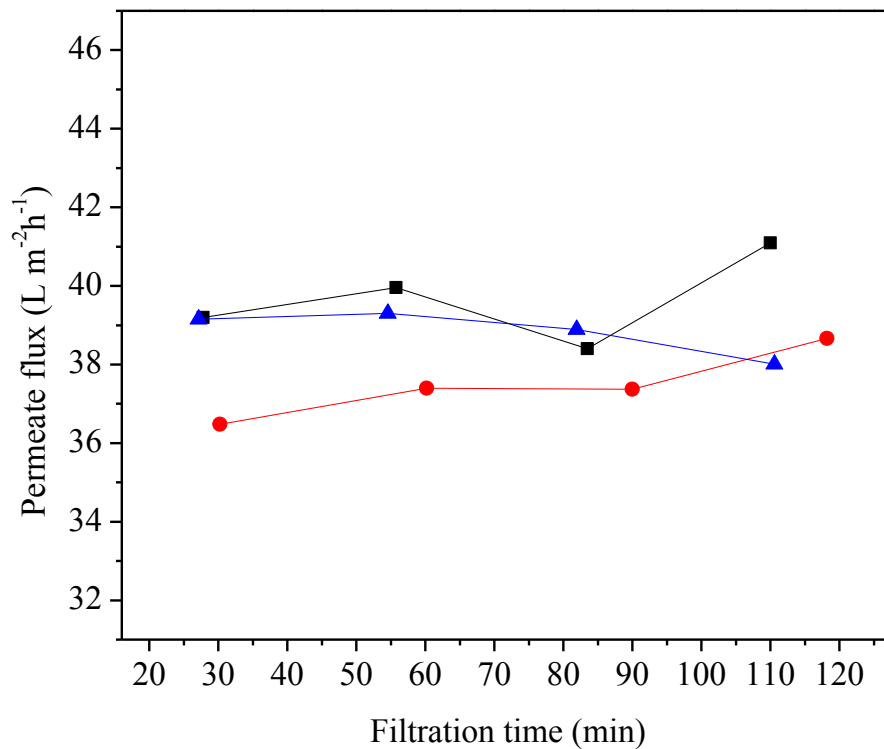
Table 22 – Filtration experiments for the selection of pH with 30 CMC of CPC and TMP of 3 bar using 10 kDa membrane.

pH	NA removal (%)
4.0	54 ± 7
8.0	56 ± 9
12.0	54 ± 12

From Table 22, it is possible to observe that the NA removals were very similar regardless the solution pH. Cationic surfactants are generally stable to pH changes, both acid and alkaline (TADROS, 2005). This result indicates that the surfactant CPC can be satisfactorily used over this pH range for MEUF experiments. In Figure 29

Figure 29, it is demonstrated that the permeate flux did not vary sharply with pH changes, although permeate flux for pH 8 was slightly lower.

Figure 29 – Permeate flux for filtration experiments using CPC under center point conditions (30 CMC and TMP of 3 bar) at pH: 4 (■); 8 (●); and 12 (▲).



Since NA removal and permeate flux were similar in the pH range analyzed, the neutral pH of 8 was selected for the following experiments due to its proximity to the real produced water condition.

4.2.4.2 Naphthenic acid removal and permeate flux

As mentioned previously, the critical micelle concentration is a fundamental parameter when working with MEUF. Deriszadeh, Harding and Husein (2009) evaluated a CPC concentration of 10 mM for MEUF runs, which corresponds to approximately 30 times the CMC of the cyclohexanecarboxylic acid. Thus, 30 times the CMC was chosen as the center point of the experimental design for surfactant concentration parameter. In order to evaluate a lower surfactant dosage and assure a high permeate flux, 10 times the CMC was tested. Fifty times the CMC was also studied as a higher surfactant dosage, to analyze the contribution of surfactant in the formation of polarization layer at the membrane surface. The pressure system was also assembled to verify micelle stability and permeate flux, as demonstrated in Table 23.

Table 23 – Filtration experiments for the experimental design with CPC.

Surfactant concentration	TMP (bar)	NA removal (%)	Average permeate flux* (L h⁻¹ m²)
-	3.0	20 ± 3	273.9
10 CMC	2.0	28 ± 5	28.1
10 CMC	4.0	27 ± 4	36.3
30 CMC	3.0	56 ± 14	26.3
30 CMC	3.0	60 ± 7	25.3
30 CMC	3.0	54 ± 4	28.7
50 CMC	2.0	68 ± 6	21.3
50 CMC	4.0	67 ± 3	25.0

*Average permeate flux of the four samples collected for each experiment.

The overall response in terms of TMP did not demonstrate difference in NA removal when analyzing the same CPC concentration. However, filtration experiments in the presence of surfactant showed higher removals compared to the filtration without surfactant for all cases. For 10 CMC, the removal showed to be approximately 7 % higher in the presence of CPC for the pressure of 2.0 and 4.0 bar. For center point (30 CMC), the average triplicate

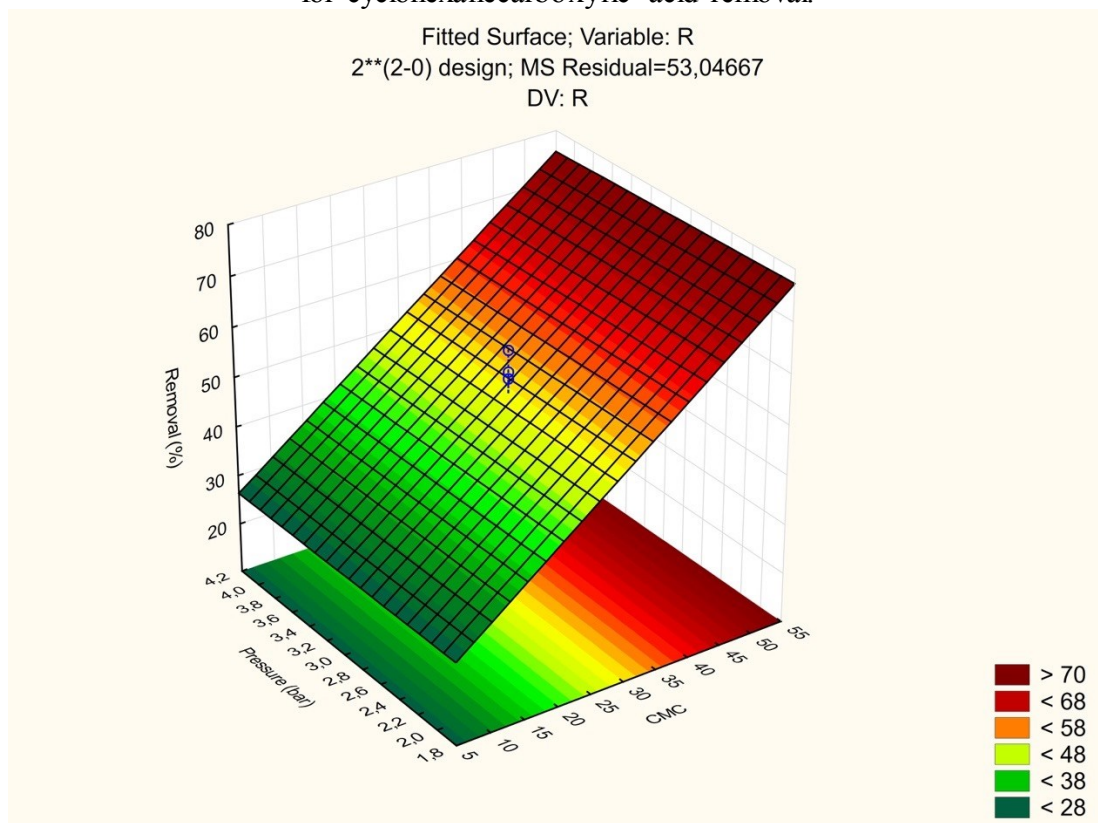
removal was 57 ± 3 %, with a standard deviation applied to all experiments of the design. The highest NA removal occurred at 50 CMC of CPC, with 68 % and 67 % for the TMP of 2.0 and 4.0 bar, respectively. The analysis of variance (ANOVA) was elaborated, as presented in Table 24, to verify the influence of critical micelle concentration (CMC) and transmembrane pressure (TMP). The analysis showed that CMC factor influences significantly on NA removal with 95 % confidence interval.

Table 24 – ANOVA data from the experimental design for NA removal using CPC.

Factor	SS	df	MS	F	p
CMC	1608.01	1	1608.01	30.31	0.01
TMP (bar)	0.490	1	0.490	0.0092	0.93
CMC x TMP	0.160	1	0.160	0.0030	0.96
Error	159.14	3	53.047	-	-
Total SS	1767.800	6			

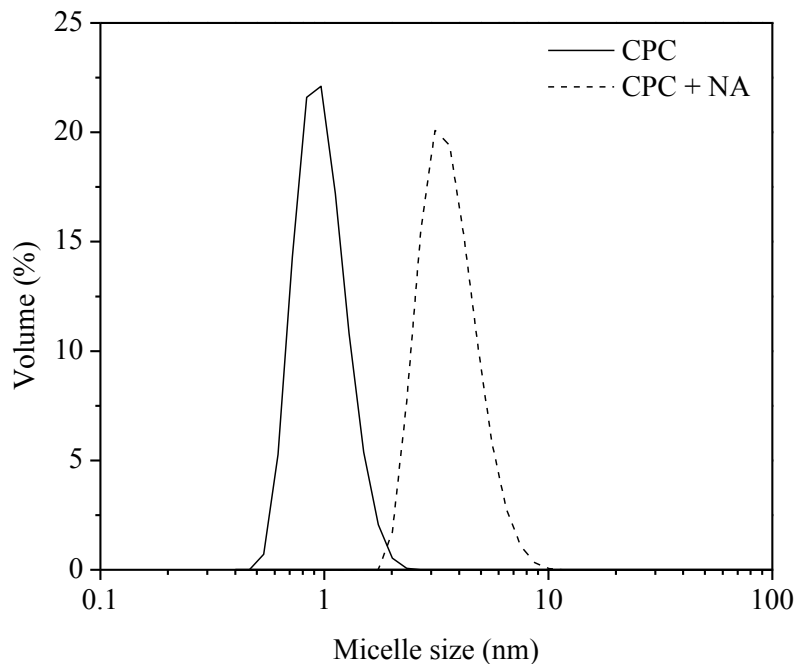
On the other hand, transmembrane pressure alone and combined with CMC were not considered significant factors by the statistical analysis. Figure 30 illustrates the effect of TMP (pressure) and CMC in terms of cyclohexanecarboxylic acid removal.

Figure 30 – Fitted surface for the experimental design using CPC, 10 kDa membrane at 25 °C for cyclohexanecarboxylic acid removal.



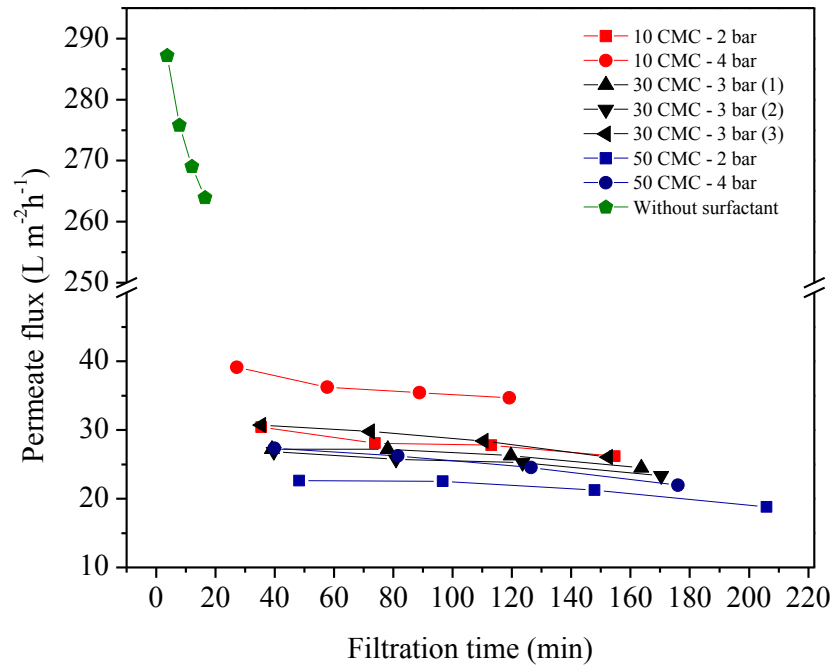
Higher surfactant dosages increased NA removal but also decreased the overall permeate flux (Table 23). This fact indicates that the micelles are being retained at membrane surface, increasing the filtration resistance. In Figure 31, it is possible to observe that there was an increase in micelle size: from 1.1 nm in aqueous solution with 10 CMC of CPC to 3.3 nm in the presence of 10 CMC of CPC and 500 mg L⁻¹ of NA. Deriszadeh, Harding and Husein (2009) found the micelle size for CPC alone approximately 1 nm, and the micelle size for CPC + pentanoic acid approximately 3 nm. Since their findings are close to the results observed in this study and the naphthenic acids have similar carbon number, it is likely that the cyclohexanecarboxylic acid is contained within the micellar structure.

Figure 31 – Micelle size in aqueous solution using 10 CMC of CPC: (—) CPC surfactant only and (---) CPC + 500 mg L⁻¹ of naphthenic acid (NA).



The permeate flux of all experiments from the experimental design using CPC were lower compared to the test without surfactant (Figure 32). The filtration test with 10 CMC and the lowest TMP (2.0 bar) presented the highest permeate flux. For the assays at 4.0 bar for 10 and 50 CMC, the permeate flux was very similar to the filtration under the condition of the center point. The lowest permeate flux was given by 50 CMC and 2.0 bar, which took more than 3 hours per batch.

Figure 32 – Permeate flux of the experimental design with CPC measured every 40 mL of filtered sample using 10 kDa membrane.



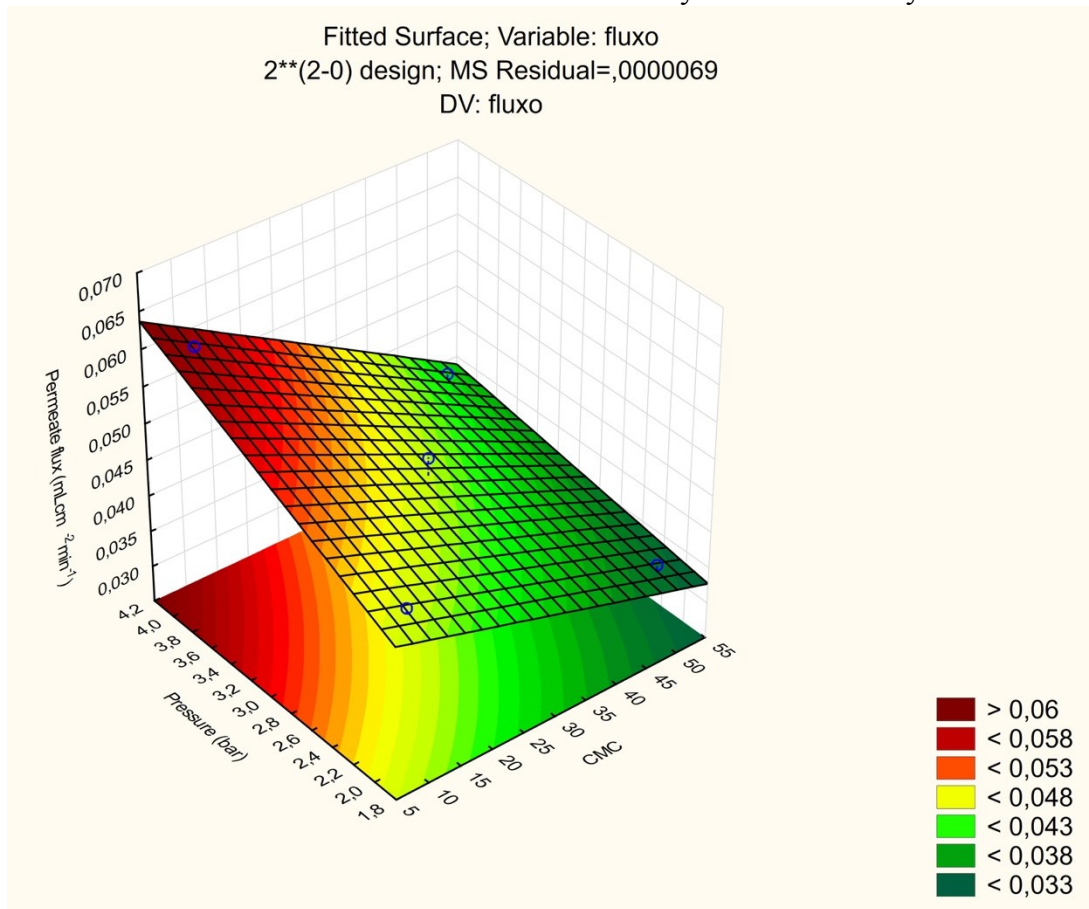
ANOVA analysis was built to assess the influence of CMC and TMP over permeate flux. Since the p value is less than 0.05 for both parameters, it is possible to affirm that the independent variables are significant for MEUF with CPC with 95 % confidence interval, as shown in Table 25.

Table 25 – ANOVA data from the experimental design for permeate flux using CPC.

Factor	SS	df	MS	F	p
CMC	0.000231	1	0.000231	33.54618	0.010239
TMP (bar)	0.000098	1	0.000098	14.25883	0.03253
CMC x TMP	0.000015	1	0.000015	2.10181	0.242995
Error	0.000021	3	0.000007	-	-
Total SS	0.000365	6			

The fitted surface for the experimental design in terms of permeate flux is shown in Figure 33. By the plotted surface, it is possible to observe that higher the CMC, lower is the permeate flux; in a similar way, the higher the TMP, the higher the permeate flux.

Figure 33 – Fitted surface for the experimental design in terms of permeate flux using CPC, 10 kDa membrane at 25 °C for the removal of cyclohexanecarboxylic acid.



Since NA removal for high and low level of TMP is very similar (approximately 67 %), the TMP of 4.0 bar is more desirable for a more efficient operation.

4.2.4.3 Evaluation of hydrophilicity and hydrophobicity

In an attempt to assess the membrane chemistry in terms of hydrophilic and hydrophobic characteristics, membranes with MWCO of 4 and 5 kDa were tested, as shown in Table 26. The pore sizes of 4 and 5 kDa were the closest available by the manufacturer Microdyn Nadir in which the only difference between the membranes was the chemical treatment to alter its chemical properties.

Table 26 – Naphthenic acid removal for hydrophilic and hydrophobic membranes.

MWCO (kDa)	Membrane chemistry	NA removal (%)
4	Hydrophilic	72 ± 2
5	Hydrophobic	72 ± 3

Hydrophilic membranes are preferable to facilitate the passage of water molecules through the membrane pore sizes (DERISZADEH; HARDING; HUSEIN, 2008). However, NA removal for both membranes are approximately 72 %, which demonstrates that there is no advantage in using a hydrophilic membrane in this case. Since the assays were run under the best condition from the experimental design using CPC (50 CMC and 4 bar), it is important to point out that NA removal using 5 kDa membrane ($72 \pm 3\%$) was slightly higher than using 10 kDa ($67 \pm 3 \%$) membrane. The permeate flux was not measured in both experiments because the main purpose of the comparison was to evaluate a hydrophilic membrane in terms of NA removal.

5 CONCLUSION

The study of micellar enhanced ultrafiltration for the removal of cyclohexanecarboxylic acid – selected in this study as the naphthenic acid model – showed to be a successful technique for NA removal in acid, alkaline and neutral pH using the surfactant CPC. Even though cyclohexanecarboxylic has high solubility in water, cyclic carbon chain and low molecular weight, the experimental design proposed in this study achieved a naphthenic acid removal of 68 % using a surfactant concentration of 50 times the CMC and transmembrane pressure of 4.0 bar. Both experiments run at 50 CMC using 2.0 and 4.0 presented similar removal percentages (68 and 67 %, respectively), which indicates that the highest TMP tested is desirable for a higher permeate flux.

The critical micelle concentration was successfully measured in the presence of cyclohexanecarboxylic acid to dose assertively surfactant concentrations used in MEUF assays. The surface tension method used in this study was also successfully verified with only surfactant species in aqueous solution: for SDS, a CMC lower than literature was found. However, the test was repeated with a higher purity grade which was in accordance to other studies. This result suggested that the impurities of the surfactant previously tested competed with surfactant monomers at the free interface, lowering the surface tension, and consequently, the CMC. In a similar way, since naphthenic acids are also surfactants (NAs have amphiphilic structure), CPC, SDS and TX100 surfactants decreased the CMC in the presence of cyclohexanecarboxylic acid in 68, 44 and 58 %, respectively.

In order to verify if the surfactant would have influence on FTIR response, a Tukey's Test revealed no difference among the average absorbances with and without surfactant for standard curve using TX100. Thus, the standard curve for cyclohexanecarboxylic acid was used without any correction factor due to the presence of surfactant. For CPC, a standard curve was satisfactorily assessed considering a loss of 4.75 % in terms of absorbance.

For Triton X-100 filtration experiments, NA removals were unsatisfactory based on the experimental design. In addition, the surfactant did not present an increase in micelle size in the presence of NA. Valeric acid was also tested in a filtration experiment with TX100; however, NA removal was also unsuccessful. A preliminary MEUF experiment using SDS took over 10 hours to finish the batch carried with 10 times the CMC, 10 kDa membrane and

TMP of 4.0 bar. For this reason, MEUF experiments were not carried out with SDS surfactant.

5.1 SUGGESTIONS FOR FUTURE STUDIES

Since the tests with 50 CMC for 2.0 and 4.0 bar presented similar removals, higher pressures can be investigated in future studies to reduce operational time. Thus, higher pressures and higher surfactant concentrations are promising parameters for further research with CPC. In addition, different surfactants and surfactant blends can be tested for micelle formation with naphthenic acids. The determination of surfactant concentration, which is permeating the membrane is also an important parameter to evaluate in future MEUF assays.

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