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Bachelor of Science in Engineering of Micro and Nanotechnologies

Oil/ water separation methods
An Overview

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"There is no justification for present existence other than its expansion into an indefinitely open future"

- *Simone de Beauvoir*.

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Abstract

Catastrophic environmental problems such as oil spill accidents, industrial oily wastewater and any other type of uncontrolled release of oils into the environment are a major global issue, since it threatens marine ecosystems, animals, plants, corals and it also leads to a big economic impact. Additionally, it can also affect the public health of communities located near the polluted area.

This present thesis addresses the study of different types of oil collecting methods, such as the use of materials that are environmentally friendly, cost friendly and easy to use and produce. With that in mind, the focus of this work will be to study different approaches on materials and technologies for oil/water separation, with special focus on water/oil emulsion separation. Emulsified oil/water mixtures are extremely stable dispersions being therefore more difficult to separate as the size of the droplets in the emulsion decreases.

Regarding oil sorption, materials can be divided into two categories absorbent or adsorbent. Oil absorbent materials, such as sponges, foams, nanoparticles, and aerogels, can be adjusted to have both a hydrophobic and oleophilic wettability while displaying a porous structure. This can be advantageous for targeting oil spills in large scale environmental catastrophes sets, since these materials can easily absorb oil. Oil adsorbent materials for example, meshes, textiles, membranes, and clays, involve the capture of the collecting material to the surface of the adsorbent material, additionally attracting more attention than other technologies by being low cost and of easy manufactures. They have ideal applications mainly in industrial wastewater treatments. On the adsorbent materials category, the utilization of nanofibrous membranes is highlighted by its benefits, among them their high surface area, and by the possibility of allowing the use of different types of materials in order to adjust its permeability, its fiber diameter, its higher surface area associated to the nanofibers and its porosity.

Keywords: Oil-adsorption materials, Oil-absorption materials, Oil-removing, Water-removing, Oil microdroplets, Oil/water emulsions, Oil/water separation

Resumo

Catástrofes ambientais como acidentes por derramamento de óleo, efluentes oleosos industriais e qualquer outro tipo de liberação descontrolada de óleos para o meio ambiente, são um grande problema a nível global, uma vez que ameaçam os ecossistemas marinhos, animais, plantas e corais, implicando também um grande impacto económico. Além disso, pode também afetar a saúde pública das comunidades próximas à área poluída.

A presente tese aborda o estudo de diferentes tipos de métodos de recolha de óleo, tais como o uso de materiais ecológicos, de baixo custo, de fácil uso e produção. Com isto em mente, o foco será estudar diferentes abordagens, materiais e tecnologias para separação óleo/água, com foco especial na separação de emulsões óleo/água. As emulsões de óleo/água são dispersões extremamente estáveis sendo, portanto, mais difíceis de separar à medida que o tamanho das gotículas na emulsão diminui.

Em relação à capacidade de sorção, os materiais podem ser divididos em duas categorias sendo por isso, absorventes ou adsorventes. Os materiais absorventes, como esponjas, espumas, nanopartículas e aerogéis, podem ser ajustados de forma a obter uma molhabilidade hidrofóbica e oleofílica e uma estrutura porosa, uma vez que possuem naturalmente a vantagem de remover o óleo em zonas de catástrofes ambientais de grande escala, uma vez que podem facilmente absorver o óleo. Os materiais adsorventes, por exemplo, malhas, tecidos, membranas e argilas, envolvem a captura do material coletor para a superfície do material adsorvente e atraem mais atenção do que outras tecnologias devido ao seu baixo custo e facilidade de fabricação. Esta categoria de material é idealmente vantajosa para tratamentos de águas residuais industriais. É de ressalvar que na categoria de materiais adsorventes, a utilização de membranas de nanofibras se destaca pelos benefícios em permitir o uso de diferentes tipos de materiais, ajustar a sua permeabilidade, diâmetro da fibra e porosidade e também pela maior área superficial associada às nanofibras.

Palavras-chave: Materiais absorventes de óleo, Materiais adsorventes de óleo, Remoção de óleo, Remoção de água, Microgotas, Emulsões óleo/água, Separação de óleo/água

Contents

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Symbols

% Percentage

µm Micrometers

nm Nanometers

g/g Gram of oil per gram of sorbent

w/w Weight by weight

mL/h Milliliters per hour

cm Centimeters

kV Kilovolts

Acronyms

TWh Terawatt-hour

TOE Tons of oil efficient

NPs Nanoparticles

CF Copper foam

TiO$_2$ Titanium dioxide

PU Polyurethane

ME Melamine

HPS Hydrophobic sílica nanoparticles

PVP Polyvinylidone

PVDF Poly (vinylidene fluoride)

PAN Polyacrylonitrile

PET Poly (ethylene terephthalate)

PS Polystyrene

MF Microfiltration

NF Nanofiltration

UF Ultrafiltration

RO Reverse osmosis

NFs Nanofibers

PTFE Polytetrafluoroethylene

PEN Poly (arylene ether nitrile)

PSf Polysulfone

PVDF Polyvinylidene fluoride

PVA Poly (vinyl alcohol)

CNC Cellulose nanocrystals

DMAc Dimethylacetamide

Motivation

Nowadays, water pollution consequence of the presence of a water/oil emulsion has been a high frequency problem of our generation. This is justified by the massive global fossil fuel consumption from most industries, and results in problems such as: oil spills, oil waste caused by machine malfunction and oily wastewater generated by agriculture, petrochemical, metallurgical, pharmaceutical, automobile and food industries [1].

Over the last few years, disastrous oil spill accidents have taken place, primarily caused by incidents in oil exportation or accidents on oil platforms. One of the major and most recent accidents was the 2019 Northeast Brazil oil spill, that affected almost 3000 km of the Brazilian coastline and released about 2500 tons of crude oil onto the sea [2]. This calamity resulted on a tremendous economic impact, and most importantly, on the degradation of the region's ecosystem, such as corals and seaweeds and the death of many sea animals. It also poses a huge health risk for the populations that live near the affected area since it affects and contaminates our food chain and water, both essential for life [2], [3].

The efficient removal of the total amount of oil in the water, resultant from oily wastewater and oil spill accidents, is a worldwide concern and action must be taken in order to avoid a large range of environmental and public health issues, such as increased cancer risk and respiratory problems [1].

One of the major issues resultant from these events is the failure on capturing microdroplets, that cannot be properly filtrated by traditional methods [4]. As a result, investigators and industries continue the search for efficient methods to capture micro sized droplets of oil, 143 article results obtained just by searching the topic "oil/water emulsion separation" in Web of Science, formed by the result of sea currents, wave action or water mixing[5]. This water movement action results on a water/oil emulsion, formed by oil microdroplets, droplets which have dimensions of 20 µm or less and are undetectable to the naked eye [6]. For that it's highly necessary the creation of materials and membranes that are environmentally friendly, efficiently adsorbent, easy to use and produce, have a low cost of production and are recyclable is a crucial step towards fighting the consequences of water/oil pollution.

1. Introduction

1.1 From biomass fuels to a fossil fuel economy

Since the discovery of fire, wood-fuels and other biomass type of fuels have been used to obtain heat, light, and other forms of energy. Over the years, with the increase in population, the advances in technology and the crescent necessity for power motivated the search for a more efficient fuel. Although, even with the advances in agriculture, in solar-based energy generation and in other types of renewable energy sources, such as wind and water power generation, the power supply was still limited and the search for an even better alternative was inevitable [7]. The turning point in the major transition from biomass fuels to fossil fuels was marked by the historic invention of the steam engine and the consequent industrial revolution era [2]. At this point the cost of wood-fuel increased significantly. The harvesting of forest trees began to be regulated and the power efficiency needed at this point was incompatible with these types of fuels. And so forth, in the 18th century coal was used as a substitute for biomass fuels and, ultimately, in the 19th century was marked by the additional introduction of natural gas, petroleum and its derivatives, thus beginning the oil age era and being invented the internal combustion engines [7].

Despite all the advantages that came from this types of fuels, with its use problems have arose, associated with its extraction and distribution, as it is the example of oil spills [8].

1.2 Oil spills- An overview

Between the 1965s and 1970s, the global oil consumption was, in average, 22,042 terawatt-hour, TWh, per year. That sums a capacity of about 1.895×10^9 tons of oil equivalent (TOE), in which an average of 635,000 tons of oil per year were accidentally spilled on the ocean [2].

Nowadays, when addressing recent worldwide oil consumption, from the years 2010 to 2018, the average of global oil consumption was approximately 51,500 TWh per year, equivalent to approximately 4.428×10^9 TOE [2]. With this number in mind, just on the last decade (2010s), the average oil spill lost rounded 164,000 tons.

In 2019, four large oil spills were recorded in North America, South Asia and Brazil, which resulted in, approximately, 3,500 tons of oil spilled on the ocean due to tankers problems, such as collisions, equipment failure and explosions [9].

Besides oil spillage, oily effluent discharges, such as oil-water emulsions resultant from a wide range of industries, for instance from the automobile industry, from the food industry, from the textile industry, from the refineries, as well as from the oil explorations, are all a major source of water pollution and of contamination [10]. These events resulted in catastrophic damage to the ecosystem and to human health, not only consequence of the oil spills or discharges themselves, but also consequence of the inherent cleaning processes [6]. Additionally, the death of surface sea organisms, the death by asphyxiation of many fishes, birds, turtles, etc., the destruction and death of corals and, finally, the exposure of organisms and humans to some toxins, directly and indirectly through our food chain, are some examples of the hazard that this situation can cause to the ecosphere [8]. Thus, it is of extreme importance to endure on the study for efficient oil capture methods, for innovative wastewater treatment and to explore new methods and techniques, primarily for oil/water emulsion separations.

1.3 Oil/water conventional separation technologies

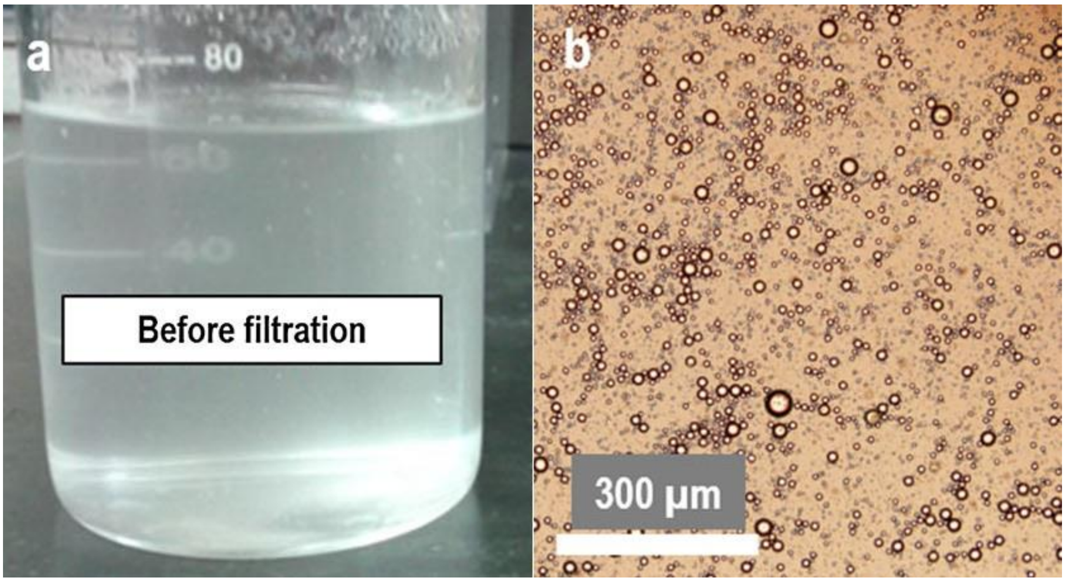

Figure 1.1- a) Photo of an oil/water emulsion; b) Optical microscopy image of an oil/water emulsion. Adapted by permission from Springer Nature: Sringer , Cellulose, All-cellulose composite membranes for oil microdroplet collection, Ana P. C. Almeida, João Oliveira, Susete N. Fernandes, Maria H. Godinho, João P. Canejo [COPYRIGHT] (2020). [6]

Micrometer sized droplets arrive from emulsified oily water [11], as seen on figure 1.1, as an after effect of oil spills or industrial oily wastewaters. These are an outcome of the economic and technological growth and are consequence of a water/oil emulsion, in which the originated microdroplets have, generally, dimensions of 20 µm or less, being undetectable to the naked eye and being unable to be captured by the conventional methods, as mentioned below [12]. In the last years, one of the most used conventional techniques in water/oil separation is air flotation [13], a physical treatment that consists on removing impurities in water using air under pressure. This will form bubbles that will cause the impurities to float to the surface, allowing them to be separated from the water. Other methods are gravity separation[14], adsorption[15], sedimentation by centrifugation, that consists on rotating the solution by centrifugal force favoring the sedimentation of the solution compounds[16], and biological treatment [17] in which microorganisms are introduced to eliminate the organic parts and stabilize pollutant compounds of the oily wastewater [10], [18]. However, these processes face some major challenges, such as expensive costs, high complexity, low efficiency and, more importantly, incompatibility with collecting oil microdroplets [19].

1.4 Microdroplets removal technologies

Currently, one of the most commonly employed physical techniques for microdroplets collection is electroflotation [10], used to treat oily wastewater and to efficiently collect micro sized droplets. It consists on generating hydrogen and oxygen bubbles on the electrode surface, while water electrolysis is simultaneously occurring. These gas bubbles will then interact with the oil droplets, which will cause the oil-gas bubbles to rise. The oil has a lower density comparing to water so it tends to rise to the surface, so that they can be easily removed by employing either skimming method, where floating oil and oil emulsions are removed by a device at the surface [20]. Electrocoagulation [21] is a similar process that is described by the dissolution of a sacrificial anode, result of applying a difference in potential between the electrodes. One of the resulting products are flocs, remains from the sacrificial anode, in the form of metallic hydroxides, within the wastewater to be treated that are capable of adsorbing its impurities, such as oil, even oil microdroplets from oil/water emulsions [22]. Hydroxyl ions formed on the cathode [22], [23], that are also released to the wastewater, form a precipitate with the pollutant particles and, hence, flocculation. This sludge can be after removed, either by floatation or sedimentation [24]. However, these approaches have limitations, for instance, high material requirement and high machinery cost, together with high energy consumption [21].

1.5 Nanotechnology

Nanotechnology is an emerging area that has been constantly evolving and revolutionizing different fields of science, such as environmental engineering [25], medicine [26], electronics [27], chemistry [28], and many more [29].

Richard Feynman introduced, for the first time, the concept of nanotechnology when addressing a new perspective for miniaturization coupled with the idea of an atomic material manipulation. This important mark happened in 1959, on his famous lecture “There’s plenty room at the bottom”, at the annual session of the American Physical Society at Caltech [30].

Over the years significant changes happened, and, nowadays, nanotechnology can be defined as the modern science and engineering involved in the design, synthesis, characterization and application of materials at nanoscale, defined between 1 and 100 nanometers (nm) [31]. Here, physical, chemical and biological properties of nanomaterials like optical properties, reactivity, thermal stability, change in comparison to the bulk material properties [31]. Features such as quantum phenomena and the relation between the decrease of particle size and consequent increase of surface area are responsible for a change in some of the materials’ properties [31].

Nanomaterials can be classified by its morphology being, for example, nanorods, nanowires, nanocrystals, nanowiskers, and others, or by its dimension, in which nanoparticles and quantum dots fit into the zero-dimensional category, while nanowires and nanorods are labeled as one-dimensional. In two-dimensional nanosheets and three-dimensional materials like nanocrystals, nanomaterials that are made up of multiple layers [32].

1.5.1 Nanoparticles

As already stated, nanoparticles are zero dimensional nanostructures. They can be classified accordingly to its morphology, chemical and physical characteristics being divided in carbon-based, metal, ceramic, semiconductor polymeric or lipid-based nanoparticles [33].

Nanoparticles (NPs) have countless applications in different areas of science. Such thing can be justified by their ability to be used as mechanical reinforcement of matrices (structural), by their high surface area and by their size influence on optical, electrical, chemical and physical properties of a substance [33]. All these properties, and mainly its high surface to mass ratio, make them interesting for use in reinforcing the surface of a material. In the case of environmental applications, NPs have a very alluring role on treating contaminated water, since contaminants like oil can be easily absorbed by some nanoparticles [33], such as magnetite nanoparticles [34], cellulose nanocrystals [35] and others [36].

2. Oil/water separation technologies

2.1 Existing methods for oil/water separation

The current global situation regarding the removal and treatment of residues from water sources, is becoming an environmental concern that can no longer be avoided nor ignored [37]. The ecosystem is being greatly harmed, as a consequence of polluters such oil spills and oily residues present in wastewater. Therefore, to address this issue, water treatment has recently gained much attention from researchers worldwide, whose focus is to find new, more efficient and cost-effective materials and removal technologies that present low toxicity, good recyclability and are of easy handling [37].

Some sorbent materials appear as an asset for oil removal in high scale environmental catastrophes since they can easily absorb the oil, meaning that the oil is integrated onto the absorbent material, without the release of residues into the ecosphere [38]. For efficient oil collection, the chosen materials must be hydrophobic and oleophilic, must be porous and must present good oil selectivity. Some sponges, gels, particles and foams are examples of materials that present these mentioned abilities and, thus, are among the most frequently studied porous oil sorbent materials in our days [39]. Adsorbent materials are another type of technology for oil recovery, and oil/water emulsions separation. This material category involves the attachment of the collecting material to the surface of the adsorbent material and stands out from other technologies by being low cost, easily fabricated and ideal for applications mainly in industrial wastewater treatments. This category includes separation materials such as meshes, filters, films, clays and membranes [39].

2.1.1 Foams and sponges

Foams and sponges are 3D materials, which are characterized by their high surface area, elevated porosity, low density, high absorption rate and for being extremely light weighted [40]. By definition, a foam is a solid or liquid substance where gas bubbles, just like air, are trapped inside, and a sponge is a porous material, that can be made by various materials, such as ceramic, metallic or even polymeric [41]. These assets, along with their ability to quickly absorb some substances, such as certain pollutant materials and, when squeezed, to release the collected material, constitutes a great advantage when collecting oil from big environmental sets [42]. Additionally, some of them display the capability to absorb oils at a high rate up to 140 g/g (gram of oil per gram of sorbent) [42]. Certain foams and sponges can also demonstrate high durability and great mechanical strength due to the ability to make use and adjust pre-existing foam and sponge structures, for oil separation purposes [42]. One example of the preeminent structural materials being studied for oil/water separation purposes, regarding its performance and its customization, is the copper foam (CF). Regarding this subject, an already bought commercial CF was surface modified with polydopamine, $AgNO_3$,n-dodecyl mercaptan and studied at each stage by Zhou *et al.* [43]. This surface modification allowed to transform a hydrophilic foam into a final superhydrophobic foam, having shown to separate different types of oils, such as hexane, sesame oil, octane, in an efficient manner, higher than 95%, displaying high performance cycles up to 30 uses, where a cycle is one separation efficiency test [43]. Polymer foams are also an efficient and cheap alternative, demonstrating good reusability[44]. The most common primal matter used in polymer-based foam production are polyurethane (PU) and melamine (ME), since they are cost effective, are easy to produce and are abundant [44]. For instance, polyurethane (PU) sponge is a light weighted polymer that demonstrates high porosity, high oil absorption capacity, cost effectiveness and the ability to be produced at large scale[4]. Liu *et al.* [4] bought a low cost commercial PU sponge that had magnetic properties, due to a Fe_3O_4 nanoparticles coating. The result was a sponge that presented a superhydrophobic and superoleophilic wettability. It was proven to be efficient in harsh environments, such as salty water or very alkaline or acidic solutions, displaying an absorption capacity up to 35 times its own weight, valid for either light or heavy density oils [4]. Besides that, the magnetic properties allowed for easy collection of the sponge from the environment [4]. In the same way, Wu *et al.* [45] manufactured a low cost, and flexible polymer-based graphene foam (PGB) by a low-cost self-assembly technique of graphene sheets on a PU skeleton, which was both superhydrophobic and superoleophilic and capable of collecting different oil types, while being efficiently, above 90% efficiencies, reusable after 300 utilization cycles. Moreover, its unique 3D structure, presenting a more wrinkled structure than a standard PU foam, allows the foam to exhibit great mechanical properties, even when bended, compressed or twisted [45]. Concluding, in addition to all the advantages mentioned above, both sponges and foams also possess the huge benefit of being easily customizable with different material coatings, depending on its specific purpose, in order to finally achieve efficient oil/water separations.

2.1.2 Aerogels

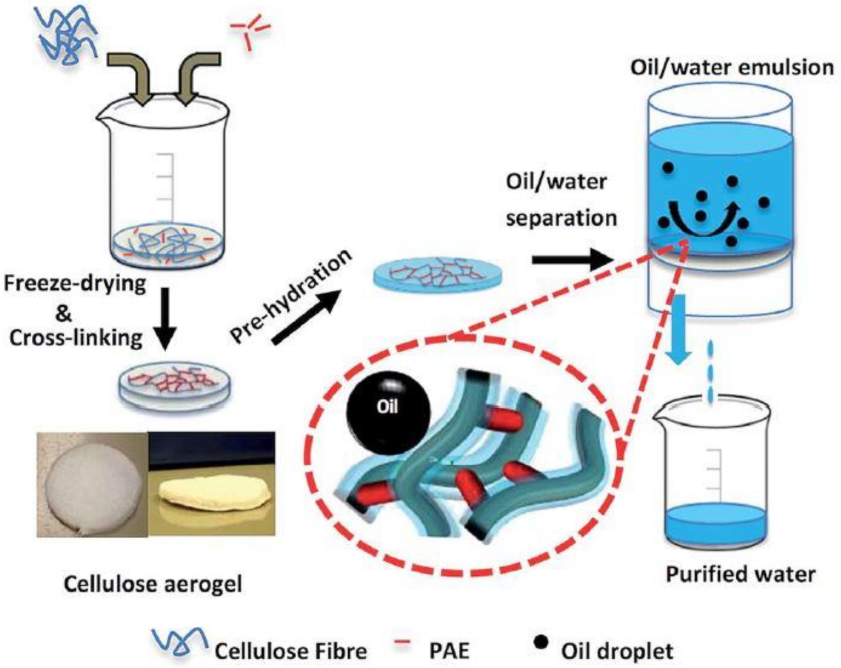

Figure 2. 1-Schematic of aerogels manufacture and application to oil/water separation. [46]

Aerogels, see figure 2.1, are 3D materials, which are produced by sol-gel synthesis, that consists, briefly explained, on the formation of a gel, a rigid and highly porous network, originated from reactions taking place between colloidal particles in solution, sol [47]. This 3D network, for oil/water separation purposes, can function as a sponge, exhibiting however higher flexibilities. They are also characterized by their high surface areas, elevated porosity and low density [48]. A sponge-like aerogel with those properties, was produced by Yu *et al.* [48] by a sol-gel method. In order to achieve hydrophobicity abilities, organoalkoxysilanes were chosen as precursors [48]. The final aerogel demonstrated good absorption capacities up to 10 cycles. In the same manner, Bo *et al.* [49] studied a hydrophobic BiOBr-silicone aerogel, fabricated by a sol-gel method, that was able to separate the oil from water, as well as to degrade, by photolytic degradation, the pollutant oil [49]. Aerogels can be immersed into the oily wastewaters, just like foams and sponges, but also can be integrated on a gravity separation process [15].

2.1.3 Nanoparticles incorporation

Certain nanoparticles have an important task in oily water treatments since oil can be easily photodegraded, absorbed, or trapped at the surface of the nanoparticles due to characteristics such as its high surface area to mass ratio and oil selectivity [33]. Nanoparticles can contribute with excellent mechanical, electrical, optical, and morphological properties, when used complementarily to customize previously made structures [33]. Gupta *et al.* [44] highlighted in their work, that the use of NPs can positively contribute to material composites, increasing its surface roughness and having the ability to help the increase of underwater hydrophobicity and oleophilicity properties of the material[44]. This is again justified by some nanoparticles properties such as, their high surface area and their size influence on chemical and physical properties of a substance [33].

Ge *et al.* [50] mentioned, in their work, the use of a previously bought polyurethane sponge that was after coated by the dip-coating method, with polyfluorowax and hydrophobic silica nanoparticles (HPS) intended to establish a superhydrophobic wettability behavior to the material. It demonstrated to maintain its absorption capacity up to 10 cycles [50].

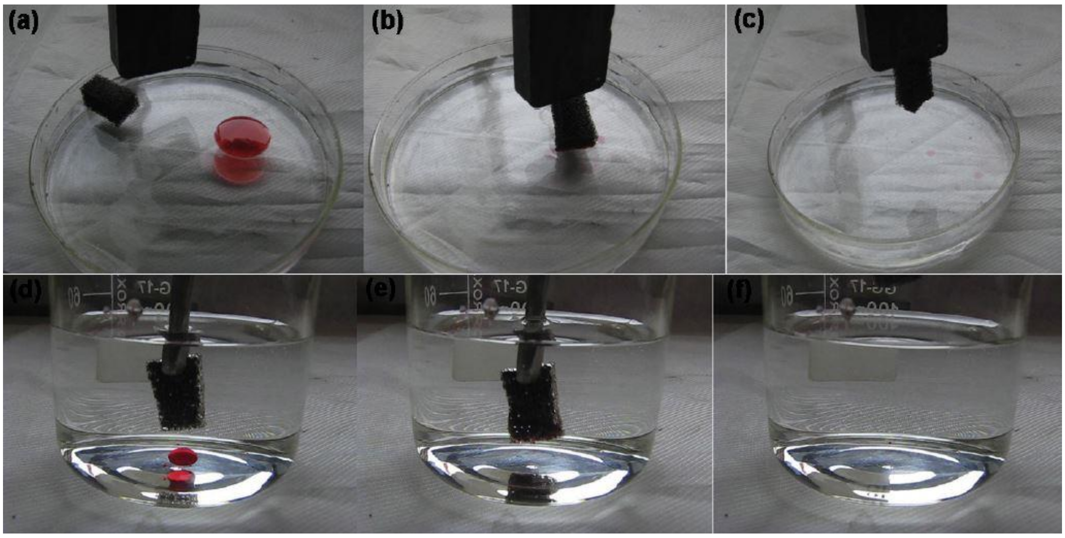

Figure 2. 2- Demonstration images for the removal of hexadecane oil, dyed with red, from the water surface using a piece of foam controlled by a magnet; Reprinted from Colloids and Surfaces A: Physicochemical and Engineering Aspects, Bo Ge, Xiaotao Zhu, Yong Li, Xuehu Men, Peilong Li, Zhaozhu Zhanga, Versatile fabrication of magnetic superhydrophobic foams and application for oil–water separation, Pages No.4 Copyright (2015), with permission from Elsevier. [51]

Magnetic nanoparticles can be attractive not only for the cleaning process, but also to manipulate the foam and remove it from the water after the separation process. For instance, Ge *et al.* [51] , in their work, functionalized a previously existing polyurethane foam with magnetic superhydrophobic nanoparticles, of Fe_3O_4, to capture oil from oily wastewaters. The foam showed a magnetic behavior due to the addition of the Fe_3O_4 NPs and had the consequent ability to be easily manipulated towards polluted areas with a magnet, as shown on figure 2.2. It also showed an oil absorption capacity up to 70 g/g, a good compressing resistance up to 200 cycles, and the possibility to scale it up in order to clean larger areas [51].

2.1.4 Meshes

The utilization of meshes became a very alluring technique for wastewater separation purposes, this is justified by their easy and cheap manufacture, for example by 3D printing [52], and by their high availability and low-cost, when commercially purchased [53]. They have also excellent efficient separation rates justified by their large pores, of about 50 µm, being, therefore, capable of separating large volumes of oil from water at low pressures and using a gravity driven separation method [54]. Typically, meshes are made from metals, such as stainless steel or aluminum and, in order to make these materials viable for oil/water separation, the mesh surface needs to be customized, to favor the adjustment of its wettability. For this purpose, materials, such as nanoparticles, oxides and polymers are being studied [55],[39].

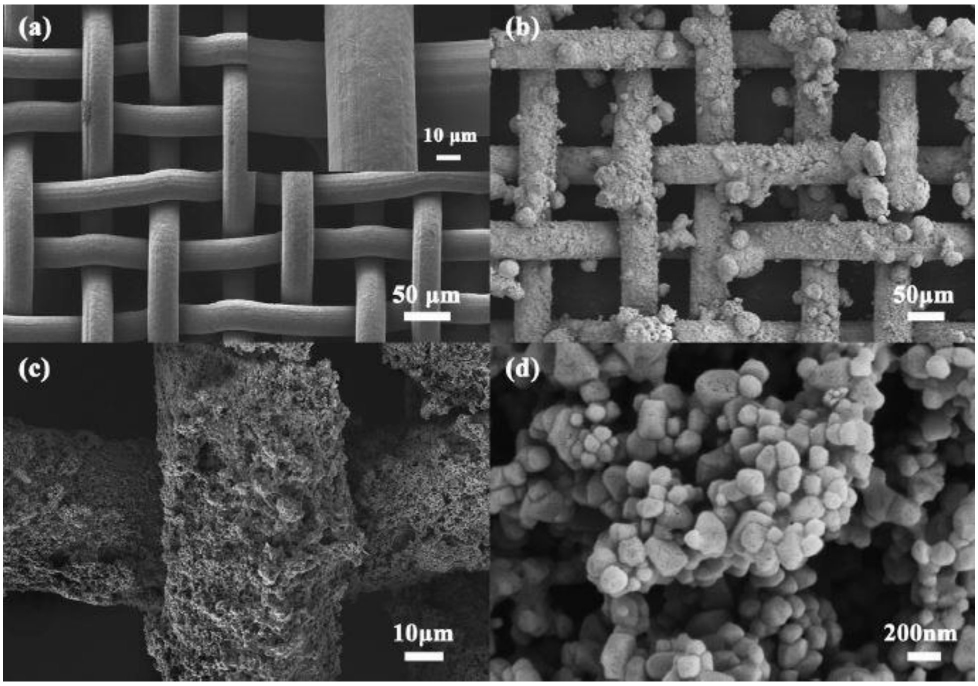

Figure 2. 3- SEM images of (a) the original stainless-steel mesh, and (b–d) the TiO2 coated mesh surface at low and high magnifications, respectively. Reprinted from Colloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 489, Jian Li,Long Yan,Wenfang Hu,Dianming Li,Fei Zha,Ziqiang Lei, Facile fabrication of underwater superoleophobic TiO2 coated mesh for highly efficient oil/water separation, Pages No. 3, Copyright (2016), with permission from Elsevier. [53]

Li *et al.* [53] produced an underwater superoleophobic TiO_2 nanoparticles coated stainless steel mesh, represented on figure 2.3. The stainless-steel mesh, which was previously commercially achieved, was coated, by spray-coating, with TiO_2 NPs and polyurethane (PU), both providing an increase in the binding forces between the NPs and the mesh. Because of its water affinity, the oil is captured by the mesh surface giving rise to a 99% separation efficiency and demonstrating a reusability of over 40 separation cycles, having also confirmed a high resistance to fouling, which occurs when the oil droplets are squeezed, using high pressure, into the membrane, thus blocking therefore the pores of the membrane [53]. Wang *et al.* [56] also manufactured an environmentally friendly MnO_2 nanocrystals coated stainless steel mesh, previously purchased and then coated with the MnO_2 nanocrystals by hydrothermal synthesis. The final mesh showed underwater superoleophobicity behavior, concentrating the oil at the coated mesh surface and, consequently, demonstrating a good separation selectivity, with efficiencies rounding 95.6% [56]. As another example, cellulosic meshes can be used, being more advantageous in terms of cost-effectiveness and environmentally friendliness than other methods displayed in literature. Koh *et al.* [52] 3D printed cellulose acetate meshes, which demonstrated anti-fouling properties and an oleophobic nature, that was able to achieve 95% separation efficiencies. Also, the printed meshes were capable of “self-cleaning”, that is, by immersing the contaminated mesh in water, the previously collected oil droplets detached themselves from the mesh, being capable of coagulating into larger droplets [52]. This 3D printing methodology allows to have a higher control of the mesh design [52], which is difficult to achieve with already purchased meshes, and cellulose acetate presents a more environmentally friendly alternative to the typical stainless steel meshes, due to its biodegradability [57].

2.1.5 Clays

Clays, alike montmorillonite and bentonite, are currently being studied for oil sorbent applications, such as oil spills and wastewater treatments, consequence of their high oil adsorption capacity [58]. These materials can be easily used as a composite material, and are known to improve both physical and chemical properties of the composite, such as enhancing the mechanical properties while reducing the materials flammability [59]. Wang *et al.* [60] studied the incorporation of montmorillonite (MMT) and polyvinylidone (PVP), a porogen, on a ultrafiltration membrane of poly(vinylidene fluoride) (PVDF), produced by phase inversion method [60]. MMT was proven to enhance, when together with the PVP, the hydrophilicity of the membrane, and it also changed its surface roughness. In this report it was concluded that the membrane showed the potential to remove pollutants from wastewater [60] , however they did not present the results for oily wastewater separation. Polymers have the advantage to efficiently disperse clay particles [61] and, considering that fact, Kahraman *et al.* [58] produced a hydrophobic and oleophilic electrospun polyacrylonitrile (PAN) membrane with cloisite 30B, an organoclay which was incorporated onto the nanofibers. It was concluded that by adding 3% of clays to the nanofibers the oil adsorption capacity increased by 160 times its own weight having a value around 180 g/g. This was mostly justified by the increase of hydrophobicity caused by the clay layers. Comparing these results to pure PAN membranes, that are naturally hydrophilic, the previous, clearly, did not displayed oil absorption capacity [58].

2.1.6 Textiles

Textiles are lightweight materials and more flexible alternative, when compared to other technologies, such as metallic meshes. Furthermore, some of them can demonstrate high adsorption rates and good mechanical strength even under harsh environments [62]. However, the textile surface needs to be functionalized in order to possess selectivity abilities. Making them capable to be only water-removal, presenting hydrophilicity and oleophobicity , or oil-removal type, demonstrating hydrophobicity and oleophilicity [63]. Zhang *et al.* [63] reported the production of a flexible and uniformly coated trichloromethylsilane polyester textile, a superoleophilic textile that demonstrated reusability and a good oil/water separation efficiency, since almost no water could be perceived. However, they did not present efficiencies results, since they claim to be difficult to attain because of the volatility octane oil [63]. In the same manner, Xue *et al.* [64] used a commercially available poly(ethylene terephthalate) (PET) textile, coated, by immersion, with a silica hydrophobic sol-gel that provided an increase in roughness of the textile surface. These demonstrated a superhydrophobic and superoleophilic behavior, a high and rapid affinity with the crude oil used in the oil/water mixture. However, after the textile immersion on the oil/water mixture, it was found some leftover crude oil in the tin, thus showing a poor oil separation efficiency [64]. In another work, Zhang *et al.* [65] also used silica to produce highly mechanically stable SiO2/polystyrene, (PS), nanocomposite coated fabrics. The fabrics were purchased from local textile stores and were made from 70% cotton and 30% polyester. For the coating, the fabrics were immersed in the SiO2/PS suspension, for approximately two minutes [65]. Contrarily to the results demonstrated by Xue *et al.* [64] work results, this final fabric displayed excellent durability, good flexibility and an excellent oil/water separation efficiency rounding 97% [65].

2.1.7 Membrane technology for oil and oil microdroplets collection

Membrane technologies arose as a way to overcome the gaps and disadvantages present in the traditional oil/water removal methods previously mentioned, these include expensive costs, high complexity, and low oil/water separation efficiencies. Industries are the number-one beneficiaries from this technique, consequence of its simple production and easy manipulation. Additionally, these membranes show the ability to easily separate oil/water emulsions, due to their small pore sizes [66]. Their mechanism of operation resembles the selective barrier of transport between two distinct phases, being those, in this case, the oil phase and the water phase [67].

One of the most common membrane methods used in industries comprises pressure driven membranes, [37], [67], which can after be categorized by their pore sizes. Microfiltration membranes (MF) present higher fluxes than nanofiltration membranes (NF) and also ultrafiltration membranes (UF), showing however a more probability to foul[68]. Ultrafiltration membranes possess smaller pore sizes than all the MFs, being capable to remove subtances of smaller sizes. They do, however, display poor antifouling properties[69]. Nanofiltration membranes, based on a thin membrane, of 0.1 to 0.2 µm in thickness, having pores ranging between diameters of 2 to 5 nm and in which separation is primarily based on electrostatic repulsion and size exclusion, demonstrate to easily permeate oily solutions [70], [71], or even the reverse osmosis membrane (RO), where the pressure exerted on the fluid flux is inversely proportional to the pressure on the layer surface[72].

Membranes can also be divided accordingly to their primary components, being polymers and inorganic materials the most commonly studied materials for developing membranes [73]. Inorganic membranes, on one hand, normally derived from ceramic materials, such as silica, alumina, or titania, when compared to other membranes, demonstrate greater temperature resistance and good mechanical properties. Unfortunately, their use translates into greater fabrication complexity and higher costs [74]. On the other hand, polymeric membranes are very cost effective and easy to produce. They display, however, rapid deterioration and have a diminished flux, justified by their tendency to foul [21],[75].

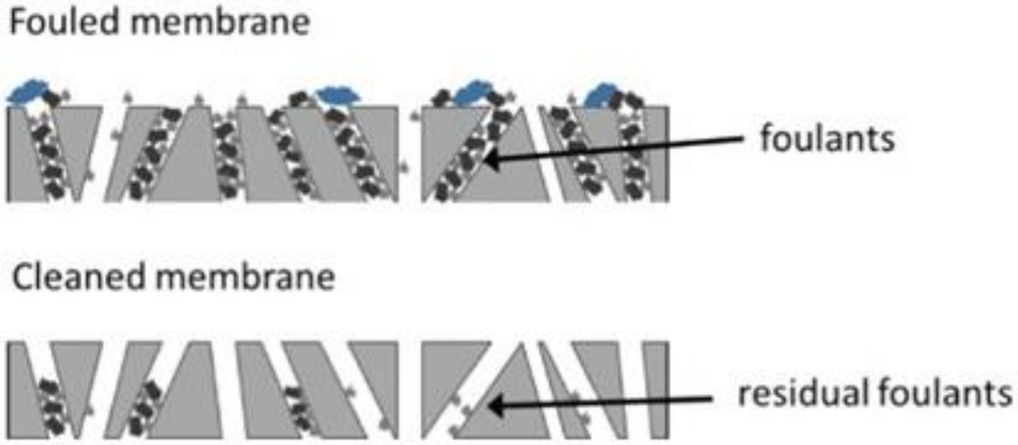

Figure 2. 4- Schematic of a fouled membrane. [76]

In order to avoid fouling, whose mechanism of operation is represented on figure 2.4, the surface of the membrane can be functionalized, thus increasing its hydrophilicity, by, for example, decreasing the oil adhesion to the surface and, therefore, reducing the probability of the membrane to foul [73]. Nanofibers can be used as a valuable solution in overcoming this issue, displaying a threadlike fiber structure, with fiber diameters ranging from 50 to 300 nanometers [77]. For that reason, they will be highlighted in the following chapter, in a form of an overview of different types of nanofiber membrane materials properties, and developments in this area of study.

2.2 Advantages in the use of nanofibers in oil/water separation

2.2.1 Nanofibers

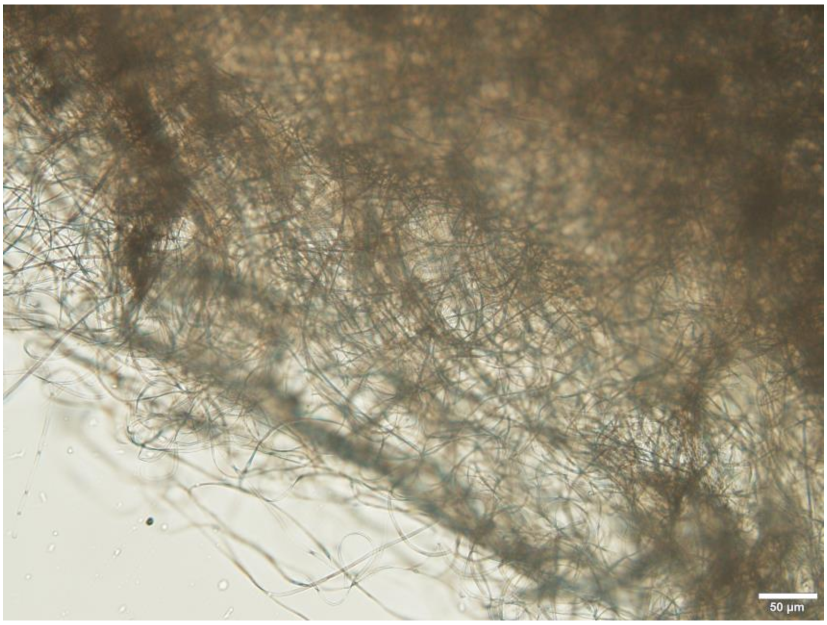

Figure 2. 5-Optical microscope image of electrospun cellulose acetate nanofibers.

Nanofibers (NFs), which are represented in figure 2.5 by an optical microscopy image displaying their morphology, have already been employed in numerous applications focusing on different types of water treatments [78] and have become alluring for applications in oil/water removal, due to their easy customization when attaining a membrane format. This trait allows for the use of a variety of different types of materials, leading to different fiber diameters/dimensions and to the possibility of producing different levels of permeability, surface area and porosity [79].

Nanofiber fabrication methods

Some of the most employed nanofibers fabrication techniques include, mechanical forces methods, such as extrusion [77], that consists of extruding one or even two polymers simultaneously from a single hole making it possible to have different types of fiber rearrangements and designs [77]. Aside from this technique, phase separation can also be used to produce nanofiber matrixes, relying on the physical incompatibility between a polymer dissolution and a solvent, after a gelation process followed by dehydration of the matrix [80]. Meltblowing is another nanofiber production technology, which consists of an one-step methodology that comprises the melting and consequent extrusion of thermoplastic polymers, such as polyester, polystyrene and polyethylene, producing, therefore, micro and nanofibers[80].

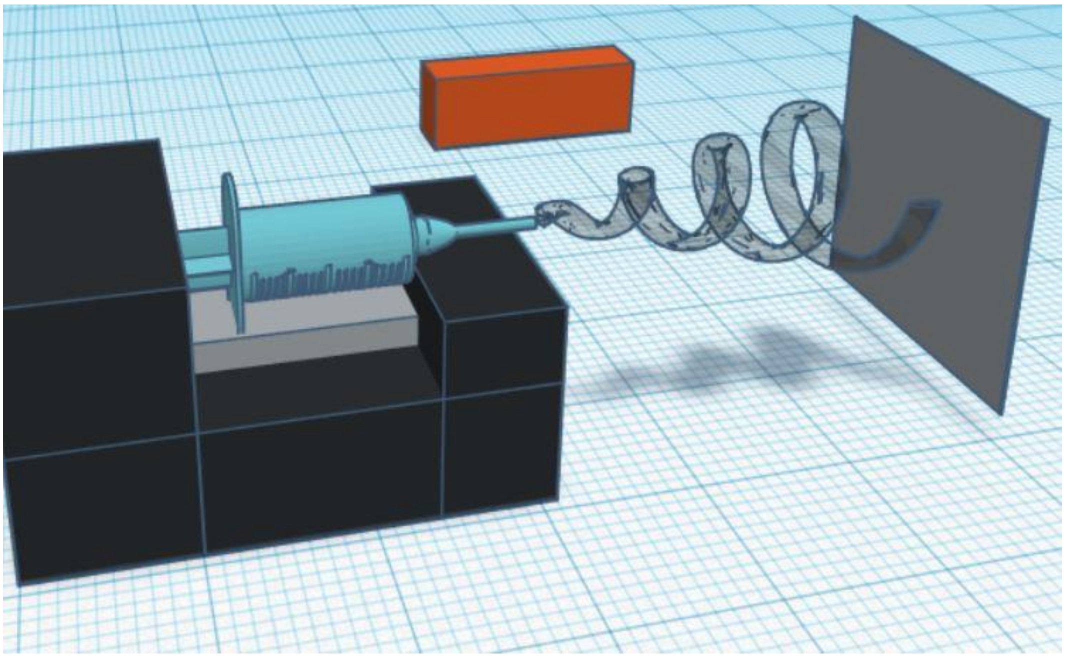

Figure 2. 6-- Schematic of a typical electrospinning setup.

Finally, one of the most commonly used methods regarding nanofibers production is electrospinning, represented in figure 2.6 its most traditionally used setup, which is a method based on electrostatic forces [81]. This technique became an attractive, cheap and a widespread technology since it allows an ability to have a certain control of the final non-woven mats, for example its porosity, its thickness and its morphology [82]. Most importantly, this technique allows to choose from a vast panoply of materials, being although polymer materials the base material, depending on the final intent. In this case, for oil/water separation, choosing the right type of materials can produce a membrane with high porosity, elevated surface area, high flexibility and a good water or oil permeability [83], which are all important features, since, as already mentioned, wettability of the membrane plays a crucial role on the filtration process [84]. In electrospinning, are several the parameters which can influence the properties of the nanofibers. These can be divided into three main categories, processing conditions, where it can be highlighted some variables such as flow rate, applied voltage, a factor that has control upon the resultant fiber diameter [85], the diameter of the needle, target geometry and the distance from the tip to the target [81]. Solution parameters, such as solvent evaporation rate [86], [87], solution viscosity [81], [88] and surface tension parameter [62], [89], and finally ambient parameters where the most important conditions are temperature [90], [91] and humidity [92].

Nanofiber membranes for oil/water separation

The use of nanofibrous membranes is a quick and environmentally friendly alternative to air flotation, centrifugation and other traditional, but more complex methods. This method is greatly advantageous, namely due to its high surface areas, its proven efficient oil/water separation, its cost effectiveness, its simplicity of manufacture and operation, along with its easy manipulation and the possibility of customization of its wetting properties [93].

When referring to wettability, these membranes can be divided into two main types, the oil removing ones and the water removing ones [84]. Oil removing membranes are characterized by its hydrophobicity and its oleophilicity, meaning that, for example, in a gravity driven separation method, it can repel water and easily adsorb and filter the oil phase [93]. Patel *et al.* [94] proposed, in their work, an oil removing electrospun polytetrafluoroethylene (PTFE) thin and porous membrane for ultrafiltration purposes. Using the latter, oil would flow under capillary separation and water would be repelled [94]. This work demonstrated to be cheap to produce due to electrospinning and showed an efficiency of oil/water separation rounding 99% for oil/water separation [94]. Also, He *et al.* [89] presented, in their study, a poly(arylene ether nitrile) (PEN) nanofibrous membrane, produced by electrospinning and hot-pressing techniques, that can be potentially used for oil/water emulsion separations in harsh environments. This conclusion arises from the displayed efficiency separation ratio of 99%, after 24 hours of use [89]. The biggest disadvantage allied to this type of membranes is membrane fouling, which reduces their efficiency of the separation and, posteriorly, leads to their deterioration [37].

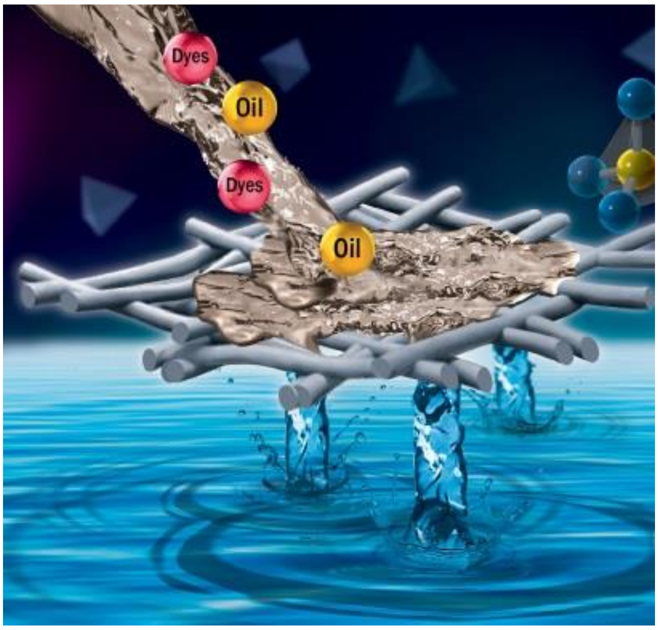

Figure 2. 7-Water removing nanofiber membrane scheme. [95]

Water removing membranes, which can be seen in figure 2.7, arrive as a better alternative to oil removing ones, since fouling is almost impossible to occur. These membranes function through water absorption and filtration, together with the surface retention of the oil. In water removing techniques, cellulose acetate, chitosan, some polymeric or ceramic nanoparticles and other materials, are used to obtain a membrane that is both superhydrophilic and superoleophobic [93]. Obaid *et al.* [37] presented, in their work, the production of a water-removing electrospun polysulfone (PSf) membrane immersed in a NaOH solution in order to obtain a membrane with underwater superoleophobicity and with a high-water flux property, which can overcome fouling. Aside from the ability to not suffer fouling, this membrane also displayed an oil/water separation efficiency of roughly 99.99% [37].

Membrane categorization can also be evaluated in terms of their primal material, being those carbon-based, ceramic-based and polymer-based nanofibrous membranes [96]. Polymer-based nanofibers membranes arose from the need to find a cost-effective alternative, which also displayed great flexibility and was of facile handling [96]. For instance, Hong *et al.*[97] produced, in their study, an electrospun cellulose acetate nanofibrous membrane with high chemical stability, being resistant to extreme conditions, namely to very acidic or alkaline environments[97]. It is important to highlight that this is normally one of the greatest difficulties and disadvantages allied to this type of membranes [97]. The developed membrane also demonstrated superoleophobicity and superhydrophilicity, having a high separation flux and, consequently, a high separation efficiency, of more than 99%, even when on harsh environments and for more than one cycle of oil/water separation [97]. The author suggest that this membrane has the ability to be used is large-scale oil/water separations. Even though the membrane presents high flux and chemical stability even in harsh environments, they did not suggest a methodology to implement it on larger scales than a laboratory gravity separation setup.

Ceramic-based nanofibrous membranes fabrication recently became very attractive, taking into consideration they are typically low-cost materials, in which the membrane demonstrates inertness, together with high chemical, thermal and mechanical stability, making them ideal when treating harsh and corrosive environments [98]. Typically, ceramic materials chosen for this type of membranes could be silica, zirconia, zeolite, alumina and other oxides [98]. Titanium dioxide, TiO_2, a semiconductor that demonstrates to be non-toxic, to be photocatalytic and to be water immiscible, is one of the most used oxides for this purpose[99]. Zhang *et al.* [100] manufactured in their work, by an easy sol-gel electrospinning and polymerization method, titanium dioxide nanofibrous membranes incorporated with TiO_2 nanoparticles, proven to demonstrate high flexibility and chemical stability, nontoxicity and good porosity [100]. The membranes also displayed high photocatalytic activity capable of eliminating organic pollutants from water [100].

When comparing ceramic-based membranes with polymer-based ones, the first ones outshine the latter ones, when performing in certain aggressive environments, such as highly acidic or highly alkaline means, since they do not deteriorate, neither suffer modifications to their structure, making them suitable for oil/water separation in almost every environment [98]. Nevertheless, these membranes demonstrate occasional occurrence of fouling, which can be explained by limitations regarding the membranes' pore sizes. Barbosa *et al.* [101]

produced in their work, by secondary growth method, a very effective hydrophilic and oleophobic zeolite membrane for oil/water separation purposes [101]. In their study, when comparing the alumina comprising zeolite membrane with the one which did not have the zeolite crystals, it was observed some oil clogging in the latter membrane. This is justified by the formation of an oil layer at the surface on both membranes, resulting on a better oil removal percentage. In spite of this fact, the zeolite crystals membrane showed a better efficiency, explained by its high porosity, in comparison to the low porosity of the ceramic-based one [101].

Finally, carbon-based membranes are the last main category existent and they stand out from the previous ones, due to their high chemical and mechanical stability, easy regeneration, which means that after physical or chemical cleaning, the membrane still presents the efficiencies that presented in the beginning, high surface area and antifouling abilities [96]. Carbon-based membranes are characterized by having a wettability intrinsically oleophobic and hydrophilic. Concerning their composition, they are primarily composed by carbon nanotubes or graphene as main material [102]. In one of the most preeminent ongoing studies regarding the use of carbon nanotubes, is their incorporation on polymer-based membranes, where, due to alignment of the nanotubes, the water flux more that duplicates, as a consequence of the surface smoothness of the nanotube walls [103]. Furthermore, this arrangement of the carbon nanotubes creates an additional porous layer, or stack of layers, in which its pore size can influence the collection of oil emulsion droplets of smaller diameters [103]. Graphene, when applied to a polymer membrane matrix, has also demonstrated improvement in the performance of the overall system. For instance, Prince et al. produced, in their work, a graphene-based PES membrane proving that graphene can enhance, by 43%, the PES membrane wettability [104].

2.3 Oil/water emulsion separation

Concerning oil/water separation, one of the most recent adversities faced by industries, as well as the scientific community, is the difficulty in collecting oil from oil/water emulsions [105]. Oil pollution is still a problem, affecting our health and environment in current times, prominently oil/water emulsions, justified by the higher difficulty inherent to the collection of such small oil droplets [6].

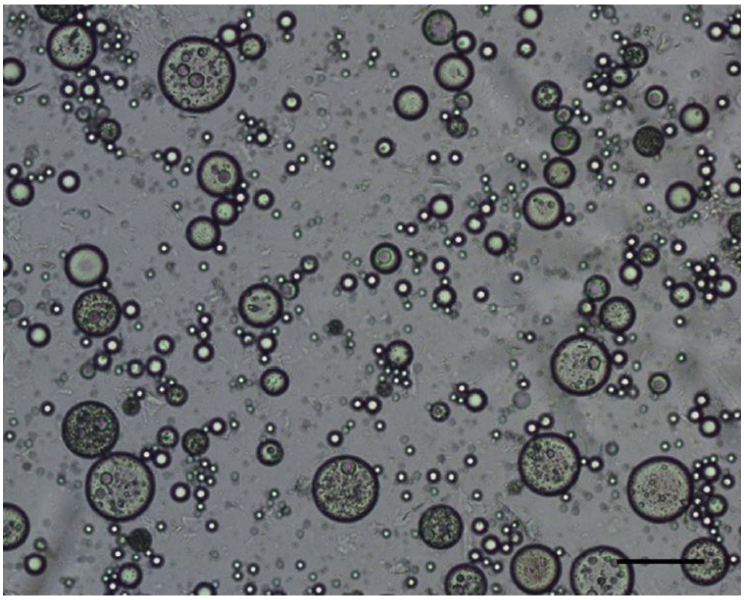

Figure 2. 8- Optical images of oil/water emulsions – The scale bar corresponds to 20µm. Reprinted from Colloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 522, Qiang Wang, Caibiao Hua, Abdelmoumin Zoghbia, Juan Huanga, Qiang Xia, Oil-in-oil-in-water pre-double emulsions stabilized by nonionicsurfactants and silica particles: A new approach for topical application of rutin, Pages No.6, Copyright 2017, with permission from Elsevier. [106]

Emulsified oil/water mixtures, as it is represented by an optical image of emulsions on figure 2.8, are extremely stable dispersions [105], since they present a highly strong oil/water interface, that becomes more difficult to separate as the size of the droplets in the emulsion decreases [107][108]. Oil microdroplets are a product from these emulsions and are categorized by having dimensions smaller than 20µm, therefore, presenting themselves as a great obstacle, since they are unable to be captured by the conventional methods, which were described in earlier chapters [13]. Lately, and as already mentioned on chapter 1.4, the most commonly used techniques, as electroflotation [10] and electrocoagulation [23], have restraints, such as high material requirement, expensive machinery together with high energy consumption [23], which justify the need to continue the study for more effective solutions, possibly by combining different types of wettability with the right porous substrate [109].

2.3.1 Foams

Foams, as before mentioned, are 3D materials characterized by their low density, light weight, and high surface area, also having great capability to absorb liquid substances, depending on their wettability [42]. Wang *et al.* [110] in their work studied a cost-effective and eco-friendly method, using a purchased polyurethane (PU) foam, that was, posteriorly, coated in a alkaline medium which contained dopamine, dodecanethiol and fly ash. Fly ash is a fine waste powder substance derived from burning fossil fuels and municipal waste. This substance, not only has proven to have an important role on the emulsion separation, as it also contributes in reducing the environmental burden, consequent of the burning of these substances [110]. The foam proved to have superhydrophobicity, even under harsh mediums (very salty, acidic, or alkaline) for 15 cycles. Additionally, it displayed the ability to separate oil/water emulsions with efficiencies of about 93% [110]. Yang *et al.* [111] prepared, in their study, a commercial Ti foam with a one-step femtosecond laser, whose function was to treat the surface to be superhydrophilic and underwater superoleophobic, achieving separation efficiencies of 99% even in oil/water emulsion separations [111]. In the same manner, Luo *et al.* [112], also purchased a commercial titanium (Ti) foam, that was after anodized in non-toxic fluorine-containing electrolyte, which is the same as introducing -O -Ti -F groups onto the Ti foam, forming a superhydrophilic foam that have demonstrated to be ideal to separate oil/water emulsions. After the emulsion separation tests, it demonstrated 99% of oil/water emulsion separation efficiency, as well as anticorrosive properties [112]. Ti-based materials have once again demonstrated high potential for water treatments, mainly due to their nontoxicity and chemical stability. As for carbon foams, Yang *et al.* [113] produced a foam, in their work, fabricated by carbonization of a 3D, commercially available, melamine foam, that was compressed afterwards. The foam compression was made in order to avoid a possible foam collapse, and to increase its mechanical properties. This foam presented underwater superoleophobicity and underoil superhydrophobicity, proved to have excellent oil/water emulsion separation efficiencies, higher than 98% and demonstrated environmental stability even in harsh environments [113].

2.3.2 Aerogels

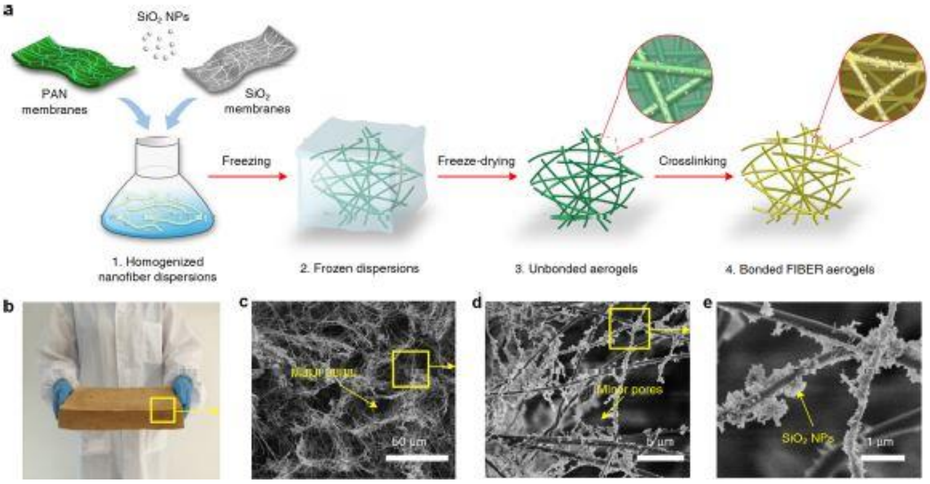

Figure 2. 9-(a) Schematic showing the aerogel synthetic steps; (b) Optical image of fiber aerogel on a large scale of 2.5 L; (c-e) Microscopic architecture of fiber aerogels at various magnifications; Y. Si et al., "Superelastic and Superhydrophobic Nanofiber-Assembled Cellular Aerogels for Effective Separation of Oil/Water Emulsions," ACS Nano, vol. 9, no. 4, pp. 3791–3799, 2015, doi: 10.1021/nn506633b. Copyright (2015) American Chemical Society. [114]

Aerogels, as seen in figure 2.9, are highly porous 3D materials that can behave as sponges, while displaying high surface areas, low-density and good flexibility [48]. Si *et al.* [114] reported, in their work, a flexible and superhydrophobic nanofiber-assembled cellular aerogel, fabricated by deposition of electrospun nanofibers made of SiO_2 and polyacrylonitrile (PAN) and having SiO_2 nanoparticles incorporated in them, originating a 3D assembly, that was after freeze-dried to obtain the aerogel. The final product resulted on a structure with very low density, high recyclability and which is capable of efficiently separating oil/water emulsions, by gravity driven separation, with about 99% efficiency, while using a simple gravity separation method and presenting antifouling properties [114]. Also, Yue *et al.* [115] presented, in their study, a lightweight and superhydrophobic aerogel derived from waste paper and banana peels, which was produced by the combination of freezing-cast, freeze-drying and pyrolysis methodologies. The separation was effectuated by means of a gravity-driven method, concluding that the aerogel presented a sportion capacity of 35 to 115 times its own weight and, even for oil/water emulsion separation, it achieved separation efficiencies up to 99.6% [115]. In a final example, Chaudhary *et al.* [116] produced, in their work, a non-toxic, hydrophilic and highly porous chitosan and agarose based aerogel, being the latter substance a polysaccharide used as a pore formation and coating agent. The result was an eco-friendly membrane, presenting biodegradability, and displaying a separation efficiency of 99%, which indicates the potential of this membrane to be used in industrial settings. Summarizing, aerogels can easily separate oil/water and oil/water emulsions, making use of rather simple separation methods and resulting in high separation efficiencies, with the additional advantage of having a tendency to display antifouling properties.

2.3.3 Membranes

Membrane filtration has played an important role in the oil/water emulsion separation subject, has they present favorable properties in the collection of such small oil droplets, consequence of their ability to achieve smaller membrane pore sizes [117]. Furthermore, electrospun membranes demonstrate, typically, a high surface area, showing the ability to have control upon the nanofibers size and the possibility to incorporate active chemistry into the network [118]. However, there are still drawbacks to overcome, since, with smaller pore sizes, the probability of the membrane to foul increases [108]. Zhou *et al.* [74] report, in their work, the fabrication of an hydrophilic membrane, in which hydrophilicity decreases the oil adhesion, therefore, reducing the probability to foul. This ceramic microfiltration membrane was made from a commercially available Al_2O_3 membrane, which was modified with a ZrO2 coating, by hydrolysis of $ZrCl_4$, making the membrane more hydrophilic. This membranes proved to have an oil rejection above 97.8% [74].

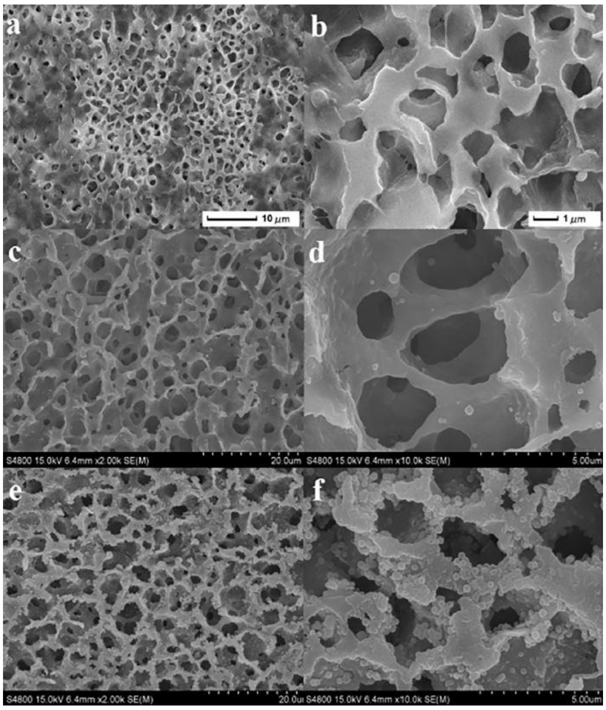

Figure 2. 10- SEM images of (a,b) a simple PVDF membrane, (c,d)a PVDF membrane with pDA coating, and (e,f) the final membrane with SiO2 nanoparticles added to the final membrane surface. Reprinted from Separation and Purification Technology, Volume 209, Jiuyun Cui, Zhiping Zhou, Atian Xie, Minjia Meng, Yanhua Cui, Siwei Liu, Jian Lu, Shi Zhou, Yongsheng Yan, Hongjun Dong, Bio-inspired fabrication of superhydrophilic nanocomposite membrane based on surface modification of SiO2 anchored by polydopamine towards effective oil-water emulsions separation, Pages No. 4, Copyright (2018), with permission from Elsevier. [119]

Cui *et al.* [119] produced, in their study, using a phase-inversion process, a SiO2 nanocomposite polyvinylidene fluoride membrane (PVDF), which displayed resistance to fouling, see figure 2.10. SiO_2 nanoparticles proved to create roughness at the surface of the membrane and also showed to decrease its pore size. Regarding wettability, the membrane exhibited superhydrophilicity and superoleophobicity, as well as a high separation efficiency, approximately 98%, when collecting oil/water emulsions even after 10 cycles [119]. This eco-friendly membrane also showed resistance to fouling and an ability to regenerate, meaning that, after a separation cycle, the membrane can be recovered and reused, by simply washing it with ethanol and water [119]. Zhang *et al.* [120], mentioned, in their work, the successful production of a polymer-based nanofiber membrane with superhydrophobic and superoleophilic properties, making use of a commercially available polyester fabric, which was dip-coated in a solution containing a polymer of intrinsic microporosity (PIM-1) and fluorinated alkylsilane (PTES). It was also capable of removing oil from an oil/water mixture and oil from oil/water emulsions, with oil droplets diameters ranging from 10 to 30 µm, displaying separation efficiencies rounding 99.95% and 99.97% respectively, up to 30 cycles [120]. Correspondingly, Almeida and coworkers [6] produced a cheap and environmentally friendly CA electrospun composite membrane with cellulose nanocrystals (CNC) stamped by screenprinting on the surface of the membrane. It successfully demonstrated a separation efficiency of 83% for oil/water emulsions containing dispersed microdroplets, with diameters ranging from 10 to 15 µm, using gravity force filtration [6]. Obaid *et al.* [121] manufactured, in another work, an electrospun Polyvinylidene fluoride (PVDF) nanofibrous membrane, that was posteriorly modified with Triethylamine to avoid fouling [121]. PVDF is commonly used in applications for treating and filtrating different types of wastewater. The result was a superhydrophilic and superoleophobic membrane with high separation flux, and an efficiency of 99% for different types of oil and also for oil/water emulsions, having the potential to be easily implemented on industries for water treatment purposes [121].

2.3.4 Clays

Clays have shown to improve the mechanical strength and wettability of the filtration material [122]. Being also cost-effective, abundant in nature and easy to integrate in membranes [71]. Due to that, and their high adsorption capacity clays have shown a high potential for oil/water emulsion wastewater treatment. In order to prove that, Mota *et al.* [123] used, as part of their study, modified Brazilian clays (green calcium bentonite-aluminum clay minerals) to further analyze its performance in oil/water emulsion separation. Clay powders were modified with surfactants into their interlayer space, becoming organoclays, in order to achieve hydrophobicity and increasing thereby their adsorption capacity for pollutants such as oils. The modified clays were weighted with 0.5 grams each sample and dispersed into 50 ml solutions containing oil/water emulsions. The clays displayed adsorption capacities up to 9.7 g/g, presenting oil removal efficiencies up to 96% [123]. Moazed *et al.* [124] used, in their study, a combination of bentonite organoclay with anthracite onto oil/water emulsions and were able to attain oil removal efficiencies up to 98%, whilst also and proved to have a quick sorption rate after 1 hour of test [124], proven therefore to be a good solution to treat oily wastewater emulsions. Finally, and employing clays into polymeric NFs, Zhu *et al.* [125] produced, in their work, a low-cost and hydrophilic ultrafiltration with attapulgite, a natural clay, and poly(vinyl alcohol) (PVA) nanofibrous membrane, via papermaking and posterior sintering technology [125]. The membrane showed to have small pore sizes, about 12 nm, and to have potential to be used for oil/water emulsion since it demonstrated a separation efficiency of around 97%, as well as, good anti-fouling properties [125]. However the authors obtained inferior efficiencies, for higher separation pressures, which can be explained by the penetration of smaller oil microdroplets into the membrane[125]. Afterall, it can be concluded that clays display good oil adsorption capacities, mostly when treated with surfactants in order to show hydrophobicity. Furthermore, when used as a composite, they have proven to improve the materials’ chemical and physical properties, constituting therefore an interesting area of study. When searching “"clays" oil/water emulsion separation” on Web of Knowledge, only 11 results were displayed, a fact that supports the existence of an investigation gap in clay usage, for oil/water emulsion separation. Due to their potential, it is suggested that research teams further endure on the study for clays for applications regarding this area.

In this manner, the premise of this work propelled the author of this thesis to get into the line of action, in a laboratory sense, which lead to the gathering of some preliminary, however, rather promising results. The work developed had the intent to produce and optimize composite membranes of cellulose acetate with montmorillonite clays , having the latter ones being produced by an electrospinning process, and, finally, evaluate the performance of the system in oil/water emulsion separation. Having both the application of the membranes and the electrospinning technique as primary goals to keep in mind, several solutions were prepared and optimized. Nanocomposites of clay and CA became an attractive choice, since polymers can disperse efficiently clay particles [125] and, additionally, the clay usage, as a composite material in an electrospun membrane, can be used to further improve its physical and chemical properties, namely its wettability and its mechanical properties [123]. Cellulose acetate was chosen consequence of its abundancy on earth [114], and of their low-cost feature, their biodegradability and their biocompatibility [52]. Cellulose acetate [115] is a very versatile biopolymer, demonstrating properties such as high flexibility, good chemical resistivity, high durability, thermal stability, and high hydrophilicity [116].

Figure 2. 11- POM images of CA/MMT nanofibers taken in transmission mode between parallel polarizers with 50 µm magnification a) short and defective nanofibers derived from an inefficient solution and electrospinning parameters; b)nanofibers with less defects due to an optimized solution having yet some "beaded" nanofibers; c) optimized nanofibers with the final solution and electrospinning parameters.

As seen on figure 2.11, the nanofibers, which were produced by electrospinning and which were resultant from the first two experiment trials, observed in a) and b), showed a lot of structural defects, such as short nanofiber dimensions, the presence of "beaded" nanofibers and, also remains of the precursor solution that were directly ejected from the needle to the target, without evaporation of the solvent. This can be explained by the viscosity of solution, which is, probably, very low. Here, after optimization of all of the controllable parameters inherent to the experiment, it was possible to attain nanofibers showing less defects, overall, as seen on figure 2.11 c). These final parameters allowed to start the production of membranes for posterior oil/water emulsion separation tests, thus having played a fundamental role on this study.

3. Conclusion

The main focus of this monographic thesis was to study the primary materials and methods that are currently being investigated and used in order to separate, efficiently, oil/water mixtures and, more importantly, oil/water emulsions.

Within the absorbent materials category, it is crucial that they present an adequate wettability, typically, both a superhydrophobic and superoleophilic behavior, a great absorption ability, good selectivity, and finally, a highly porous structure. Foams and sponges are of extreme lightweight and of low-density, with 3D porous structures having the potential to be introduced and directly used, for example, at the oil spill site. Beyond the high range of materials that can be used in these kinds of applications, there are polymers, such as polyurethane, and metals, i.e. copper, which display the advantage of being commercially available and of easy posterior modification. They present oil/water separation efficiencies of around 95% and a good mechanical strength to compression, from 30 to 300 cycles. As for oil/water emulsions, they also have demonstrated to be a good separation method. Polyurethane, titanium, and carbon foams were observed to have successfully separated both phases, with efficiencies rounding 93 to 99%. These characteristics make them one of the technologies of choice for oil/water separation, in case of environmental disasters or of vast oily wastewater spots. In the same way, aerogels are also highly porous networks that possess high surface, low density, and good flexibility. They can be made from silicone, chitosan, and even from biomass, such as banana peels and paper waste. They are normally produced through sol-gel synthesis and have the tendency to be manufactured to display an oleophilic wettability. However, since they can be employed as a filter to separate oil/water mixtures and emulsions, by means of gravity separation, they can also be hydrophilic. As result, separation efficiencies rounded 99%, even for oil/water emulsions. As for nanoparticles incorporation, these have the advantage of not only being highly absorbent, but also of providing other properties to the composite materials. For example, Fe_3O_4 NPs, provides magnetic properties to the composite, while silica NPs incorporation provides hydrophobicity to the material.

At the other side of the spectrum, adsorbent materials, such as meshes, films, membranes, and clays, are typically used in industrial settings as filters. For instance, meshes are able to adsorb high volumes of oil, due to its larger pore sizes. They are usually made from stainless steel or aluminum and, can either be manufactured by, for example, a low-cost 3D printing method, or attained commercially. When addressing separation efficiencies, meshes are capable to separate oil/water mixtures with an effectiveness rounding 95 to 99%, also being capable of reusage, up to 40 separation cycles. The biggest disadvantage is it inefficiency in collecting oil from an oil/water emulsion, due to their larger pore size, when comparing to the oil microdroplets sizes. Clays, such as montmorillonite and bentonite are materials with high potential for oily wastewater separation purposes. They have not received much attention yet, however, have shown to have oil adsorption capacities up to 160 times their own weight and to improve the composite materials' hydrophobicity and physical properties, such as mechanical strength. Even for oil/water emulsion separations, the efficiency reached up to 98%. Textiles possess higher flexibility, comparing to meshes, and good mechanical strengths. Regardless, they have to be functionalized in order to possess selectivity for oil/water separation, that can reach efficiency values up to 97%. Finally, membranes are, generally, easy to produce and cost effective. Additionally, unlike meshes, their ability to achieve small pore sizes make them suitable to separate oil/water emulsions, presenting efficiencies rounding 99% for oil/water mixtures and 97% for oil/water emulsions, having, although, a higher tendency to experience membrane fouling. Nanofibrous membranes, can be used as a valuable solution to overcome fouling, because of its high surface areas, along with its easy manipulation and customization of its wetting properties, its fiber sizes and its membrane pore sizes, mainly when produced by electrospinning. Membranes can be divided into ceramic membranes, such as silica, alumina or titania based, being those more expensive than polymer-based ones, however, having higher temperature resistance. Carbon membranes, based on carbon nanotubes or graphene, help increase water flux and have the ability to adjust its pore sizes. Polymeric membranes, are more cost effective and easier to produce, having, although, a higher tendency to deteriorate or to experience membrane fouling. Roughly, membranes can present separation efficiencies almost up to 99.99% to water/oil mixtures and between 83 to 99.97% to oil/water emulsions. Their biggest and most valuable advantages are their ability to be produced making use of a wide range of materials, the fact that a large amount of them is eco-friendly and, at last, their ability to be produced in a low-cost and simple manner. They also can incorporate nanoparticles, clays, or different materials, with the possibility of achieving optimized composite membranes, with complementary properties, making them a valuable option for oily wastewater cleaning in industrial settings.

4. Future perspectives

As discussed before, membranes have proven to be an efficient technology to help clean and prevent oily wastewater from industries. With that in mind, it is suggested to endure on the study for new and more efficient clays for oil/water and oil/water emulsions separation purposes, with special focus on polymer-clay membrane nanocomposites, for example, by integrating clays on a cellulose acetate membrane. Here, it will be of interest to study the separation efficiencies, the reusability per cycles of performance and possible cleaning protocols for the membranes. Also, as a follow up to Almeida *et al.* [6] work, it is suggested the addition of clays to their all-cellulose composite membranes. It is also suggested to, as Mota *et al.*[123] mentioned, to study treatments for the clays using cationic surfactants, such as ammonium compounds, since they have shown to increase their hydrophobicity and their oil adsorption capacity.

For the treatment of oily wastewater resulted from environmental catastrophes, it is suggested to pursuit on study of new foams and sponges, due to their high absorption capacity, high durability and facile cleaning and reusability. Focusing on the ones with magnetic properties, in order to be easily re-collected from the treated spill areas.

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7. Annex

In this chapter it is reported in more detail, a short experimental work that had the intent to produce and optimize cellulose acetate composite non-woven membranes, incorporated with montmorillonite clays, and produced by an electrospinning process for oil/water emulsion separation. For that, optimization of the solution and electrospinning parameters played a fundamental role on this study.

Electrospinning parameters

In electrospinning, are several the parameters which can influence the properties of the nanofibers. These can be divided into three main categories, processing conditions, where it can be highlighted some variables such as flow rate, applied voltage between the needle and the collector, a factor that has control upon the resultant fiber diameter [115], the diameter of the needle, target geometry and the distance from the tip of the needle to the target [80]. Solution parameters, such as solvent evaporation rate [116], [117], solution viscosity [80], [118] and surface tension parameter [62], [86], and finally ambient parameters where the most important conditions are temperature [119], [120] and humidity [121].

7.1 Clay and cellulose acetate solution preparation and deposition

Initially the cellulose acetate solution was prepared with a 12% concentration in weight of cellulose acetate, with 50.000 Mn, in a proportion of 33.4% of dimethylacetamide and 66.7% of acetone in weight (w/w). However due to the incorporation of clays to the mixture, the final solution presented low viscosity, and, in order to provide better results, the solution parameters had to be adjusted.

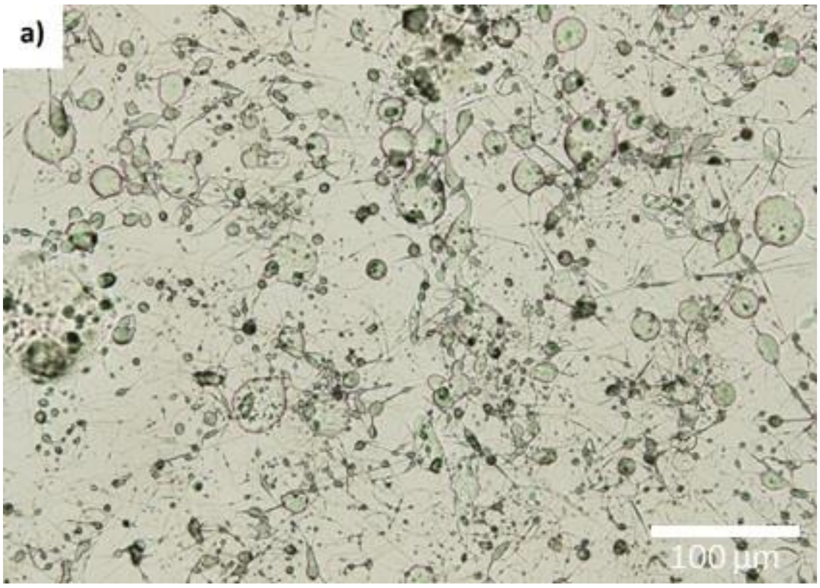

Figure 7. 1- POM images taken in transmission mode, between parallel polarizers, with a 50 µm magnification of short and defective CA/MMT nanofibers derived from an inefficient solution and electrospinning parameters;

As seen on figure 7.1, the nanofibers resultant from the first experiment trial, showed a lot of defects such as short nanofibers, some "beaded" nanofibers and solution directly ejected from the needle to the target. This can be explained by a probable low viscosity solution since the experiment started with a 12% cellulose acetate solution. Here, the electrospinning parameters presented an applied voltage of 18kV, a flow rate of 0.3 mL/h, a 15 cm distance from the needle to the target, a temperature of approximately 23 Celsius degrees and a humidity of near 51%.

Figure 7. 2- POM images taken in transmission mode, between parallel polarizers, with a 50 µm magnification of CA/MMT nanofibers with less defects due to an optimized solution having yet some "beaded" and short nanofibers;

Analyzing the image7.2 it can be seen less defects yet there are some beaded nanofibers. In this case the fibers were made with the optimal solution mentioned above, being therefore more viscous, and with the electrospinning parameters of, 24 kV applied voltage, and the rest of the parameters were equal to the latter case, a flow rate of 0.3 mL/h, a 15 cm distance from the needle to the target, a temperature of approximately 23 Celsius degrees and a humidity of near 53%.

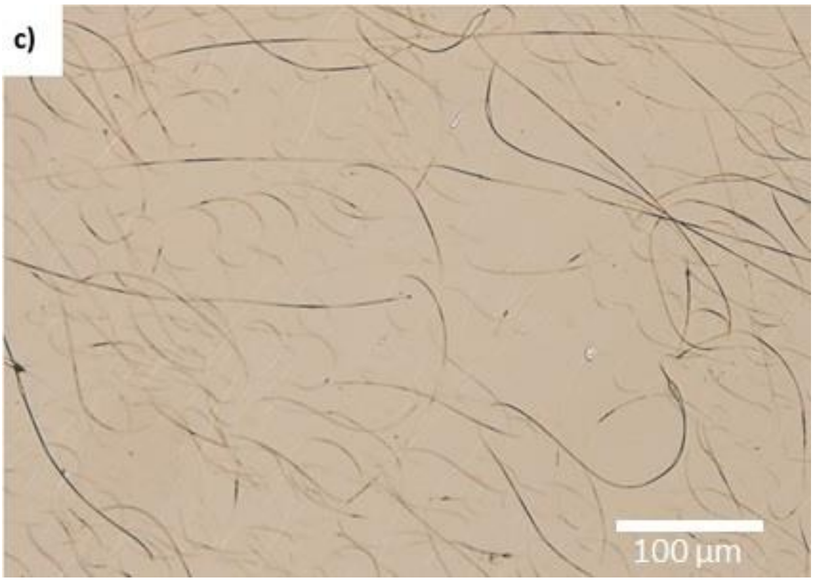

Figure 7. 3- POM images taken in transmission mode, between parallel polarizers, with a 50 µm magnification of CA/MMT optimized nanofibers with the final solution and electrospinning parameters;

It was concluded that using a more viscous solution, of 16% and a smaller applied voltage, of 18 kV, were the optimal parameters to obtain better fibers since, as seen on figure 7.3, the fibers presented less defects overall. The applied voltage is a factor that has control upon the resultant fiber diameter, and it is concluded that, by decreasing the potential, was possible to obtain fibers of cellulose acetate with incorporated nanoparticles of montmorillonite clay.

Here, using ImageJ to measure the nanofiber diameters from image 7.3, for 50 measures, it was obtained an average value of 1.306±0.449 µm, which is a valid value comparing to literature [126]. The final cellulose acetate solution was produced with a 16% (w/w) concentration of cellulose acetate, from Sigma-Aldrich with 50.000 Mn, in 84% (w/w) mixture of solvents (50% of dimethylacetamide plus 50% of acetone in volume). The acetone was purchased from fisher chemical and dimethylacetamide (DMAc) from Lab-scan analytical sciences. Montmorillonite clays were added beforehand to the dimethylacetamide in a 5% percentage compared to the final weight of DMAc used. The solution was after poured into a syringe with an eighteen-gauge needle. The final optimized electrospinning parameters during the fiber deposition were, an applied voltage of 18kV, a flow rate of 0.3 mL/h, a 15 cm distance from the needle to the target, a temperature of approximately 23 Celsius degrees and a humidity of near 53%. These final parameters allowed the production of non-woven membranes for posterior oil/water emulsion separation tests.