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APPLICATIONS OF PURE AND RECYCLED POLYMERIC MICRO-NANOFIBER FOR THE REMOVAL OF OIL SPILLS

Afra Gharib Khamis Al-Blooshi

This thesis is submitted in partial fulfilment of the requirements for the degree of Master of Science in Chemistry

Under the Supervision of Dr. Mohamed Alazab Alnaqbi

May 2015
Declaration of Original Work

I, Afra Gharib Khamis AlBlooshi, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled “Applications of pure and recycled polymeric micro-nanofiber for the removal of oil spills”, hereby, solemnly declare that this thesis is an original research work that has been done and prepared by me under the supervision of Dr. Mohamed Alazab Alnaqbi, in the College of Science at UAEU. This work has not been previously formed as the basis for the award of any academic degree, diploma or a similar title at this or any other university. The materials borrowed from other sources and included in my thesis have been properly cited and acknowledged.

Student’s Signature __________________________ Date 09/06/2015
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Abstract

Cleaning oil spills is a universal concern due to its environmental impact. The aim of this study is to study the effectiveness and applications of pure and recycled polymers in clean-up and the recovery of crude oil from oil spills. In this study, micro-nanofibers of analytical-grade and commercial polystyrene samples were prepared by electrospinning technique. Fiber size distribution was shown to vary with the electrospinning parameters and type of polymer. Fibrous sorbents prepared hereafter were investigated for their efficiency in removing oil spills. Results showed a variation in the sorption capacities of the fibers to various types of crude oils with the morphology of the fibers and the conditions at which they were prepared. Results also showed a variation of the sorption capacities with the original properties of the crude oils investigated. To fine-tune the sorption process, optimization of the electrospinning process was carried out including electrospinning setup parameters as well as polymeric solution and electrospinning chamber parameters. Correlations were established between each of the parameters and the sorption efficiency of the fibrous sorbents prepared thereafter. A high potential of the fibrous sorbents in the removal of crude oil spills was, therefore, proven with experimental evidences and structure-property relationships.

Keywords: Oil spills, electrospinning, micro-nanofibers, sorption capacity, retrieval.
تطبيقات ألياف النانو والميكرو بوليمرية بنوعيا النقلي والمعاد تدويرها في إزالة التلوث النفطي

المؤلف

تعد إزالة البلاستيك من أكثر الأمور اهتماما على المستوى العالمي وذلك لتأثيرها الواضح على البيئة. يهدف هذا البحث لدراسة استخدام لدائن مخلطة وأخرى أعيد تدويرها في إزالة بقع النفط الخام وإعادة استرجاعها. تم استخدام تقنية الغزل الكهربي في تحضير ألياف نانوية و找个غوية من لدائن البوليستر المخلقت ومعاد تدويرها. وقد أثبتت الدراسة استدام أبعاد الألياف المحضررة على العوامل المختلفة لتقنية الغزل الكهربي وقد تم اختبار الممصات الليفية التي تم تحضيرها من هذه الألياف لدراسة كفاءتها في إزالة البلاستيك النفطية.

وقد أثبتت النتائج تفاوت في نسبة امتصاص بقع البلاستيك بتغيير نوع وخصائص البلاستيك وشكل الألياف المستخدمة في تصنيع الممصات الليفية والتي اعتمدت بدورها على العوامل المختلفة التي تم تحضير الألياف عندها. كما قام البحث بإعادة تدقيق العوامل التي تم تحضير الألياف عندها للحصول على نسبة أعلى للاستدام. وضمت هذه العوامل ما يخص محالل اللدائن المحضررة بالإضافة إلى العوامل الخاصة بتقنية الغزل الكهربي. وقامت الدراسة باستنتاج علاقات مختلطة بين كل من هذه العوامل ومقدرة الممصات الليفية المحضررة عندها على امتصاص البيع النفطي. وانتهت الدراسة بنتائج المقدرة العالية للممصات الليفية التي تم تحضيرها على إزالة البيع النفطية وإعادة تدوير البلاستيك الذي تم إزالته.

الكلمات المفتاحية: بقع البلاستيك، الغزل الكهربي، ألياف ميكرو، نانوية، قدرة الإمتصاص، الاسترجاع.
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I dedicate this thesis to the memory of my dear late mother.

Though she is not with me physically, I always feel surrounded by her presence, prayers and support!
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Figure 74: High magnification SEM micrographs of fibrous sorbents obtained by electrospinning 20 wt% solutions of PSII at different Humidity % at (a) (70-88)%, and (b) (89-99)% in DMF

Figure 75: Extent of retrieval (%) of TOTAL crude oil adsorbed onto fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions at different Humidity % at 49% -Normal, (70-88)%, and (89-99)% in DMF
Figure 76: Sorption capacities to TOTAL crude oil of fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions at different Needle diameters at 18G, 21G, 23G, and 29G in DMF.

Figure 77: SEM micrographs of fibrous sorbents obtained by electrospinning 20 wt% solutions of PSII at different Needle diameters at (a) 18G, (b) 21G, (c) 23G, and (d) 29G in DMF.

Figure 78: Extent of retrieval (%) of TOTAL crude oil adsorbed onto fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions at different Needle diameters at 18G, 21G, 23G, and 29G in DMF.
List of Abbreviations

DMF N, N-dimethylformamide
FT-IR Fourier Transform Infrared Spectroscopy
GPC Gel Permeation Chromatography
PSI Polystyrene $M_w = 100,000$ g/mol
PSII Polystyrene $M_w = 350,000$ g/mol
PSClIII Recycled Polystyrene
SEM Scanning Electron Microscope
THF Tetrahydrofuran
Chapter 1: Introduction

Water pollution is known worldwide to be induced directly or indirectly by humans into the marine environment. It includes estuaries, which effect and damage the living resources and marine life. In addition to directly affecting the human health, pollution is also considered an obstruction to marine activities, causes a deterioration of sea water usage and a reduction of amenities. Williams (1996) concluded that water pollution is not only related to hazardous materials in aqueous media but air pollutants, which eventually end up accumulated in different types of aqueous media as well.

Pollution of water has been always attributed to the increase in industrialization and human activities in the world. As a result, and according to the World Health Organization (WHO), three billion people in the world lack access to clean water. Most of the sources of aquatic pollution are well-known, 50% of which is a direct result of the agriculture sector. Domestic and municipal wastes also cause massive damage to ecosystems. Such wastes may contain a broad range of the pollutants, like pathogens, organic substances, heavy metals, and oil. Due to the population growth, the amount of wastes produced by people is significantly increasing. It is supposed, that water pollution will increase at least twice over the next 20 years. The environmental response of an aquatic system to pollutants greatly depends on its inherent susceptibility, i.e., a natural capacity to absorb environmental stress and still easily recover stability.

Oil pollution has been receiving increasing attention since the middle of the 19th century with the increase in tanker operations, oil use, frequent marine tanker collisions and accidents resulting in oil spills. Unfortunately, every year, millions of
gallons of oil are being added to the coastal and marine environments from different sources, as shown in Figure 1. Smith (1971) reported that as many as half a million tons of persistent oils are discharged into the sea every year. Reed (1972) suggested a similar figure and reported that the annual release of hydrocarbon is around 600,000–1,000,000 tons. Under still conditions, the oil traps silts and other suspended matters and sinks to the bottom where it is deposited. Coastal refineries institute another distinct risk of continuous oil pollution since millions of gallons of crude oil and its products are processed and stored there. Crude oil is purified and processed in refineries to produce a variety of fuels, lubricants, and solvents. During these operations, a continuous small-scale pollution occurs through leakages, spills, breakages, etc. Water is used in many processes and inevitably becomes contaminated with oil and derivatives, and when discharged, it carries appreciable fuel loads. Spillages et al. (2007) reported that Australia's largest spill was the loss of 17,000 tons of light crude oil from the tanker Kirki off the coast of Western Australia in July 1991. There have been 13 incidents involving the loss of more than 100 tons of oil in Australian marine environments since 1970 as shown in Table 1. In addition, the largest offshore spill in U.S history took place in spring-summer 2010, known as “Deepwater Horizon disaster”. It presented a significant threat to the coastline and the marine ecosystem of the Gulf of Mexico, and was estimated around 33,000 barrels/day. Moreover, the worst environmental maritime disaster took place in New Zealand in 2011. It was attributed to the rupture of one of the ship's main fuel tanks. As a result, it released between 130 and 350 tonnes of heavy oil into the water. The fresh damage was caused after the ship's hull dragged in heavy winds and swells of up to four metres.
The United Arab Emirates is one of the world's leading countries of oil production, and its marine environment along the Arabian Gulf and the Gulf of Oman is subjected to increasing quantities of oil spills. Similar to most of the countries in the Arabian Peninsula, UAE registered desalination plants as the main supply for fresh water. Consequently, and being all built close to the shore, these plants are subjected to the threat of oil spills, hence introducing toxic materials, which directly affect marine life. Smith (1970) reported mortality and elimination of sea stars (*Pisaster* spp.) and sea urchins (*Strongylocentrotus* spp.) as a result of diesel oil pollution and reported that as little as 0.1% emulsion of the oil may inactivate the tube feet of the urchins.
Figure 1: Extent of oil pollution from different sources into the coastal and marine environment worldwide each year from different sources.
Table 1: Recent oil spills in Australia (>100 tonnes).\textsuperscript{17}

<table>
<thead>
<tr>
<th>Ship</th>
<th>Year</th>
<th>Ship type</th>
<th>Estimated oil lost (&gt;100 tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kirki</td>
<td>1991</td>
<td>Oil tanker</td>
<td>17000</td>
</tr>
<tr>
<td>Metaxata</td>
<td>1999</td>
<td>Oil tanker</td>
<td>1400</td>
</tr>
<tr>
<td>Oceanic Grandeur</td>
<td>1970</td>
<td>Oil tanker</td>
<td>1067</td>
</tr>
<tr>
<td>Korean Star</td>
<td>1988</td>
<td>Bulk carrier</td>
<td>800</td>
</tr>
<tr>
<td>Sanko Harvest</td>
<td>1991</td>
<td>Bulk Carrier</td>
<td>700</td>
</tr>
<tr>
<td>Bethioua</td>
<td>1976</td>
<td>Oil tanker</td>
<td>350</td>
</tr>
<tr>
<td>Iron Baron</td>
<td>1995</td>
<td>Bulk carrier</td>
<td>300</td>
</tr>
<tr>
<td>Laura D'Amato</td>
<td>1999</td>
<td>Oil tanker</td>
<td>300</td>
</tr>
<tr>
<td>Era</td>
<td>1992</td>
<td>Oil tanker</td>
<td>296</td>
</tr>
<tr>
<td>Port Stanvac</td>
<td>1999</td>
<td>Pipeline</td>
<td>270</td>
</tr>
<tr>
<td>Al Qurain</td>
<td>1988</td>
<td>Livestock carrier</td>
<td>184</td>
</tr>
<tr>
<td>Esso Gippsland</td>
<td>1982</td>
<td>Oil tanker</td>
<td>180</td>
</tr>
<tr>
<td>World Encouragement</td>
<td>1979</td>
<td>Oil tanker</td>
<td>110</td>
</tr>
</tbody>
</table>
The rate of recovery of the ecosystem as a result of contamination with oil spills is debatable. Shriadah (1998) observed a rapid reduction in the contamination level and recovery of the ecosystem along the Gulf of Oman in one of the oil spill incidents which caused a temporary elevation of contamination levels. On the other hand, Yamamoto et al. (2003) concluded that the recovery rate is dependent on the pollution sites and the intensity of contamination.

Consequences of oil spills have direct environmental and economical impacts. Concerning the environmental impact, oil spills cause a decrease in the concentration of dissolved oxygen in water, as it is well known that film formation of oils obstructs O₂ transferring between air and water. Moreover, dark oil (e.g. crude and residue fuel oil) tends to absorb more solar energy than light oil (e.g. gasoline and diesel), hence raising the water temperature, which might be cause a fire hazard. In addition, oil slick disturbs the amount of light reaching marine plants, algae, and planktons hence affect their photosynthesis. Figure 2 describes the changes that usually take place in the physical and chemical properties of water as a result of the presence of oil slick onto aquatic media.

In addition to all of the above consequences, oil spills have acute-to-chronic effects on organisms, depending on the amount of oil released. Metabolic processes of the affected plants can also increase the toxicity of the well known toxic agents, such as n-paraffin, by converting it to other derivatives that are more toxic than the original. Reptiles and amphibians can also be killed directly by petroleum. In a temperate region, mammals (polar bear, otter, fur seal, and muskrat) that rely on fur insulation are frequently killed by oil. Seabirds are often killed by oil spills, primarily because of plumage oiling and oil ingestion. An example of a chronic biological
Figure 2: Weathering processes that change oil properties
impact is the reduction in the thickness of eggshells of the next generation seabirds. It should be also mentioned that damages caused by an oil spill will be greater if occurring near coral or mangrove areas. Economical impact of oil spills are difficult to assess because it depends on the type of oil, and the geographical details of the region where oil spill took place.

Crude oil is considered a precious commodity. Therefore, any spillage or inefficient extraction implies economic and environmental concerns. Thus, efficient systems are significantly essential for the treatment and recovery of the spilled oil. In addition to accidents, such as well drilling, shipping or bunkering incidents, or by deliberate discharge from the vessels, oil spills may also arise as a result of natural leakage from the sea floor. These events have encouraged environmental scientists to develop techniques to deal with oil spills, both at sea and on shorelines. Depending on the approach taken in the treatment, these techniques include physical, chemical, and biological in origin. Some of these methods were debated and as a result, significant research efforts have been devoted to this subject in the recent years. The following sections provide more details about these approaches.

1.1 Physical Methods

Some of the most common practical and environmental physical methods of the oil spill cleanup are based on mechanical recovery. This approach is the largest class of the recovery techniques, and includes a broad variety of skimmers, booms, and oil-collecting vessels. The mechanical methods do not involve chemicals and do not, therefore, require special official permission to be implemented, unlike dispersants, whose use is limited or even forbidden in many regions. The mechanical oil recovery systems are provided to the oil spill location by the specially designed
and equipped spill response vessels. A boom is a device used to control oil spreading and restrict discharge into a limited area. Booms can be made from various polymer-based materials which are tolerant to oil, UV light, and other handling conditions. Examples include nylon, polyester, polyurethane, and PVC, etc., and are variable in design and construction. A boom is made of essential components: a freeboard, a skirt, and a longitudinal support. A "freeboard" is a top part that contains the oil and helps preventing waves from splashing oil over the top part of the boom. A "skirt" is an underwater part of the boom, and it helps collecting the oil and contributes in reducing the amount of oil lost in the boom. A "longitudinal support", which is usually a chain or cable running along the bottom of the skirt, strengthens the boom against wind and wave action, and may also serve as a weight or ballast to add stability and help keep the boom upright as shown in Figure 3.33

Skimmers are usually used together with the booms. The skimmers remove oil from the water surface without causing changes in its physical or chemical properties and transfer it to the storage tanks onboard the vessel. During severe winter conditions where ice covers is found onto the water surface, there is usually no need to use the booms because the ice serves as a barrier against oil spreading. A variety of skimmer designs have been optimized to operate efficiently in different weather conditions, as well as in the Arctic sea with a high concentration of ice. Although designs vary, all skimmers rely on specific gravity, surface tension, and a moving medium to remove floating oil from the water surface as shown in Figure 4.34
Figure 3: Use a boom for oil clean up.\textsuperscript{35}

Figure 4: Use skimmer for oil clean up.\textsuperscript{36}
Oil-collecting vessels are motorized vessels, which are integrated with some of the above-mentioned technologies. They perform an independent collection of the oil spill on the water, and are, therefore, considered the most reliable and possible technology in the future. This is based on the fact that they have the ability to handle large volumes of the inflow to be treated with minimal negative impact on the environment, compared to other technologies. Most of the vessels combine several oil spill response technologies onboard.\(^{37}\)

1.2 Chemical Methods

In many cases, physical methods are not sufficient for a complete removal of an oil spill. In addition, the time used for oil spill removal is very critical. In these situations, chemical methods are suitable alternatives. However, chemical methods are relatively more expensive and have other side effects, which are considered disadvantages of these methods. Chemical methods are mainly composed of chemical solidifiers, which have chemical structure that makes it different from chemical dispersants. Their main function is to change the physical and chemical properties of an oil spill to form coagulate, which then either sinks to the bottom of the water media or floats onto the water surface then collected using special boats. However, due to their high costs, solidifiers are not so common and are only used in some countries. Chemical dispersants are chemical agents that are composed of surfactant and petroleum-based solvents. Additionally, some reagent aids may be added to control the spreading of the dispersed oil. The primary function of dispersants is to reduce surface tension of an oil slick as shown in Figure 5.\(^ {38}\)
Figure 5: Schematic representation showing the principles behind the use of dispersants.
Sorbents makes up another class of materials with the ability of soaking up oil spills from water. The main advantage of sorbents is the convenience of removing oil slick from contaminated area, unlike other methods. However, it is well known that oil-containing sorbents should be collected for oil recovery or for further elimination. Thus, adsorbents should be low in density to make them buoyant for long periods and be able to adsorb oil. Therefore, sorbents should be designed with high porosity for a maximum efficiency of oils spill removal.

Oleophilic materials are preferred as sorbents as they possess high affinity towards the hydrophobic oils spills, hence removal efficiency is expected to be high. On the other hand, sorbents should not be hydrophilic to avoid the adsorption of water. An example of a polymeric boom is shown in Figure 6. Additionally, ideal sorbents should have the following properties:

1. During pick up of the saturated adsorbents, soaked oil should be minimum.
2. Application and transportation of sorbents should be convenient.
3. Sorbents should be non-toxic and non-harmful to the environment.
4. Sorbents should be less expensive than other materials used on oil spill removal.
I.3 Biological Methods

These methods are also known as “bioremediation”, which are usually applied as a secondary on-site treatment, after mechanical or chemical methods, especially when the oil spill layer thickness is not less than 0.1 mm. Few microorganisms are capable of digesting the petroleum hydrocarbons, such as bacteria of the genus Pseudomonas and some species of fungi and yeasts. It becomes more accessible to other types of oil-eating bacteria if the oil spill is more finely divided. Bioremediation typically involves biostimulation, which means the addition of the rate-limiting nutrients in order to accelerate the biodegradation of the oil. Namely, in order for the microorganisms to digest carbon-based materials, significant amounts of nitrogen and phosphorus, which are essential ingredients of protein and nucleic acid, are needed. Maintaining sufficient nitrogen is considered the biggest challenge. Biological methods involve the use of living organisms such as; bacteria, yeast, algae, and fungi to degrade oil spill. The main advantage of biological methods is its low negative impact on ecology. However, the disadvantage of biological methods is the slow rate of degradation as long time is always needed for a complete degradation of the oil spill products.
Figure 6: A boom filled up with polypropylene sorbent, applied to collect oil.
1.4 Other Approaches

A number of other technologies may also be used such as inorganic minerals, natural materials, synthetic chemical and biological materials: these include the use of polymeric materials. Recently, Wang et al. have used kapok fibers for high oil absorbency. In another recent work by Likon et al., used seed fibers as a natural source for oil absorbents. Table 2 shows the advantages and limitations of each of the various treatment methods. Examples of physical and mechanical methods are skimmer, gravity separation, micro and ultrafiltration, and membrane filtration. The biological method includes the use of microorganisms to remove oil. Chemical treatment can be realized by coagulation and flocculation, electrocoagulation, and flotation techniques. Granular or fibrous filter materials are used for surface and depth filtration method. Meanwhile, adsorption method utilizes booms, dispersants, and sorbents to remove oil. In the following sections, more focus will be given to sorption of oil using fibrous sorbents and various methods of preparing those sorbents.
<table>
<thead>
<tr>
<th>Methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Good oil removal efficiency, Simple operation, Low processing cost</td>
<td>Labor intensive, Poor removal of fine emulsions (&lt;100 µm)</td>
<td>48–51</td>
</tr>
<tr>
<td>Coagulation and flocculation</td>
<td>Good oil removal efficiency</td>
<td>High initial and operating cost, Labor intensive, Generation of a secondary pollutant</td>
<td>43,52,53</td>
</tr>
<tr>
<td>Electrocoagulation</td>
<td>High oil removal efficiency, Low operating cost</td>
<td>High initial cost</td>
<td>42,54</td>
</tr>
<tr>
<td>Flotation</td>
<td>High oil removal efficiency</td>
<td>Complex operation (involves coagulants/flocculants), Inadequate removal of fine oil droplets (&lt;50 µm), High operating cost</td>
<td>44,55–57</td>
</tr>
<tr>
<td>Coalescences (depth filtration)</td>
<td>Good oil removal efficiency, Simple operation, Low initial and Operating cost</td>
<td>Oil removal efficiency highly depends on the quality of filter bed media, Slow oil removal process</td>
<td>45,46,58–62</td>
</tr>
<tr>
<td>Membrane filtration</td>
<td>High oil removal efficiency</td>
<td>Requires pre-treatment of wastewater, High initial and operating cost, Premature membrane fouling</td>
<td>63–65</td>
</tr>
<tr>
<td>Biological treatment</td>
<td>Good oil removal efficiency, Low operating cost</td>
<td>Extremely temperature and pH sensitive, Requires skilled operator Requires wide space</td>
<td>41</td>
</tr>
</tbody>
</table>
1.5 Fibrous Sorbents

Fibrous sorbents of different origins; natural and synthetic, have been investigated for oil spill removal. Figure 7 shows some types of fibrous materials and their classification. In the textile industry, fibers are considered the basic unit of textile products, which are characterized by flexibility, fineness and high aspect ratio (length-to-thickness) of $\geq 100$. Textile technology has evolved over millennia, and the term textile now has a very broad meaning. In general, this term applies to product forms (fiber, yarn, and fabric); either from natural or synthetic sources as well as the products derived from them. This includes all types of yarns or ropes (threads, cords, ropes and braided), all kinds of fabrics (woven, knitted and nonwoven), hosiery (knitwear and garments), household fibrous, furnishing and upholstery, industrial and technical fibrous (e.g. geotextiles, medical fibrous and fibrous composites). Moreover, an earlier classification of fibrous material as reinforcements was established by Scardino. Numerous types of synthetic inorganic and organic fibers are used for commercial, industrial, and even medical purposes. Some of the major commercial uses of fibers are for thermal and acoustical insulation, filtration, and reinforcements. Thus, fibrous products aid in energy conservation (thermal insulation) and the removal of pollution (filtration). Medical uses of fibers include blood filtration and implant reinforcements.

Polymeric man-made fibers are fabricated from natural or synthetic sources. The consumption of man-made fibers based on synthetic polymers, frequently referred to as synthetic fibers, has grown rapidly since their introduction into the market in the 1940s and 1950s. Today in the United States, more than 50% of the fibers used in textile applications are man-made. The worldwide production of man-made fibers amounted to about 27 million metric tons in 1996.
Fibrous materials and their classification

Figure 7: Fibrous materials and their classification
The first man-made fiber was presented in 1889 at the World Exhibition in Paris. Developments in the polymer and chemical industries – as well as in electronics and mechanics – have led to the introduction of new types of man-made fibers, especially the first synthetic fibers, such as nylon\textsuperscript{73}, polypropylene\textsuperscript{74} and polystyrene\textsuperscript{75,76}. Regenerated cellulosic fibers are a class of man-made fibrous materials manufactured from wood pulp or other natural sources of cellulose. Besides the application of unmodified cellulose products, cellulose can be converted into regenerated cellulosic materials, which have been widely applied in many fields.\textsuperscript{77}

Sorption by natural fibrous materials takes place by adsorption and coalescence method. Adsorption and coalescence (via depth filtration) showed reasonable and attractive results if appropriate media are used.\textsuperscript{68} In these mechanisms, no additional chemicals are required to emulsify oil in water, and high removal efficiencies of chemical oxygen demand (COD) from wastewater were demonstrated\textsuperscript{78}. In general, natural fibrous oil sorbents contain micro and macroporous structures that permit an oil attachment and entrapment within inter- and intrafiber structures. Adsorption and coalescence mechanisms are often separately studied, although there is a very high probability that both mechanisms occur simultaneously. In both mechanisms, oil adsorption performance is commonly measured in terms of oil removal efficiency (\% removal) and sorption capacity (mass of oil sorbed per gram sorbent).\textsuperscript{67}
A number of natural sorbents have been studied in this regard such as straw\textsuperscript{79}, sawdust\textsuperscript{48}, corn cob\textsuperscript{80}, rice\textsuperscript{81}, coconut husk\textsuperscript{82}, cotton\textsuperscript{83}, wood\textsuperscript{84}, wool\textsuperscript{85}, kenaf\textsuperscript{66}, cattail\textsuperscript{41}, and kapok fibers\textsuperscript{69}. However, it has been shown that most of them have disadvantages such as poor buoyancy, relatively low oil absorption capacity, low hydrophobicity, and high affinity towards water absorption\textsuperscript{68}. Considering the high hydrophobicity of oil, the most proper sorbents should possess high hydrophobic as well. Therefore, the attention of environmental scientists has been driven towards the use of synthetic hydrophobic polymers, such as polypropylene\textsuperscript{87}, polyurethane foams\textsuperscript{88}, and polystyrene\textsuperscript{89}. These synthetic sorbents have excellent hydrophobic and oleophilic properties\textsuperscript{68}, and could be further treated to enhance their hydrophobic characteristics\textsuperscript{90}. In addition to high hydrophobicity, fibers with high surface area are also expected to have higher sorption capacities. When the diameters of polymeric fibers are shrunk from micrometers (e.g. 10–100 µm) to submicron or nanometers (e.g. 10–100 nm), there appear several surprising and useful characteristics such as very large surface area to volume ratio (this ratio for a nanofiber can be as large as 100 times of that of a microfiber), flexibility in surface functionalities, and superior mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material. These outstanding properties make the polymer nanofibers to be optimal candidates for many critical applications\textsuperscript{91}.

1.6 Fabrication of Fibrous Sorbents – Electrospinning Technique

A number of processing techniques such as drawing\textsuperscript{92}, template synthesis\textsuperscript{93}, self-assembly\textsuperscript{94,95}, electrospinning\textsuperscript{44}, etc. have been used to prepare polymeric micro- to-nanofibrous sorbents in recent years\textsuperscript{91}. Electrospinning has been recognized as an efficient technique for the fabrication of polymer nanofibers. The process of
"electrospinning", was first discovered in 1934 by Formhals. Within the following 10 years (1934-44), Formhals published a series of patents describing an experimental setup for the production of polymer fibers using an electrostatic force. The first spinning method adopted by Formhals had some technical disadvantages, such as the difficulty of completely drying the fibers obtained from spinning due to the short distance between the spinning and collection area, which resulted in a less aggregated web structure. In a subsequent patent, Formhals refined his earlier approach, where the distance between the feeding nozzle and the fiber collecting device was altered to provide more drying time for the electrospun fibers. Subsequently in 1940, Formhals patented a method for producing composite fiber webs from multiple polymeric sources by electrostatically spinning polymer fibers on a moving base substrate.

The major advantage of the electrospinning process is its technical simplicity and ease of adaptability. Electrospinning unit is simple to construct. It consists of a high voltage electric source with positive or negative polarity, a syringe pump with capillaries or tubes to carry the solution from the syringe or pipette to the spinneret, and conducting collector. The collector could be metallic in origin such as aluminum, which can be shaped as flat plates, rotating drums, etc. A schematic drawing of the electrospinning unit is shown in Figure 8. Previous researchers have used an apparatus similar to the one given in Figure 8 with modifications depending on process conditions to spin a wide variety of fine fibers. Electrospun fibers can be made from solutions or melts of polymers, which are then forced through a syringe pump to form a pendant drop of the polymer at the tip of the capillary. High voltage is applied to the polymer solution into the syringe through an immersed electrode, or by direct contact with the syringe metallic needle, thereby inducing free charges into
the polymer solution. These charged ions move in response to the applied electric field towards the electrode of opposite polarity: grounded collector.\textsuperscript{105} At the tip of the capillary, the pendant hemispherical polymer drop takes a cone-like projection in the presence of an electric field. Additionally, when the applied potential reaches the critical value required in order to overcome the surface tension of the liquid, a jet of liquid is ejected from the cone tip.\textsuperscript{106} Various instability modes that occur during the fiber forming processes are expected to occur by the combined effect of both the electrostatic field and the material properties of the polymer. It has been suggested that the onset of different modes of instabilities in the electrospinning process may depend on the shape of the jet initiating surface and the degree of instability, which efficiently produces changes in the fiber morphology.\textsuperscript{107}
Figure 8: Schematic diagram of electrospinning set-up.\textsuperscript{104}
In electrospinning, the charge transport due to the applied voltage is mainly
due to the flow of the polymer jet towards the collector, and the increase or decrease
in the current is linked to the mass flow of the polymer from the nozzle tip. Deitzel et
al. (2011) have inferred that the change in the spinning current is correlated to the
change in the instability mode\(^{108}\). They experimentally showed that an increase in
applied voltage causes a change in the shape of the jet initiating point, and hence the
structure and morphology of fibers\(^{107}\). Earlier in 1971, Baumgarten while carrying
out experiments with acrylic fibers observed an increase in fiber length of
approximately twice with small changes in fiber diameter with an increase in applied
voltage\(^{109}\). Similarly, Megelski et al. (2013) have investigated the voltage
dependence on the fiber diameter using polystyrene (PS) and showed that the PS
fiber size decreased from about 20 \(\mu\)m to 10 \(\mu\)m with an increase in voltage from
5KV to 12KV, while there was no significant change observed in the pore size
distribution, as shown in Figure 9\(^{110}\).

It has also been shown that varying the applied voltage has a significant effect
on the formation of the Taylor cone. At relatively low applied voltages a pendant
drop (depicted in light gray in Figure 9) is formed at the tip of the capillary, where
after the Taylor cone (represented in dark gray) then forms at the tip of the pendant
Figure 9: Effect of varying the applied voltage on the formation of the Taylor cone.\textsuperscript{110}
drop. However, as the applied voltage is increased (moving from left to right) the volume of the pendant drop decreases until the Taylor cone is formed at the tip of the capillary. Increasing the applied voltage further results in the fiber jet being ejected from within the capillary, which is associated with an increase in bead defects as shown in Figure 10.111

The structure and morphology of electrospun fibers are easily affected by the nozzle to collector distance because of their dependence on the deposition time, evaporation rate, and whipping or instability interval.112 Megelski et al. (2013) observed bead formation in electrospun PS fibers on reducing the nozzle to collector distance while preserving the ribbon shaped morphology with a decrease in the nozzle to collector distance.113

The flow rate of the polymer from the syringe is another important process parameter as it influences the jet velocity and the material transfer rate. In the case of PS fibers, Megelski et al. (2013) observed that the fiber diameter and the pore diameter increased with an increase in the polymer flow rate. As the flow rate increased, the fibers had pronounced beaded morphologies and the mean pore size increased from 90 to 150 nm Figure 11 shows the FESEM images of these PS fibers as a function of flow rate.113
Figure 10: Variation of beaded fibers as the mass ratio of water/ethanol was changed. Electric field is 0.5 kV/cm. weight fraction of PEO is 3.0%. The horizontal edge of each of the figures is 20 microns long.\textsuperscript{111}
Figure 11: FESEM images of PS fibers as a function of flow rate: (a) 0.004 mL/min (5 kV, WD 9.5 mm); (b) 0.07 mL/min (15 kV, WD 5.5 mm); (c) 0.1 mL/min (15 kV, WD 5.2 mm); (d) 0.14 mL/min (15 kV, WD 5.5 mm); (e) 0.24 mL/min (15 kV, WD 5.5 mm).\textsuperscript{113}
Research activity on the electrospinning of nanofibers has been successful in spinning submicron range fibers from different polymeric solutions and melts. Although a vast amount of literature is available on the structure and morphological properties of polymeric micro- and nanofibers, there is very little published information on the electrohydrodynamics of the electrospinning process. Polymers with attractive chemical, mechanical, and electrical properties like high conductivity, high chemical resistance, and high tensile strength have been spun into ultrafine fibers by the electrospinning process, and their potential application in areas like filtration, optical fibers, drug delivery system, tissue scaffolds, and protective textiles have been examined.\textsuperscript{107}\textsuperscript{115} MacDiarmid et al. (2001) have electrospun polystyrene using THF as a solvent to produce nanofibers with a minimum diameter of 16 nm and an average diameter of 30.5 nm. He observed higher temperature in fibers due to higher conductivity.\textsuperscript{116}

The production of nanofibers by the electrospinning process is influenced by both the electrostatic forces and the viscoelastic behavior of the polymer. Process parameters, like solution feed rate, applied voltage, nozzle-collector distance, and spinning environment, as well as material properties, like solution concentration, viscosity, surface tension, conductivity, and solvent vapor pressure, influence the structure and properties of electrospun nanofibers. Significant work has been done to correlate fibers' characteristics to process parameters, and to characterize the properties of fibers as a function of process and material parameters.\textsuperscript{103}

In terms of materials properties effect, solution concentration has been shown to limit boundaries for the formation of electrospun fibers due to variations in the viscosity and surface tension.\textsuperscript{107} Low strength solution forms droplets due to the
influence of surface tension while higher concentration prohibits fiber formation due to higher viscosity. Previously published literature has documented the difficulties in the electrospinning of polymers; for example, Megelski et al. (2002) have reported on the fiber morphology and pore formation of PS in THF in varied concentrations from 18 to 35 wt %. They found that the viscosity of the solution increased as the PS concentration increased while all other spinning parameters were kept constant. Optical micrographs showed an increase in fiber diameter from 0.8 to 20 (±10) μm with increasing solution concentration. The PS fibers form beads up to a concentration of 30 wt %, with the occurrence of beads decreasing with increasing solution viscosity. As can be seen in Figure 12, the size of the beads as well as the size of the fibers increased with higher PS concentration.114

In addition to the above, electrospinning process can also be influenced by choices in nozzle configuration (single, single with emulsion, side-by-side, or coaxial nozzles). Depending on the application, a number of nozzle configurations have been employed. Perhaps the simplest and most common configuration is the single nozzle technique. In this configuration, a charged polymer solution flows through a single capillary. This configuration is very versatile and has been used to electrospun only polymer solutions117 as well as polymer blends (with soluble polymers) in common solvent.110

Many synthetic and natural polymers have been electrospun using a variety of solvents, and their effect on the formation of pores was briefly described only by Bognitzki et al (2000).118 Some work has been carried out on PS membranes, where the pores were found to be either a function of solvent density or created by thermally induced phase separation techniques.119-121 In the study as mentioned earlier the physical properties of the solvents play a significant role in this process
and hypothesize that the solvent volatility plays a critical role in the pore formation process.
Figure 12: Optical microscope images of PS fibers electrospun from THF as a function of PS concentration: (a) 18 wt %; (b) 20 wt %; (c) 25 wt %; (d) 28 wt %; (e) 30 wt %; (f) 35 wt %.\textsuperscript{114}
In general, a very high density of pores was observed on PS fibers electrospun from THF, and the resulting microtexture induced at the fiber surface increases the surface area by as much as 20 to 40% depending on the diameter of the fiber.\textsuperscript{122} Substitution of THF observed the influence of the solvent vapor pressure with DMF, with the microtexture and nanopores of the PS fibers disappearing as the volatility of the mixed solvent system decreased.\textsuperscript{114}

The characterization of fibers produced by the electrospinning process remains one of the most difficult tasks as the chances of getting single fibers are rare. In order to empirically understand electrospinning process, assessment of the entire process from polymer selection to mechanical testing needs to be carried out accurately. In electrospinning, the polymers used are characterized into four distinct categories: physical, structural, mechanical, and chemical.\textsuperscript{123} Presently, nanofibers have attracted the attention of researchers due to their remarkable micro and nanostructural characteristics, high surface area, small pore size, and the possibility of their producing three-dimensional structures that enable the development of advanced materials with sophisticated applications.\textsuperscript{124} Physical characterization is associated with structure and morphology of the sample and the nanofibers internal structure determines the physical and mechanical properties. Geometric properties of nanofibers include fiber diameter, diameter distribution, fiber orientation, and fiber morphology (e.g. cross-section shape and surface roughness). For the characterization of geometric properties, techniques such as scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) were used.\textsuperscript{125,126,114,127-130} SEM has been used by many researchers to observe the morphology of the fibers produced,\textsuperscript{109,125,126,131-133} as SEM is capable of detecting
fiber diameters and morphologies, but the resolution is less at extreme magnifications. Figure 13 shows the typical SEM image of Polystyrene electrospun fibers. For SEM, there is a requirement for the samples to be electrically conductive, therefore, for most of the electrospun polymers produced, a gold or platinum coating must be applied that may alter the diameter readings at higher magnifications. Nevertheless, SEM remains a quick method for observing the fibers produced, and it requires a slight sample size for its operation.\textsuperscript{124}
Figure 13: SEM images of spun fibers electrospun from a 30 wt % PS/DMF solution under (a) 43%, (b) 37%, (c) 24%, (d) 22%, (e) 15%, (f) 11% with relative humidity (scale bar: 5 μm).\textsuperscript{134}
Chapter 2: Objectives

The following is a detailed list of objectives of the current work:

1) Prepare the appropriate polystyrene solutions with different concentrations suitable for electrospinning

2) Fabricate fibers with micro and/or nano diameters of synthetic (pure) and recycled polymers with variable fiber size distribution

3) Optimize the electrospinning conditions that will yield fibers with uniform size distribution within the mm -nm scale, and to characterize the fibers prepared there of.

4) Evaluate the electrospun fibers of all types of polystyrene polymers for the removal of various types of oil spills from aqueous media

5) Model the process of oil spills using prepared fibers and correlate the efficiency of oil pick-up capacity with the structure and morphology of the prepared fibers.
Chapter 3: Materials and Methods

3.1 Materials

The starting materials included two types of polystyrene PSI ($M_w = 100,000$ g/mol) and PSSL ($M_w = 350,000$ g/mol), were purchased from Avocado Research Chemicals Ltd. and Sigma-Aldrich Companies. In addition, a recycled polystyrene (PSCIII) was also used by using foam and Styrofoam cups. Solvents included N, N-dimethylformamide (DMF) (>99.8%), and was purchased from Fluka, while tetrahydrofuran (THF) (>99.8%) was purchased from LiChrosolv. Polymers used in the current study were designated as PSI, PSSL, and PSCIII, respectively, and were all used as received. Crude oils used in the current study were supplied by ADNOC, TOTAL, and ADCO; all in Abu Dhabi, UAE with labeled densities. The Crude oil properties investigated are listed in Table 3.

Table 3. Properties of the Crude oil, measured at room temperature.

<table>
<thead>
<tr>
<th>Crude Oil Types</th>
<th>Density (g/cm$^3$)</th>
<th>Viscosity cP @50RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADNOC</td>
<td>0.869</td>
<td>38.5</td>
</tr>
<tr>
<td>TOTAL</td>
<td>0.867</td>
<td>7.0</td>
</tr>
<tr>
<td>ADCO</td>
<td>0.829</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Each crude oil’s viscosity was measured using viscometer (Brookfield Viscometer by using spindle S34).
3.2 Methods

3.2.1 Fabrication of PS Microfibers

Homogeneous solutions of PSI, PSII and PSCI containing 20, 30, and 40 w/v% were prepared by dissolving the corresponding amounts of the polymer beads in DMF, THF or a mixture of both. Polymer microfibers were made using an electrospinning technique where each of the polymer solutions was injected at a feeding rate of 10 ml/hr using an automatic syringe pump, and a voltage of 15 kV, provided by a Gama High Voltage Research power supply, towards a grounded metallic collector. The collector is located at a distance of 15 cm from the syringe needle. The electrospinning process was carried out under laboratory humidity and at room temperature. The whole electrospinning assembly was kept inside a Plexiglas box to avoid the effect of external airflow and change in temperature and humidity around the system when in use. Electrospun fibers were collected on a flat square aluminum foil sheet and were left till complete dryness before studying their morphology and before evaluating their sorption capacities.

In order to study the effect of electrospinning parameters on the sorption capacities of the fibrous sorbents, an optimization procedure was carried out in which six electrospinning parameters were evaluated. In the following sections, details about each variable will be given. It should be mentioned that each parameter was separately varied while keeping all other parameters constant, in order to carefully optimize the electrospinning process and produce fibers with maximum affinity towards crude oil collection.
Effect of Solvents: Polystyrene solutions (PSI, PSII and PSCIII) of concentrations 20%, 30% and 40% were prepared by dissolving each of them in DMF, THF and their mixtures at volume ratios of 100/0, 75/25, 50/50, 25/75, and 0/100. All other electrospinning parameters were kept constant.

Effect of Applied Voltage: Microfibers were collected at applied voltages of 10KV, 15KV, 20KV, 25KV and 30KV.

Effect of Feeding Rate: Polymer solutions were fed through the syringe using an automatic syringe pump at feeding rates of 1, 5, and 10 ml/h.

Effect of Distance: As mentioned above, this is the distance between the tip of the syringe needle and the grounded metallic collector. Distance was varied at 10, 15, and 20 cm.

Effect of Humidity: The presence of humidity is known to affect the fibers' surface topography. It should be mentioned that electrospinning setup and experiment was all carried out in a closed plexiglass box to avoid external air flow, temperature and humidity effects on the fibers during their formation. In the current study, microfibers were collected under the effect of relative humidity adjusted at 49, 70-80, and 80-90% by using humidifier.

Effect of Needle Diameter: It is known that diameter of the needle determines the starting size of the fibers before their deposition onto the grounded collector. In this regard, needles with gauge numbers of 18G, 21G, 23G and 29G were used.
3.2.2 Characterization of the Sorbents

Starting polymers (as-received) were characterized for their composition using FT-IR spectroscopy to characterize the polymer composition. This was carried out on a polymer thin film cast a solution containing 20% of each of the polymers in DMF. Electrospun PSI, PSII, and PSCIH microfibers were characterized for their morphology, BET surface area, and pore size distribution. Analysis of the fibers morphology was carried out using a scanning electron microscope (JOEL-6010) after being gold-coated. Fibers size and distribution were calculated using image analysis software (ImageJ, National Institutes of Health, Bethesda, Maryland). BET surface area, porosity, and pore size distribution were carried out using a nitrogen gas adsorption at 77 K employing a Quantochrome NOVA 1000 volumetric gas sorption instrument: Autosorb, USA.

3.2.3. Sorption Experiments

In a typical sorption experiment, 10 ml of crude oil was poured into a 250-mL beaker containing 100 mL artificial seawater (3.5% NaCl). Different amounts of each of the polymeric microfibrous sorbents (0.005, 0.01, 0.05, and 0.1g) were then evenly placed onto the oil surface. After various time intervals, namely, 0.5, 1, 2, 5, 10 and 30 minutes, the sorbent containing the adsorbed oil was collected, drained for one minute, and placed on a watch glass for weighing. All experiments were performed at ambient temperature and all weighing performed using an analytical balance with readability up to 0.01mg (5 decimal places). The oil sorption capacity (g/g) of the sorbent was determined by following equation (Tanobe et al., 2008)\textsuperscript{135}. 

\textsuperscript{135}
\[
Q = \frac{m_o - m_s}{m_s}
\]

Where \( Q \) is the oil sorption capacity (g/g), \( m_o \) is the total mass of sorbent after the oil drained, and \( m_s \) is the mass of the dry sorbent. Results are expressed as an average of triplicate readings.
Chapter 4: Results and Discussion

In the following sections, characterization of the starting materials will be first shown, followed by discussing the application of the fabricated polymeric microfibers in the removal of crude oil spills. In the second part of this chapter, detailed optimization of the electrospinning process will be discussed and the effect of optimizing the electrospinning parameters on the sorption capacities of the fibers prepared thereafter will be deliberated.

4.1 Characterization of the Starting Materials

4.1.1 Crude Oil

Three types of crude oils were used in the current study. These were obtained from oil companies in UAE. Studying the density and viscosity of these oils showed their variability. Figure 14 (a,b) shows densities and viscosities of the oils, respectively. Although the three oils showed minor variation in their densities, a more pronounced variation in their viscosities was found. ADNOC crude oil showed the highest viscosity, while ADCO crude oil had the lowest. It should be mentioned that variation in the densities and viscosities of crude oil depend on the composition of the oil, where crude oil is essentially a mixture of many different hydrocarbons, all of varying chain lengths and complexities.
Figure 14: Density (a) and Viscosity (b) of crude oils used in the current study
4.1.2 Polystyrene

In the current study, polystyrene of different origins were used. Analytical-grade polystyrene (PSI and PSII) were obtained from Sigma-Aldrich, while commercial polystyrene (PSCIII) was prepared by recycling styrofoam sheets and cups. In order to confirm phase composition, all types of polystyrene were analyzed by FTIR; Figure 15. All polystyrene bands were shown at their corresponding wave numbers known in the literature. Bands such as those at 3081.2-3001.1 cm\(^{-1}\) and 2923.91 cm\(^{-1}\) and 2850.40 cm\(^{-1}\) corresponding to the stretching mode of aromatic C-H and at 1943.2-1728.3 cm\(^{-1}\) corresponding to the aromatic CH asymmetric stretching mode were all observed in the IR spectra of all types of polystyrene. These findings indicate the high purity of the analytical-grade polystyrene and surprisingly indicate the exceptional high purity of the recycled polystyrene samples. No evidence of non-polystyrene reagents, which are usually used in manufacturing polystyrene foam, was found.

Molecular weights of PSI and PSII starting polymers were confirmed by GPC analysis (University of Sharjah) to match the information of the supplier. In addition, molecular weight of PSCIII was also measured using GPC analysis. Results are shown in Figure 16.
Figure 15: FT-IR spectra for PSI, PSII, and PSCIIII polymers

Figure 16: Weight-based Molecular weight of PSI, PSII, and PSCIIII polymers
4.2 Characterization of the Polymeric Microfibers

Polystyrene of different origins (PSI, PSII and PSCIIII) were electrospun into fibers using a pre-organized set of electrospinning conditions. Those were voltage of 15 kV, feeding rate of 10 ml/hr, spinning distance of 15 cm and laboratory humidity (47% relative humidity). Under these conditions, solutions containing 20, 30, and 40 wt% of each of the polymers were electrospun into fibers. Those were characterized for their morphology using SEM, and surface area and pore size distribution using \( \text{N}_2 \)-adsorption. Figures 17-19 show SEM micrographs of microfibers electrospun from solutions containing 20, 30, and 40 wt%, respectively. All samples showed the formation of randomly distributed micro-scale fibers with cylindrical morphology. No signs of other non-fibrous morphologies, such as beads, ribbons, islands, or films, were found. Results of the fiber size distribution of these fibrous samples are shown in Figures 20-22. An average fiber size of 3.5 mm was shown in the fibers produced from 20, 30, and 40 wt% solutions of PSI with a slight increase with increasing the initial concentration of the polymer solutions; Figure 20. On the other hand, average fiber size of 5, 7, and 10 mm were shown in the fibrous samples produced by the electrospinning of 20, 30, and 40 wt% PSII solutions; Figure 21. The relatively higher average fiber size produced from the spinning of PSII solutions than the PSI solutions could be related to the higher molecular weight of PSII than PSI (100,000 vs. 350,000 Da, respectively). Fibers produced from the spinning of solutions containing 20, 30, and 40 wt% of recycled polymer (PSCIIII) showed an average sizes of 1, 4.5 and 7 mm, respectively; Figure 22. These confirm the effect of initial molecular weight of the polymer on the average size of fibers, where molecular weight of PSCIIII was midway between that of PSI and PSII: 216,000 Da. Increasing the molecular weight of the polymers is
known to highly affect the viscosity of solutions prepared thereof. This, in turn, is also known to be yield coarser fibers. High magnification micrographs of fibers produced from the spinning of 20wt% solutions of the three polymers are shown in Figure 23. Micrographs confirmed the cylindrical morphology of the fibers with low surface roughness and signs of internal porosity. Surface roughness and internal porosity could be related to the immediate evaporation of the solvent as a result of fibers deposition during electrospinning.
Figure 17: SEM micrographs of a) PSI, b) PSII, and c) PSCIII fibrous sorbents obtained by electrospinning 20 wt% solutions of each polymers in DMF.
Figure 18: SEM micrographs of a) PSI, b) PSII, and c) PSCIII fibrous sorbents obtained by electrospinning 30 wt% solutions of each polymers in DMF
Figure 19: SEM micrographs of a) PSI, b) PSII, and c) PSCI fibrous sorbents obtained by electrospinning 40 wt% solutions of each polymers in DMF.
Figure 20: Fiber size distribution of fibrous sorbents obtained by electrospinning of (a) 20%, (b) 30%, and (c) 40% solutions of PSI polymers in DMF
Figure 21: Fiber size distribution of fibrous sorbents obtained by electrospinning of (a) 20%, (b) 30%, and (c) 40% solutions of PSII polymers in DMF.
Figure 22: Fiber size distribution of fibrous sorbents obtained by electrospinning of (a) 20%, (b) 30%, and (c) 40% solutions of PSCIII polymers in DMF.
Figure 23: High magnification SEM micrographs of fibrous sorbents obtained by electrospinning 20 wt% solutions of (a) PSI, (b) PSII, and (c) PSCI III polymers in DMF.
Assessment of the fibers porosity was carried out by adsorption-desorption experiments using N$_2$ adsorption. **Figure 24** shows adsorption-desorption hysteresis of fibers produced from the electrospinning of 20 wt% solutions of the three polymers. All fibers showed type IV isotherms with a low extent of N$_2$ adsorption, which is related to the low surface roughness of the fibers. As a result of the non-woven nature of the fibers, pore size distribution was measured; shown in **Figure 25**. The absence of high surface roughness of the fibers of all polymers was reflected in the presence of minor meso- and micro-porosity within the fibers. The distribution curves showed, on the other hand, macro-porosity, which could be related to the interconnected porosities present within the fibrous sorbents.
Figure 24: Adsorption Isotherms of fibrous sorbents obtained by electrospinning solutions containing 20 wt% of each of the polymers in DMF

Figure 25: Pore Size distribution of fibrous sorbents obtained by electrospinning solutions containing 20 wt% of each of the polymers in DMF
4.3 Oil Sorption Experiments

4.3.1 ADNOC Crude Oil

Electrospun polystyrene fibers fabricated from solutions containing 20, 30, and 40 wt% PSI, PSII and PSCI are evaluated for their efficiency in collecting ADNOC crude oil spills in simulated salty water. In addition, sorption capacity was evaluated as a function of the sorbent weight. Figures 26 show the sorption capacity (g/g) of the crude oil using 0.0044, 0.0066, 0.05 and 0.1 g of fibrous sorbents prepared from solutions containing 20 wt% of PSI, PSII, and PSCI polymers. Sorption experiments were conducted for 30 minutes. All sorption curves showed a similar pattern with an instant sorption of the crude oil by the fibrous sorbent within the first 30 seconds of the sorption experiment. Initial sorption did not take place on a gradual basis similar to the adsorption of gases onto solid sorbents. Instead, sorption was instant and is attributed to the strong hydrophobic-hydrophobic interaction between the polymeric fibrous sorbent and the crude oil floating on the surface of an aqueous medium. Figure 27 shows the maximum sorption capacities achieved after 30 seconds using various weights of the fibrous sorbents that were prepared from solutions containing 20 wt% of PSI, PSII, and PSCI. A general trend can be derived from this graph, where the instantaneous sorption decreased with increasing the weight of the sorbent regardless of the type of polymer. It should be mentioned that all experiments were conducted at a constant volume of the oil. This indicates that a minimum amount of each of the sorbents was essentially used for collecting the crude oil from water. In addition, the cotton-like visual morphology of the fibrous sorbents and the random distribution of the fibers indicate that increasing the sorbent weight will increase the volume-to-weight ratio, which will make it difficult for the highly
Figure 26: Sorption capacities of ADNOC crude oil onto (a) 0.0044g, (b) 0.0066g, (c) 0.05g, and (d) 0.1g fibrous sorbents prepared from electrospinning of 20 wt% solutions of the polymers in DMF
Figure 27: Maximum sorption capacities achieved after 30 seconds using various weights of the fibrous sorbents that were prepared from solutions containing 20 wt% of PSI, PSII, and PSCIII.
viscous crude oil to penetrate within the interconnected porosities of the fibrous sorbents. Figure 28 shows photographs taken during sorption experiments. They clearly indicates the cotton-like nature of the fibrous sorbents and strong interaction between the crude oil and the sorbent.

Fibrous sorbents prepared from 30 and 40% polymeric solutions showed a similar pattern, with overall lower sorption capacities. Figures 29 and 31 show the corresponding sorption capacities, respectively, as a function of the sorbent weight. The highest achieved sorption capacities after 30 seconds were also recorded and plotted in Figures 30 and 32, respectively. Results also indicate that maximum sorption was achieved when 0.0044 g of sorbent was used. Figure 33 summarizes the sorption capacities of sorbents prepared from 20, 30, and 40 wt% solutions of PSI, P$\text{SII}$, and PSCIII at a constant sorbent weight of 0.0044 g. It can be shown that the initial instantaneous sorption decreased with increasing the initial concentrations of the polymers. This could be attributed to the increase in the fibers dimensions as the initial concentrations of the polymer solutions were increased. This is reflected in an overall decrease in the surface area of the fibers; a major property that dictates the high sorption capacity of the fibers. On the other hand, results shown in Figure 33 do not clearly indicate the effect of molecular weight of the polymers on their sorption capacity as a function of the concentrations of the polymer solutions.
Figure 28: Steps of the sorption capacity experiments
Figure 29: Sorption capacities of ADNOC crude oil onto (a) 0.0044g, (b) 0.0066g, (c) 0.05g, and (d) 0.1g fibrous sorbents prepared from electrospinning of 30 wt% solutions of the polymers in DMF.
Figure 30: Maximum sorption capacities achieved after 30 seconds using various weights of the fibrous sorbents that were prepared from solutions containing 30 wt% of PSI, PSII, and PSCIII
Figure 31: Sorption capacities of ADNOC crude oil onto (a) 0.0044g, (b) 0.0066g, (c) 0.05g, and (d) 0.1g fibrous sorbents prepared from electrospinning of 40 wt% solutions of the polymers in DMF
Figure 32: Maximum sorption capacities achieved after 30 seconds using various weights of the fibrous sorbents that were prepared from solutions containing 40 wt% of PSI, PSII, and PSCIII.
Figure 33: Highest achieved sorption capacities after 30 sec of fibrous sorbents (0.0044g/each) prepared from electrospinning of 20, 30, and 40 wt% solutions of each of the polymers in DMF
Upon initial adsorption of the crude oil onto and into the fibers, desorption of the un-adsorbed oil started to take place on a gradual basis within the following 30 minutes duration of the experiment. This pattern was observed in all experiments. Desorption could be related to the presence of weakly adsorbed layers of oil that were not directly attracted to the fibrous sorbent through the hydrophobic-hydrophobic interaction. Therefore, it could be stated that the high cohesive forces between various hydrocarbons in the crude oil predominated in these externally adsorbed layers, leading to their desorption. In addition, the gradual desorption could be related to the high viscosity of the crude oil. Figure 34 shows the 30 minutes sorption capacities of the oil onto fibrous sorbents of the three polymers at a constant sorbent weight of 0.0044g. These results also imply the percent oil remaining into and onto the fibrous sorbent after 30 minutes of adsorption. A pattern similar to that shown in Figure 33 was observed where the amount of adsorbed oil remaining in the fibrous sorbent was directly related to that initially adsorbed after 30 seconds.
Figure 34: Highest achieved sorption capacities after 30 min of fibrous sorbents prepared from electrospinning of 20, 30, and 40 wt% solutions of each of the polymers in DMF.
It should be mentioned that sorbent loaded with oil was removed from the media after 30 seconds and left for dripping in a petri dish. Therefore, the desorbed oil was dripped in the petri dish, and is was retrieved. This means that the removed oil spill is completely collected despite the desorption of the externally bound layers of oil. The retrieved water-free oil can therefore be recycled. To estimate the extent of retrieval of oil, the following equation was applied:

\[
\% \text{ Retrieval} = \left( \frac{w_f - w_i}{w_i} \right) \times 100
\]

Where:

- \( w_i \) is the sorption capacity (g/g) after 30 seconds (initial)
- \( w_f \) is the sorption capacity (g/g) after 30 minutes (Final)

Figures 35 show the extent of retrieval of crude oil after desorption from the fibrous sorbents of different weights electrospun from solutions containing 20, 30, and 40 wt% of PS I, PS II, and PSCI III. These results indicate that a maximum of 40% oil can be retrieved during the process of its removal from aqueous media. Despite the absence of a direct correlation between the type of polymer, its concentration or the weight of sorbent, a general trend can be derived where PSII sorbents of all percentages showed the highest percent of retrieval followed by PSCI III then PSI sorbents.
Figure 35: Extent of retrieval (%) of ADNOC crude oil adsorbed onto PSI, PSII, and PSIII fibrous sorbents (a) 0.0044 g, (b) 0.0066 g, (c) 0.05 g, and (d) 0.1 g prepared by the electrospin of 20, 30, and 40 wt% solutions of each of the polymers in DMF.
4.3.2 TOTAL Crude Oil

Based on the findings of the sorption of ADNOC crude oil onto PSI, PSII and PSCIII fibrous sorbents, two weights of the sorbent were chosen for further evaluation on their performance on removal TOTAL crude oil from simulated salty water. Those were 0.005 and 0.01 g. As was previously mentioned, TOTAL crude oil was shown to have a close density to that of ADNOC crude oil, but was found to be 20% less viscous. Fluidity of the oil during the sorption experiments is, therefore, expected as compared to that of ADNOC crude oil. Figures 36-38 show the sorption capacities of 0.005 and 0.01 g – sorbents prepared from solutions containing 20, 30 and 40 wt% of PSI, PSII, and PSCIII polymers, respectively. All sorption experiments showed an initial instantaneous sorption onto the fibrous sorbents after 30 seconds of sorption. However, the maximum achieved sorption capacities were inferior to those obtained during the sorption of ADNOC crude oil onto the same sorbents. These results could be related to the difference in viscosity of the oils, hence their variation in fluidity during sorption. Highly viscous ADNOC crude oil was shown to highly adsorb onto the fibrous sorbents. As was mentioned before, viscosity is related to the presence of long chain hydrocarbons in the oil. The higher viscosity of ADNOC crude oil could be related to the presence of higher molecular weight hydrocarbons than those present in the less viscous TOTAL crude oil. This brings in an important hypothesis where higher molecular weight hydrocarbons indicate higher degree of hydrophobicity, which was reflected in higher sorption capacities onto the hydrophobic fibrous sorbent. On the other hand, the low viscosity of the TOTAL oil indicates the presence of lower hydrophobic species, which could strongly explain the lower sorption capacities of this oil onto the fibrous sorbents.
Figure 36: Sorption capacities to TOTAL crude oil of fibrous sorbents (a) 0.005g, and (b) 0.01g prepared from electrospinning of 20 wt% solutions of the polymers in DMF.
Figure 37: Sorption capacities to TOTAL crude oil of fibrous sorbents (a) 0.005g, and (b) 0.01g prepared from electrospinning of 30 wt% solutions of the polymers in DMF.
Figure 38: Sorption capacities to TOTAL crude oil of fibrous sorbents (a) 0.005g, and (b) 0.01g, prepared from electrospinning of 40 wt% solutions of the polymers in DMF.
Figure 39 (a-c) shows a comparison between the highest achieved sorption capacities of the sorbents prepared from 20, 30, and 40% solutions of the three polymers, respectively as a function of the sorbent weight after 30 seconds of sorption. An overall trend can be derived where doubling the weight of the sorbent showed a slight increase in the initial instantaneous sorption capacities in all experiments. On the other hand, there was an insignificant effect of the initial solution concentration, from which sorbents were prepared, on the sorption capacities. Moreover, the effect of molecular weight of the polymer on the sorption capacities was also insignificant.

Upon instant adsorption of the TOTAL crude oil onto the fibers, desorption of the weakly adsorbed oil started to take place during the 30 minutes duration of the experiment. This behavior was observed in all experiments involving TOTAL crude oil and is similar to that shown in the desorption of ADNOC crude oil from the fibrous sorbents. Calculations of percent retention and percent retrieval of the TOTAL oil after 30 minutes are plotted in Figures 40-41, respectively. A direct relationship can be also derived between the remaining oil in the fibrous sorbent and the initially adsorbed oil after 30 seconds. These results also indicate the possibility of retrieving 60% of the adsorbed TOTAL oil. Compared with 40% retrieval of the ADNOC crude oil, the difference could be related to the lower viscosity of the TOTAL oil and the lower extent of initial adsorption with the fibrous sorbents.
Figure 39: Highest achieved sorption capacities capacities to TOTAL crude oil after 30 sec of fibrous sorbents (0.005g & 0.01g) prepared from electrospinning of (a) 20 wt%, (b) 30 wt%, and (c) 40 wt% solutions of each of the polymers in DMF
Figure 40: Highest achieved sorption capacities capacities to TOTAL crude oil after 30 min of fibrous sorbents (0.005g & 0.01g) prepared from electrospinning of (a) 20 wt%, (b) 30 wt%, and (c) 40 wt% solutions of each of the polymers in DMF.
Figure 41: Extent of retrieval (%) of TOTAL crude oil adsorbed onto PSI, PSII, and PSCIII fibrous sorbents (a) 0.005g, and (b) 0.01g prepared by the electrospinning of 20, 30, and 40 wt% solutions of each of the polymers in DMF.
4.3.3 ADCO Crude Oil

Fibrous sorbents prepared from solutions containing 20, 30, and 40 wt% of PSl, PSII, and PSCIII polymers were also used for the sorption of ADCO crude oil. Based on the results shown in Figure 14, ADCO oil is less viscous than both ADNOC and TOTAL crude oils. Its viscosity is around 10% that of the viscosity of ADNOC oil but is closer to the viscosity of TOTAL oil, hence it has more fluidity than both oils. Figures 42-44 show sorption capacities of fibrous sorbents (0.005 and 0.01 g) to ADCO oil. Despite the lower viscosity of the oil than the other oils, it showed an instant adsorption onto the fibrous sorbents within the first 30 seconds of the experiment. This behavior is similar to what was shown with both ADNOC and TOTAL.
Figure 42: Sorption capacities to ADCO crude oil of fibrous sorbents (a) 0.005g, and (b) 0.01g prepared from electrospinning of 20 wt% solutions of the polymers in DMF
Figure 43: Sorption capacities to ADCO crude oil of fibrous sorbents (a) 0.005g, and (b) 0.01g prepared from electrospinning of 30 wt% solutions of the polymers in DMF
Figure 44: Sorption capacities to ADCO crude oil of fibrous sorbents (a) 0.005g, and (b) 0.01g prepared from electrospinning of 40 wt% solutions of the polymers in DMF.
Figure 45 shows highest achieved sorption capacities after 30 seconds of experiment. Values shown in these graphs are closer to those achieved with TOTAL crude oil, where the highest achieved sorption capacity was 68 g/g. Externally adsorbed oil started to desorb from the surfaces of all sorbents within the following 30 minutes of the sorption experiment reaching a plateau after 10 minutes of sorption. This is comparable to the time at which plateau was achieved in desorption of TOTAL crude oil. On the other hand, desorption of ADNOC crude oil took place after ≤ 5 minutes of experiment. This variation is attributed to the difference in viscosity between the three oils. Figure 46 shows the lowest sorption capacities; an indication of the amount of oil remained onto the fibrous sorbent, after 30 minutes of experiment. The amount of oil remained in the sorbent was directly proportional to those initially adsorbed after 30 seconds, showing a similar pattern to what was observed on the other crude oils. As a result, the percent retrieval after 30 minutes was calculated in all experiments, and plotted in Figure 47. A maximum of 48% of ADCO crude oil was retrieved. Compared with a maximum of 60% retrieval extent with TOTAL crude oil, the difference could be attributed to the relatively lower viscosity; hence lower hydrophobicity of the ADCO crude oil than that of the TOTAL crude oil. These findings indicate that initial adsorption of the crude oil could be followed by higher extents of desorption in case of lower viscosity crude oils, as was observed with TOTAL and ADCO oils. On the other hand, higher initial adsorption, as was shown in the experiments involving ADNOC crude oil, was followed by a retrieval extent of 48%, which could be attributed to the higher cohesive forces between the long chain hydrocarbons which highly contribute to the elevated viscosity of the crude oil.
Figure 45: Highest achieved sorption capacities to ADCO crude oil after 30 sec of fibrous sorbents prepared from electrospinning of (a) 20 wt%, (b) 30 wt%, and (c) 40 wt% solutions of each of the polymers in DMF
Figure 46: Highest achieved sorption capacities to ADCO crude oil after 30 min of fibrous sorbents prepared from electrospinning of (a) 20 wt%, (b) 30 wt%, and (c) 40 wt% solutions of each of the polymers in DMF.
Figure 47: Extent of retrieval (%) of ADCO crude oil adsorbed onto PSI, PSII, and PSCIII fibrous sorbents (a) 0.005g, and (b) 0.01g prepared by the electrospin of 20, 30, and 40 wt% solutions of each of the polymers in DMF.
Based on the sorption results of all crude oils with fibrous sorbents, it was observed that on average sorbents prepared from solutions containing 20 wt% of PSII showed the highest sorption capacities among other polymers. Figure 48 shows a comparison between the sorption capacities of the three types of crude oil onto fibrous sorbents fabricated from solutions containing 20 wt% of PSII. Highest achieved sorption values were summarized in Figure 49. It is evident that ADNOC crude oil showed the highest sorption capacities than the two other crude oils. This was attributed to difference in viscosity between the oils, where high viscosity indicates longer chain hydrocarbons, hence higher hydrophobicity and as a consequence higher extent of attraction to the hydrophobic fibrous sorbents. The close sorption capacities of TOTAL and ADCO crude oils on the same fibrous sorbents confirms this hypothesis where both oils were close in viscosity and were both inferior to that of the ADNOC crude oil. It can be also shown in Figure 48 that all crude oils showed a similar plateau after 10 minutes of sorption where desorption of the weakly adsorbed oil was ceased. Figure 50 summarizes the retrieval % of all crude oils onto the PSII fibrous sorbents. The highest retrieval rate was achieved when TOTAL oil was involved.
Figure 48: Comparison between the sorption capacities to ADNOC, TOTAL, and ADCO crude oils of fibrous sorbents (a) 0.005g. and (b) 0.01g. each prepared from electrospinning of 20 wt% solutions of PSII in DMF.
Figure 49: Highest achieved sorption capacities to ADNOC, TOTAL, and ADCO crude oils after 30 sec of fibrous sorbents (0.005g & 0.01g) prepared from electrospinning of 20 wt% solutions of PSII in DMF

Figure 50: Extent of retrieval (%) to ADNOC, TOTAL, and ADCO crude oils of fibrous sorbents (0.005g & 0.01g) prepared from electrospinning of 20 wt% solutions of PSII in DMF
4.4 Effect of Electrospinning Parameters on Sorption of TOTAL Crude Oil on PSII Fibrous Sorbents

In the previous sections, it was shown that polystyrene fibrous sorbents were successfully used to collect three different types of crude oil from simulated salty water media. The main hypothesis behind this high efficiency was attributed to the high surface area of the fibers and their hydrophobic nature. Based on these findings, fine tuning of the characteristics of the fibers produced by electrospinning of 20, 30 and 40 wt% PSI, PSII, and PSCIIP solutions was attempted. The main objective was to study the effect of varying the electrospinning conditions on the performance of the fibers towards the sorption of TOTAL crude oil. Results will be discussed in the following sections.

4.4.1 Effect of Solvent

It should be mentioned that fibrous sorbents evaluated in the previous sections for the removal of ADNOC, TOTAL and ADCO crude oils were prepared by electrospinning solutions of each of the polymers in dimethyl formamide (DMF). This is one of the commonly used solvents for dissolving polystyrene\textsuperscript{136}. Another common solvent; tetrahydrofuran (THF) has been studied as well\textsuperscript{136}. Solvent mixtures based on formulations of DMF and THF were used to dissolve PSI, PSII, and PSCIIP making 20, 30 and 40 wt% solutions thereof, and were electrospun at constant voltage 15KV, feeding rate 10 ml/hr, spinning distance 15cm, humidity (normal) 47%, and needle size 21G. Proportions of DMF and THF in the solvent mixtures are given in Table 4.
Table 4: Composition of solvent mixtures of THF and DMF

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solvent Composition (% by volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>100</td>
</tr>
<tr>
<td>DMF</td>
<td>0</td>
</tr>
</tbody>
</table>

Under these conditions, fibrous sorbents (0.005 g/each) were evaluated for their efficiencies in removing TOTAL crude oil from salty water. Results are shown in Figures 51-53 for fibrous sorbents prepared from solutions containing 20, 30, and 40% of PSI, PSII, and PSCIII, respectively. An overall trend was shown where all fibrous sorbents showed an instantaneous sorption within the first 30 seconds of experiment, followed by a sustained desorption throughout the remaining 30 minutes of experiments. On average, sorbents prepared from pure DMF and 50:50 (DMF:THF) solvents showed the highest sorption capacities achieved after 30 seconds. A close comparison between sorption capacities after 30 seconds of sorbents prepared from pure DMF and DMF:THF (50:50) are shown in Figures 54-55. Sorbents prepared from solutions containing 20 wt% of all polymers showed the highest sorption capacities in both solvents. The highest achieved sorption capacities in these cases reached 80, 55, and 95 g/g for polymers PSI, PSII, and PSCIII dissolved in pure DMF, while those dissolved in DMF:THF (50:50) showed 87, 60 and 84 g/g, respectively.
Figure 51: Sorption capacities to TOTAL crude oil of fibrous sorbents (0.005g/each) prepared by the electrospin of 20 wt% solvent of each (a) PSI, (b) PSII, and (c) PSCIII in various solvent systems.
Figure 52: Sorption capacities to TOTAL crude oil of fibrous sorbents (0.005g/each) prepared by the electrospinning of 30 wt% solvent of each (a) PSI, (b) PSII, and (c) PSCI in various solvent systems.
Figure 53: Sorption capacities to TOTAL crude oil of fibrous sorbents (0.005g/each) prepared by the electrospin of 40 wt% solvent of each (a) PSI, (b) PSII, and (c) PSCIII in various solvent systems.
Figure 54: Highest achieved sorption capacities to TOTAL crude oil after 30 sec of fibrous sorbents prepared by electrospinning of 20, 30, and 40 wt% of (a) PSI, (b) PSII, and (c) PSCIII solutions in 100% DMF
Figure 55: Highest achieved sorption capacities to TOTAL crude oil after 30 sec of fibrous sorbents prepared by electrospinning of 20, 30, and 40 wt% of (a) PSI, (b) PSII, and (c) PSCIII solutions in (50:50)-(THF:DMF)
Correlating these values with the SEM micrographs of these sorbents Figure 56 explains the relatively higher performance of PSI and PSCHIII sorbents where their fiber size was in the range of 1-1.5 mm, while fibers produced from PSII 20% solution showed a higher size range; up to 2.5 mm. The smaller the size of the fibers the higher is their surface area, and consequently this is known to enhance their sorption capacity. The SEM micrographs of PSII sorbents shown in Figure 56 also indicates more surface roughness of the fibers, as compared with sorbents prepared from other polymers. Considering sorbents prepared from other concentrations of the PSII polymer, Figure 57 compared SEM micrographs of sorbents prepared from 20, 30, and 40 wt% of PSII. The decrease in the sorption capacities with increasing the concentration of the solutions from which the PSII sorbents were prepared can be related to the relative increase in the size of the fibers, hence the decrease in the surface area of those fibers and their tendency towards oil sorption. It should be mentioned that surface roughness of the fibers obtained from PSII-20% solutions was not mentioned in the micrographs of sorbents prepared from 30 and 40% solutions in both solvents. These findings indicate an insignificant variation in the sorption capacities of sorbents prepared in both pure DMF and DMF:THF (50:50). Figures 58-9 show the percent retrieval of oil from sorbents of 20, 30, and 40 wt% PSI, PSII, and PSCHIII polymers dissolved in pure DMF and DMF:THF (50:50), respectively. Despite the variable % retrieval with percentage of polymer solution in pure DMF from which sorbents were prepared, sorbents made from solutions in DMF:THF (50:50) showed an increasing % retrieval with increasing the initial concentration of the polymers solutions. This was opposite to the decreasing sorption capacity with increasing the polymer solutions after 30 seconds; shown in Figure 55. This related
to the relative increase in the size of the fibers, hence the decrease in the surface area of those fibers and their tendency towards oil sorption.

Based on the above findings, sorbents prepared from solutions containing 20 wt% of PSl, PSII and PSCI in pure DMF and DMF:THF (50:50) were selected for further investigation of the effect of other electrospinning parameters on their performance in the removal of TOTAL crude oil.
Figure 56: SEM micrographs of fibrous sorbents obtained by electrospinning 20 wt% solutions of PS at different solvent concentration (a) PSI (100%DMF), (b) PSI (50:50, THD:DMF), (c) PSI (100% DMF), (d) PSI (50:50, THD:DMF), (e) PSCI (100% DMF), and (f) PSCI (50:50, THD:DMF)
Figure 57: SEM micrographs of fibrous sorbents obtained by electrospinning of PS at different solvent concentration (a) 20 w% PSII (100%DMF), (b) 20 w% PSII (50:50, THD:DMF), (c) 30 w% PSII I (100% DMF), (d) 320 w% PSII (50:50, THD:DMF), (e) 40 w% PSII I (100% DMF), and (f) 40 w% PSII I (50:50, THD:DMF)
Figure 58: Extent of retrieval (%) of TOTAL crude oil adsorbed onto (a) PSI, (b) PSII, and (c) PSCI fibrous sorbents (0.005g/each) prepared by the electrospin of 20, 30, and 40 wt% solutions of each of the polymers in 100% DMF
Figure 59: Extent of retrieval (%) of TOTAL crude oil adsorbed onto (a) PSI, (b) PSII, and (c) PSCIII fibrous sorbents (0.005g/each) prepared by the electrospin of 20, 30, and 40 wt% solutions of each of the polymers in (50:50)% - (THF:DMF)
4.4.2 Effect of Applied Voltage

Solutions containing 20 wt% of PSI, PSII and PSCI in pure DMF, and DMF:THF (50:50) were electrospun into sorbents at applied voltages of 10, 15, 20, 25 and 30 kV. Fibrous sorbents prepared hereafter were evaluated for their efficiency in removal of TOTAL crude oil. Figures 60-62 show the sorption capacities for sorbents made of PSI, PSII and PSCI polymers, respectively. It should be mentioned that non-fibrous sorbents were obtained at an applied voltage of 10 kV as a result of electrospinning solutions containing 20 wt% of PSI in DMF:THF (50:50) and PSCI in pure DMF and DMF:THF (50:50) solvents. Therefore, their sorption capacities were not considered since the main objective of the work was to evaluate high surface area fibrous sorbents for their performance in removing oil spills.

Results shown in Figures 60-62 indicate a similar pattern to what has been observed before in the sorption experiments of crude oil. An instantaneous sorption took place within the first 30 seconds of the experiment, followed by a slow pattern of partial desorption of the weakly adsorbed oil from the fibers for the remaining 30 minutes of the experiments. The highest achieved sorption capacities after 30 seconds were plotted in Figure 63. An overall trend can be derived where increasing the applied voltage during the preparation of the sorbents led to an overall enhancement in the sorption capacities of the sorbents. Figure 64 shows SEM micrographs of sorbents prepared by electrospinning 20 wt% PSII in pure DMF at 10, 15, 20, 25 and 30 kV. Fibers prepared at 10, 15, 20, and 25 kV showed the same size and size distribution, while deformed fibers were obtained at an applied voltage of 30 kV. Variation in the sorption capacities are, therefore, related to the relative increase in the surface roughness of the fibers with increasing voltage, as shown in
the inserts of the SEM micrographs at different voltages. Figure 65 shows the percent retrieval of the oil after 30 minutes of sorption from all fibrous sorbents. Despite the fact that insignificant correlation could be found between the percent retrieval and the applied voltage, percent retrieval was found to increase with increasing the applied voltage during the preparation of PSII 20 wt% solution. This could be attributed to the initial sorption performance of these samples after 30 seconds of experiment.

As a result of these findings, an applied voltage of 25 kV was selected for the preparation of PSII sorbents from solutions containing 20 wt% in pure DMF solvent. These conditions were maintained for studying the following parameters.
Figure 60: Sorption capacities to TOTAL crude oil of fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSI solutions (a) 100% DMF, and (b) (THF:DMF) (50:50) at different applied voltages
Figure 61: Sorption capacities to TOTAL crude oil of fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions (a) 100% DMF, and (b) (THF:DMF) (50:50)% at different applied voltages
Figure 62: Sorption capacities to TOTAL crude oil of fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSCIII solutions (a) 100% DMF, and (b) (THF:DMF) (50:50)% at different applied voltages
Figure 63: Highest achieved sorption capacities to TOTAL crude oil after 30 sec of fibrous sorbents prepared by electrospinning of of 20 wt% of (a) 100% DMF. (b)THF:DMF-(50:50) solutions of each of the polymers at different applied voltages
Figure 64: SEM micrographs of fibrous sorbents obtained by electrospinning 20 wt% solutions of PSII in DMF at different applied voltages (a) 10kV, (b) 15kV, (c) 20kV, (d) 25kV, and (e) 30kV
Figure 65: Extent of retrieval (%) of TOTAL crude oil adsorbed onto fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions (a) 100% DMF, and (b) (THF:DMF) (50:50)% solutions of each of the polymers at different applied voltages.
4.4.3 Effect of Feeding Rate

Fibrous sorbents were prepared at 25 kV from solutions containing 20 wt% of PSII in pure DMF, while varying the feeding rate during electrospinning at 1, 5, and 10 mL/hr. Sorbents prepared here with were evaluated for their performance in removing TOTAL crude oil. Results are plotted in Figure 66. All sorbents showed a typical sorption pattern with high instantaneous sorption capacities of 29, 27, and 50 g/g for sorbents prepared at feeding rates of 1, 5, and 10 mL/hr, respectively. All sorbents also showed a sustained slow-rate desorption of the weakly adsorbed oil with time during the following 30 minutes of experiment. SEM micrographs of these sorbents are shown in Figure 67, where sorbents prepared at different feeding rates showed fibrous morphology. However, sorbents prepared at a feeding rate of 1 mL/hr showed inhomogeneous fiber size distribution and fibers were distorted. Surface cracks are evident on the fibers in the insert of this micrograph. On the other hand, sorbent prepared at a feeding rate of 5 mL/hr showed the presence of beads as well as inhomogeneous size distribution of the fibers. Beaded morphology provides sites of low surface area which could be considered the reason for the decreased oil sorption in sorbents prepared at 5 mL/hr feeding rate, while un-beaded slightly cracked fibers (prepared at a feeding rate of 1 mL/hr) showed moderate sorption capacities. In contrast, sorbents prepared at a feeding rate of 10 mL/hr showed a non-beaded fibrous morphology with a homogeneous size distribution. This morphology explains the high performance of those sorbents prepared at 10 mL/hr as compared with sorbents prepared at other feeding rates. In addition, sorbent prepared at a feeding rate of 10 mL/hr achieved a 56% retrieval after 30 minutes Figure 68. Based on these findings, a feeding rate of 10 mL/hr was selected as an optimum parameter
for the following set of experiments towards the fabrication of fibrous sorbents by electrospinning.
Figure 66: Sorption capacities to TOTAL crude oil of fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions at feeding rate (1ml/hr, 5ml/hr, and 10ml/hr) in DMF.
Figure 67: SEM micrographs of fibrous sorbents obtained by electrospinning 20 wt% solutions of PSII in DMF at feeding rate at (a) 1ml/hr, (b) 5ml/hr, and (c) 10ml/hr
Figure 68: Extent of retrieval (%) of TOTAL crude oil adsorbed onto fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions at feeding rate (1ml/hr, 5ml/hr, and 10ml/hr) in DMF.
4.4.4 Effect of Distance

Figure 69 shows sorption capacities of sorbents prepared at an applied voltage of 25 kV, a feeding rate of 10 mL/hr of 20 wt% solution of PS II in pure DMF, and electrospinning distances of 10, 15 and 20 cm. Increasing the spinning distance is known to elongate the travel pathway of the fibers towards the grounded collector, hence more thinning of the fibers. Therefore, size of the fibers should decrease with increasing the spinning distance. However, the SEM micrographs shown in Figure 70 do not support this concept. An insignificant change in the size of the fibers was observed. In addition, more beading was shown in the microstructures of the sorbents prepared at spinning distances of 10 and 20 cm. On the other hand, a homogeneous non-beaded morphology was achieved when sorbents were prepared at a spinning distance of 15 cm. The presence of beads indicates a lowering in the surface area of the fibers, which explains the low sorption capacity of sorbents prepared at a spinning distance of 10 cm. In contrast, sorbents prepared at a spinning distance of 20 cm showed the highest initial sorption capacity after 30 seconds despite the fact that beads were also found in the micrograph of this sorbent. This could be related to the homogeneous distribution of the size of the fibers in the sorbent. The absence of beads, and the homogeneous size distribution of the sorbent prepared at a spinning distance of 15 cm suggested this distance to be selected as an optimum spinning distance for the rest of the optimization process. Figure 71 shows a linear increased pattern for the percent retrieval of the oil with increasing the spinning distance. This pattern could be related to the difference in the initial instantaneous sorption capacities of all samples.
Figure 69: Sorption capacities to TOTAL crude oil of fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions at distance (Needle to collector) at 10, 15, and 20cm in DMF
Figure 70: SEM micrographs of fibrous sorbents obtained by electrospinning 20 wt% solutions of PSII at distance (Needle to collector) at (a) 10 cm, (b) 15 cm, and (c) 20 cm
Figure 71: Extent of retrieval (%) of TOTAL crude oil adsorbed onto fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions at distance (Needle to collector) at 10, 15, and 20 cm in DMF.
4.4.5 Effect of Humidity

In the presence of humidity, electrospinning was previously shown to produce fibers with surface roughness and internal porosity. The main objective of studying the effect of humidity was to see whether or not created surface roughness would affect the sorption capacities of the produced fibrous sorbents at different degrees of relative humidity. It should be mentioned that humidity was changed inside the electrospinning chamber by saturating it with water vapor before electrospinning was to be carried out.

Figure 72 shows the sorption capacities of fibrous sorbents formed under the previously optimized conditions and under the effect of various degrees of humidity. Typically to what was observed in the previous sorption experiments, all sorbents showed instantaneous sorption capacities of various extents depending on the degree of humidity under which sorbents were prepared. The overall sorption capacities decreased with increasing the degree of humidity. Figure 73 show the SEM micrographs of sorbents prepared under various degrees of humidity. An overall increase in the average size of the fibers with increasing the degree of humidity can be seen. Average fiber size of 2, 3, and 5.7 μm were calculated for the fibers electrospun at 47, 70-88, and 89-99% relative humidity, respectively. These findings indicate a possibility of impregnation of the water of humidity within the fibers during their formation. In order to confirm this assumption, SEM was carried out at a high magnification of the fibers created under 70-88, and 89-99% relative humidity; Figure 74. Both micrographs showed a maximum degree of internal porosity and a less rough surface morphology.
Figure 72: Sorption capacities to TOTAL crude oil of fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions at different Humidity % at 49% -Normal, (70-88)%, and (89-99)% in DMF
Figure 73: SEM micrographs of fibrous sorbents obtained by electrospinning 20 wt% solutions of PSII at different Humidity % at (a) 49% - Normal, (b) (70-88)%, and (c) (89-99)% in DMF
Figure 74: High magnification SEM micrographs of fibrous sorbents obtained by electrospinning 20 wt% solutions of PSII at different Humidity % at (a) (70-88)%, and (b) (89-99)% in DMF
These features were only observed when the relative humidity during preparation was increased to the said values. These micrographs, therefore, confirm the assumption that water of humidity was impregnated within the fibers during their formation and as a result of its evaporation porous fibers were created. The presence of increased porosity was expected to increase the overall surface area of the fibers, hence reflected on an increased sorption capacity. The opposite was found where increased degree of relative humidity produced fibers that showed a decreased sorption capacity. These results are attributed to the following two observations: First, the surfaces of the fibers were not as porous as their interiors, and should therefore not be expected to have elevated sorption capacities. Second, and during the sorption experiments of the sorbents produced at higher degrees of humidity, it was observed that brittleness of the fibers increased with increasing the degree of humidity. Moreover, fibers were shown to breakdown after mixing with the oil, leading to a loss of the fibrous architecture of the sorbents. These observations, therefore, explain the decrease in the sorption capacity of the sorbents with increasing the degree of relative humidity under which fibers were prepared. Figure 75 shows the percent retrieval of the oil after 30 minutes of sorption within the porous sorbents created at different degrees of relative humidity. Under normal humidity conditions, 60% of the oil was retrieved. This high value was in accordance of its sorption behavior where a continuous desorption of the weakly adsorbed oil was observed throughout the 30 minutes of the experiment. On the other hand, the decreased percent retrieval of the sorbent prepared under 70-88% relative humidity is attributed to the low initial adsorption after 30 seconds. In contrast, the highly increased percent retrieval (> 70%) of the
fibers prepared at the highest degree of relative humidity could be attributed to the low mechanical stability of the fibers and their breakdown during the sorption experiments; hence oil was mechanically retrieved from the fibers. In conclusion, a normal degree of relative humidity (47%) was selected as an optimum value for the preparation of sorbents.
Figure 75: Extent of retrieval (%) of TOTAL crude oil adsorbed onto fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions at different Humidity % at 49% -Normal, (70-88)%, and (89-99)%) in DMF.
IV.4.6. Effect of Needle Diameter

Previous studies showed that needle diameter has an important effect on the diameter of the fiber emerging from the needle. In the market, syringe needles are known by gauge number where increasing the gauge number decreases the internal diameter of the needle. In the current study, needles with 4 various gauges were studied. Those were 18, 21, 23, and 29. Table 5. shows the nominal internal diameter of needles.

Table 5. Gauge number - nominal internal diameter conversion of needles used in the current study

<table>
<thead>
<tr>
<th>Gauge number</th>
<th>18</th>
<th>21</th>
<th>23</th>
<th>29</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Internal Diameter (mm)</td>
<td>0.838</td>
<td>0.514</td>
<td>0.337</td>
<td>0.184</td>
</tr>
</tbody>
</table>

Fibrous sorbents prepared using these needles were investigated for their sorption capacities. Results are shown in Figure 76. All sorbents showed a typical pattern of sorption with time starting with initial instantaneous sorption capacities after 30 seconds of sorption, followed by a slow desorption pattern throughout the remaining 30 minutes of the experiments. Figure 77 shows SEM micrographs of fibrous sorbents prepared using these different gauge needles. It is evident from these micrographs that the average size of the fibers decreased by increasing the gauge number of the needles, which is in accordance with the conversion data shown in Table 4. However, more beads were observed by increasing the gauge number, as pointed by arrows in the micrographs of fibrous sorbents electrospun using 23 and 29.
gauges. On the other hand, fibrous sorbents prepared using gauge number 21 showed un-beaded fibers with a homogeneous size distribution, which was reflected on a relatively high sorption capacity; Figure 76.
Figure 76: Sorption capacities to TOTAL crude oil of fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions at different Needle diameters at 18G, 21G, 23G, and 29G in DMF.
Figure 77: SEM micrographs of fibrous sorbents obtained by electrospinning 20 wt% solutions of PSII at different Needle diameters at (a) 18G, (b) 21G, (c) 23G, and (d) 29G in DMF.
In addition, fibrous sorbents prepared using gauge 21 showed the highest percent retrieval (60%) among all investigated fibrous sorbents; Figure 78. The low sorption capacity of the fibrous sorbents prepared using needles of other gauges was also reflected in low retrieval percentages within the range of 33-37%.
Figure 78: Extent of retrieval (%) of TOTAL crude oil adsorbed onto fibrous sorbents (0.005g) prepared by the electrospinning of 20 wt% PSII solutions at different Needle diameters at 18G, 21G, 23G, and 29G in DMF.
This study investigated the potential of using high surface area fibrous sorbents in the removal of crude oil spills from salty water media. Three types of polystyrene with various molecular weights were investigated. Those were PSI (100,000), PSII (350,000), and PSIII (225,000). PSIII was prepared by recycling polystyrene foam and coffee cups made of the same material. Three types of crude oils were investigated. Those included: ADNOC, TOTAL and ADCO with various viscosities. Polymeric solutions containing 20, 30, and 40% of each of the polymers were prepared by dissolving the corresponding amount of the polymer in THF, DMF or a combination of the two solvents. Polymeric solutions were electrospun into microfibrous sorbents, which were then characterized for their microstructure using SEM technique and porosity as well as pore size distribution using $N_2$-adsorption technique. Sorbents were evaluated for their efficiency in the removal of crude oil spills from simulated salty water media using a standardized ASTM method.

Results showed a strong correlation between the characteristics of the fibrous sorbents in terms of the size, size distribution and morphology of the fibers, and their sorption capacities of the crude oils spills. Results also confirmed the possibility of retrieving around 70% of the collected crude oil spills with a confirmation of absence of water in the adsorbed oil. Based on these findings, detailed optimization experiments were carried out, where the effects of varying the electrospinning conditions on the characteristics of the fibers and consequently the sorption performance of the fibrous sorbents prepared thereafter, were studied. These factors included: solvent in which polymer solutions were prepared, applied voltage, feeding rate, spinning distance, humidity inside the electrospinning chamber, and spinneret
(needle) gauge. The main objectives were to obtain bead-free fibrous sorbents with unified size distribution, pore size distribution, and consequently consistent sorption capacities.

Correlations were drawn between each of the electrospinning parameters and the sorption capacities and electrospinning conditions were optimized at the following:

1. Pure DMF and DMF:THF (50:50), as proper solvents
2. 25kV as an applied voltage
3. 10 ml/hr as a feeding rate
4. 15 cm as a spinning distance
5. Normal relative humidity (47%) inside the electrospinning chamber
6. 21 G (0.514 mm) as a gauge of the spinneret (needle) used in the electrospinning

Based on the overall findings of the current work, a high potential for the removal and retrieval of the crude oil spills was proven. In addition, the study showed the possibility of solving three environmental problems via the recycling of polymeric waste, removing crude oil spills, and retrieving the collected oil spills. The author, therefore, strongly recommend the continuation of these studied with more efforts towards the maximization of the efficiency of removal and retrieval of crude oils pills from aqueous and non-aqueous as well as dry media.

Our future plane related to this study, is to scale-up the electrospinning of the PS microfibers for possible testing under ‘real life’ conditions. We are also interested in exploring ways to possibly recycle or regenerate the sorbed oil from the PS fibers.
In addition, we would like to test the possibility of using our PS microfibrous sorbents for oil spill clean up in non-aqueous environment such as beaches.

Finally, it will be nice to study the mechanism for oil sorption onto PS microfibrous sorbents.
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