

QATAR UNIVERSITY

COLLEGE OF ARTS AND SCIENCES

PREPARATION AND CHARACTERIZATION OF POLYMERIC FOAMS FOR

REMOVAL OF FREE OIL FROM WATER

BY

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ABSTRACT

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Title: PREPARATION AND CHARACTERIZATION OF POLYMERIC FOAMS FOR REMOVAL OF FREE OIL FROM WATER

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Development of polymeric foams for removal of oily pollutants (spills) from water is a key target of this thesis. Pollutants occur in the form of free oil (floating on the water surface) or oil/water macroscopic, non-stabilized mixtures. The foams designed for an efficient oil removal should have a high sorption capacity for oil but low affinity to water. This is insured by either chemical composition of polymeric materials themselves (e.g. polyolefines), or by post chemical and physical treatment of suitable materials (polyurethane and melamine foams) reducing their hydrophilicity and thus water sorption capability. In this thesis, two different strategies have been chosen. Firstly, low molecular oligomer (paraffinic) material was used for synthesis of foamy structures through crosslinking and foaming of an original material. This material, arbitrarily marked as Qwax is the waste material formed during polyethylene synthesis, and it was offered by QAPCO. The foamy, elastic structures were prepared through crosslinking by dicumyl peroxide and foaming by 1,1'-azobiscarbamide. The target of this research was a preparation of porous, hydrophobic and hydrophilic material with an appropriately high sorption ability for oil and low sorption of water, suitable for removal of free oil from water surfaces. The porosity of foam determined by computer micro-tomography was found of 58.9 %, and the bulk density of 0.42 g.cm⁻³

³. The hydrophobic character of foam was observed under both air and oil as the contact angle values of water are 114° and 128°, respectively. On the other hand, super oleophilicity was observed for Qwax foam under both air and water as the contact angle values were 0°. The foams are thermally stable up to 360°C. Secondly, commercial melamine foam, commonly used for cleaning was modified by graphene oxide to enhance oleophilicity of material and, particularly reduce its hydrophilicity. Sorption ability as well as reuse of both foams for different type of oil (crude oil, diesel oil, and motor/engine oil) was studied.

DEDICATION

*This work is dedicated to my family for the support, you have made me stronger
better, and more fulfilled than I could have ever imagined.*

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Table of content

DEDICATION	v
ACKNOWLEDGMENTS	vi
Table of content	vii
List of tables.....	x
List of figures.....	xi
Chapter 1: INTRODUCTION.....	1
1.1 Oil spills	1
1.2. The needs of solution for water treatment.....	1
1.3 Research objectives	2
Chapter 2: LITRATURE REVIEW	4
2.1 Removal of free oil from water in general	7
2.2 Removal of free oil from water by sorbents.....	8
2.3 Removal of free oil from water by polymeric foams	8
2.4 Polyolefin based foams	10
2.5 Materials for oil sorbent based on the chemical composition.....	11
2.5.1 Natural organic and inorganic sorbents	11
2.5.2 Synthetic sorbents.....	11
2.5.3 Carbon and carbon nano tube-based sorbent.....	12
2.5.4 Graphene and graphite-based sorbent.....	12

2.5.5 Polymeric sorbents	13
2.5.6 Oleophilic porous absorbent.....	14
2.5.7 Polyolefin based absorbent.....	14
2.5.8 Recycled waste as sorbent for oil	15
Chapter 3: EXPERIMENTAL WORK.....	17
3.1 Materials.....	17
3.2 Viscosity of oils.....	18
3.3 Sample preparation.....	19
3.3.1 Preparation of Qwax foam.....	19
3.3.2 Determination of gel content in crosslinked samples.....	22
3.3.3 Preparation of melamine foam treated with graphene oxide.....	24
3.4 Characterization techniques	25
3.4.1 Surface wettability	25
3.4.2 Surface Morphology Analysis	27
3.4.3 Thermogravimetric analysis (TGA)	28
3.4.4 Porosity analysis, CT analysis	29
Chapter 4: RESULTS AND DISCUSSION	30
4.1 Qwax foam.....	30
4.1.1 Morphological characterization (SEM image) of Qwax foam	30
4.1.2 Thermal stability of Qwax foam.....	31

4.1.3 Surface wettability (contact angle) of Qwax foam	32
4.1.4 CT analysis for Qwax foam.....	33
4.1.5 Kinetics of absorption of Qwax foam.....	34
4.1.6 Reusability of Qwax foam.....	38
4.2 Neat melamine (ME) and polyurethane (PU) foams compared to Qwax foam .	40
4.2.1 Comparison of multiply sorption ability for melamine (ME), polyurethane (PU) and Qwax foam.	40
4.3 Melamine foam treated with graphene.....	45
4.3.1 Morphological characterization (SEM image) of neat ME foam and ME foam treated with graphene.....	45
4.3.2 Surface wettability (contact angle) of neat ME foam and ME foam treated with graphene	46
4.3.3 Sorption kinetics and oil absorption capacity of ME foam treated with graphene.....	47
4.3.4 Reproducibility and multiply cycling sorption ability of ME foam treated with graphene	49
Chapter 5: CONCLUSION.....	53
REFERENCES	55

List of tables

Table 1: Materials used and their basic properties	17
Table 2: Viscosity of Diesel, Crude and Engine oil determined at 21°C	19
Table 3: Preparation of Qwax foam according to the following ratios	21
Table 4: Selected properties of Qwax foam	23
Table 5: Results from 3D image analysis of Qwax foams	34
Table 6: Parameters of FL-LDF, and power law models	36
Table 7: The parameters characterizing sorption ability of the foam during four sorption/desorption cycles	39
Table 8: Sorption capacity of neat PU and ME foam	42
Table 9: The parameters characterizing sorption ability of MA, PU and Qwax foam	43
Table 10: Experimentally sorption parameters for neat ME foam in water	43
Table 11: Experimentally sorption parameters for neat PU foam in water	44
Table 12: Sorption capacity of neat ME foam	48
Table 13: Sorption capacity g/g of ME foam with graphene (G) in crude oil, engine oil, diesel oil, and water	49
Table 14: Experimentally sorption parameters for ME foam in crude oil	50
Table 15: Experimentally sorption parameters for ME foam in diesel oil	51
Table 16: Experimentally sorption parameters for ME foam in engine oil	51

List of figures

Figure 1: Different types of oil sorbent, such as rolls, pillow, granules, and pads	12
Figure 2: Images of tested oils	18
Figure 3: Viscometer, SV-10 series	19
Figure 4: The dependence of gel content in crosslinked Qwax on peroxide concentration	20
Figure 5: Preparation of Qwax foam using hot plate and mounting press.....	22
Figure 6: Extraction experiment using xylene	24
Figure 7: Preparation of melamine foam treated with graphene oxide.....	25
Figure 8: Different contact angle on a solid surface, representing the interaction	26
Figure 9: Contact angle goniometer, OCA system, and contact angle measurement under diesel oil condition.....	27
Figure 10: SEM device, and simplified illustration of the SEM mechanism	28
Figure 11: Thermogravimetric analyzer (TGA)	29
Figure 12: SEM image for Qwax foam.....	31
Figure 13: TGA curve for neat Qwax and Qwax foam; shows polymer degradation .	32
Figure 14: Water and oil contact angle values for Qwax foam	33
Figure 15: Space cross sections and 3D model of the foam sample Q-Wax. Size of sample 5,5 mm (diameter), 6 mm (height)	34
Figure 16: Absorption capacity (S_w) of foam for diesel, motor and crude oil.....	35
Figure 17: Photographs and SEM micrographs of MA (A), PU (B), and Qwax (C) foams used for the sorption test.	41
Figure 18: Mass of absorbed water for both melamine and polyurethane foams.....	42
Figure 19: Mass of absorbed crude oil for both foams melamine and polyurethane...	42

Figure 20: Water contact angle on neat PU foam under air, oil, and oil contact angle under water.....	44
Figure 21: SEM image for neat ME foam	46
Figure 22: SEM image for ME foam treated with graphene	46
Figure 23: Water and oil contact angle values for ME foam treated with graphene ...	47
Figure 24: Mass of absorbed oil and water for neat ME foam	48
Figure 25: Mass of absorbed oil and water for ME foam treated with graphene	49
Figure 26: Cyclic foam average absorption capacity for crude, engine, and diesel oils	52
Figure 27: Cyclic ME foam treated with graphene (absorption-squeezing for crude, engine, and diesel oil)	52

Chapter 1: INTRODUCTION

1.1 Oil spills

Oil spills can be defined as the discharge of liquid petroleum hydrocarbons into the environment, and particularly within aquatic and marine systems[1]. Several different scenarios can lead to crude oil spills accidents, such as spills from a tanker or pipeline carrying crude oil into the ocean, or from an offshore platform[2], [3]. Some oil spills are not accidents as they can incidents of anthropogenic misconducts in disposing. Unfortunately, the oil spills incidences are on the rise and their occurrence started to become frequent. Some of the famous accidents include but not limited to the Amoco Cadiz, in 1978[4], the Exxon Valdez oil spill in Alaska in 1989[5] , Gulf war marine oil spills[6], The Erika oil spill in 1999[7] , Aegean Sea oil leak at Galicia in Spain[8], The Prestige in Spain2002[9]; and Deepwater Horizon in the French coast in 2010[10]–[13]. Other causes of oil spills other than accidents could be from cleaning of tanks on oil platforms, refineries, or ocean-going ships[14][15]. After washing up on rocky shorelines and open and protected sandy beaches, the oil either settles to the bottom of the ocean or is carried away by the currents to be eventually deposited in deeper or shallower waters. When oil is spilled, it can seep into the hair and feathers of birds and mammals, weakening their capacity to protect themselves from the elements and making them prone to hypothermia and suffocation[16]–[18]

1.2. The needs of solution for water treatment

Almost everywhere in the planet, there is a plentiful supply of water. However, not all the water available naturally can be used for our daily activities[19]. Most of the water we use in our daily lives is drawn from rivers, lakes, and other sources of surface water[20]. However, our water sources are becoming increasingly polluted due to a lack of general attention and proper protection and treatment mechanisms. A growing disparity exists between the available public financing and the measures required to

implement the number of water pollution solutions which could be challenging in solving a crucial problem.

Numerous water treatment media processes are required to purify the water so that it is safe to consume. Contaminants and unwanted components are removed from water, or their concentration is reduced so that the water is fit for its intended usage[21]. For human health, this treatment is essential for the benefit of both drinking and irrigation. In addition to reducing or eliminating contaminants like pesticides, organic matter, and other pollutants from the water, water purifiers also remove chlorine, which can degrade the taste and odor of the water[22].

Methods for removing impurities from drinking water include physical filtration[23], sedimentation[24], chemical processes like chlorination[25] and UV light[26], and biological processes like sand filters and active carbon[27] [28] For both industrial and home water and wastewater treatment, there is a growing demand for ecologically friendly, sustainable techniques that are also cost-effective[30][31], [32].

1.3 Research objectives

The key target of this thesis is a development of suitable polymeric sorbents with high affinity to oil and suppressed affinity to water for a potential applicability as sorbents of oil spills. There are two strategies how to design such type of materials. Firstly, oleophilicity and hydrophobicity can be a consequence of a chemical composition of a material. Common examples are hydrocarbons (polyolefines and paraffin waxes). Secondly, a required wettability can be introduced to materials by additional treatment in order to change an inherent wettability given by chemical composition by various chemical and/or physical treatments. For example, polyurethane and melamine foams have excellent sorption ability for both oils and water. Maintaining their oleophilicity, and suppression hydrophilicity we can get suitable sorbents for oil spills removal.

In this thesis, the research objectives are defined as follows:

- i.) The synthesis of hydrocarbon-based oil sorption materials. The preparation will be based on crosslinking and foaming of paraffinic waste (Qwax) obtained from QAPCO, what is a waste material formed during synthesis low density polyethylene. This material will be transformed into porous structure with sufficient sorption ability for oils, and low/negligible sorption for water.
- ii.) The modification of wettability of commercial melamine foams. This type of foam has high sorption ability for both oil and water. The treated foams should possess high oleophilicity and hydrophobicity. Hydrophobicity will be insured by a treatment with graphene oxide and silicon rubber.

Chapter 2: LITRATURE REVIEW

The sources of oil and grease are various. The contamination of environment by the discharge of a liquid petroleum, known as an oil spill, is an accidental, negative consequence of oil and gas processing and transport, such as a tanker or pipeline carrying crude oil or an offshore platform may spill it into the ocean[33]. Large amount of oily polluted wastewater comes also from petrochemical industry, metal processing, food industry, and households[34]. In all these cases, the efficient treatments, meaning a removal of O&G from water under requested limit is needed. In very general case it can be said that the approaches for a removal of O&G from water depend on the composition and morphology of water/oil systems as well as on a magnitude of treated volumes, and targeted purity. The morphology of water/oil systems primarily determines the treatment strategy. According to the most commonly cited classification introduced by Patterson[35] and Rhee[36], which is based on the droplets' size, the oil in water can occur as i.) free oil, mostly floated on the water surface (droplets' diameter range $> 15 \mu\text{m}$, ii.) dispersed oil $20\text{-}150 \mu\text{m}$, iii.) emulsified oil ($< 20 \mu\text{m}$), and iv.) soluble or dissolved oil ($< 5 \mu\text{m}$).[33], [35], [36] In fact, if time factor is taken into account, a free oil is almost always formed as a final stage of intrinsic or induced de-emulsification processes in oil in water (o/w) emulsions and mixtures because they are not thermodynamically stable, only kinetic stable in some extent, and this stability is perturbed over time leading to the free oil formation through different mechanisms such as coalescence and coagulation.[37] Various routes have been invented and practically used for free oil removal such as mechanical, chemical, thermal, and biological methods.[38], [39] Here, we briefly highlight oil separation based on sorption processes, which is one of the most traditional routes of water treatment on one hand, but permanently attract an attention of scientific community focused on improvement

of sorption ability, utilization of natural and plastic waste, an improvement of sorbents' reuse, recycling or safer disposal, as well as an integration of sorbets into complex apparatuses. The utilization of sorbent materials is a suitable approach for removal of free oil from water surface, particularly if oil layer is thin and spread at large area, so mechanical removal cannot be effectively applied. Powdered sorbent media involve inorganic porous materials (ash, talc, clay, silica aerogel, *etc.*)[40], [41], and organic natural materials (agricultural waste, cotton mats, wood), which are mostly cheap and easily available on the one hand, but they possess a low sorption ability, and limited possibility for oil removal (recovery) what contributes to the accumulation of solid waste [42]. From this reason, new sorbent media have been developing over last decades, and polymeric sorbents belong to the most prospective ones due to their high sorption ability, easy synthesis and tuning of surface properties, possibility of oil recovery, and relatively low price [43]. Oil can be captured by sorbents on their surface, mostly having high surface porosity increasing a special surface area (adsorption), and in their bulk structure (absorption)[43]. Bulk structure is composed by a material itself (matrix) and internal pores formed by air (foams, sponges). Materials, which absorb oil (or any other liquid) in their bulk can swell, if liquid is mostly localized within a solid matrix, or maintain their original volume if liquid occupy only empty space (pores) within a structure. Nonswellable, highly porous foams (e.g., polyurethane (PU), melamine (MA),) are most common polymer structures employed for free oil removal. PU and MA foams attract particular interest due to very high porosity (95 - 99 vol.%), mechanical (compression, bending), and thermal stability, worldwide availability (common PU and MA foams used for cleaning are available in any shop), a simple use and low price[44], [45]. MA and PU foams are thermosetting materials, which do not swell when absorb liquids due to their highly cross-linked structure.[44], [45]. These

foams can be also easily chemically and physically modified in order to tune their wettability[46]. MA and PU foams strongly absorb both oils and water, what is not favorable for practical use, so suppression of water sorption through hydrophobic treatment on the surface or in the bulk is an essential requirement. A comprehensive review concerned various aspect of MA and PU foams modification, utilization and recycling was published very recently. Except surface treatment, a pore size, and pores' connectivity play considerable role in the rate of oil sorption.[46] This problem is much less studied unlike physical and chemical treatments of foams regarding their wettability.

Among other common polymeric sorbents belong polymeric fibers (e.g. polypropylene, polystyrene),[47], [48] and polydimethylsiloxane.[49], [50]. Melt-blown polypropylene (PP) pads and booms[51] are the most commonly used polymeric oil sorbent materials, adsorbing oil within their interstices via capillary forces.

Another group of polymeric materials are crosslinked elastomers (e.g. styrene-butadiene-styrene copolymer, butyl rubber),[52], [53] and thermoplastics, which are, unlike MA and PU, inherently hydrophobic and thus need not to be (but may be) additionally hydrophobised. These materials, dependently on their composition, porosity, degree of crosslinking can absorb significant amount of oil undergoing swelling of their structure. Particularly interesting are specially designed polyolefin-based absorbents synthesized by olefin polymerization from suitable vinyl monomers having high porosity, an ability to swell, and natural hydrophobicity and olephilicity[54]. Nam *et al.* recently published a set of papers related to a synthesis, characterization, and large-scale application of interlaced polymer network sorbents (called i-Petrogel).[54]–[59]. Two grades of polyolefin-based materials were investigated, namely semicrystalline poly(ethylene-co-1-octene) that is commonly

known as Linear Low-Density Polyethylene (LLDPE) with low and cross-linked amorphous copolymer poly(1-decene-co-divinylbenzene), marked as x-d-DVB. Whereas the former due to crystalline domains, which work as physical cross-links, mostly swells in organic solvents (at room temperature), the latter must be chemically cross-linked to suppress its dissolution. Sorption ability of those materials depend on crosslinking density, and the molecular weight between cross-links. Obviously, physical parameters of tested oils) molar mass, density, viscosity, surface tension) also play significant role, so low molecular toluene, or hexane induce much higher swelling than for instance motor oil or crude oil. It was also demonstrated that absorption capacity, as well as rate of sorption of various LLDPE grades is inversely proportional their density, melting temperature, and density because such materials display less compact (more loose) morphology resulting in shorter diffusion path for molecules of oil [54]–[59] .

2.1 Removal of free oil from water in general

It becomes problematic when a free oil is floating above or underwater. Since it's inevitable, it becomes a necessity to treat the oily wastewater[60]. Therefore, methods have been developed and optimized over the past 70 years for the removal of free oil from water. There are some common or traditional methods to remove free oil from water such as mechanical devices that include skimmers and booms[61], textiles[62], foams[63], and sponges[64]. Nevertheless, these options have downsides such as the required energy and pressure in mechanical devices and the poor absorption textiles, foams, and sponges. In addition, they are not easy to recycle, dispose, nor biodegrade. Other recent progress and research direction include meshes and membranes, fabrics and nanofibers, 3D porous materials and micro-nanoparticles[65].

2.2 Removal of free oil from water by sorbents

A sorbent is a material that is used to absorb or adsorb liquids or gases and usually in the water purification field it's made of fibers and more precisely natural fibers[66]. In a technical review paper from Florida, sorbents are identified based on three bases: 1) organic 2) inorganic 3) synthetic. In addition, they are classified as not the main clean up technique for huge spills. Instead, it is the final step or used for small spills[67]. Sorbents studies for oil spills or free oil removal have extended and branched as it became a hot area of research due to the efficiency of the sorbents[68]. The modification of the sorbents and their research are based on two criteria: 1) modification of the hydrophobicity of the fibers 2) biodegradability and disposal methods of the sorbents[69].

2.3 Removal of free oil from water by polymeric foams

Nowadays, there are many synthetic and natural clean up methods such as polymeric foams absorbents[70]. Melamine (MA) foams is a formaldehyde- melamine sodium bisulfite copolymer[71]. Melamine foams has many physical properties such as low flame and smoke ability which prevent it from being a fire hazard[72]f. Also, it has good absorbent capacity, feasible and it has a high demand because of it efficient to remove oils from wastewater. Some studies shown that the advantages of zinc oxide (ZnO) produced by atomic layering deposition with carbon moieties hybridization it shows decrease in wettability which mean a perceivable hydrophobicity. So, it will turn the melamine foam from a hydrophilic polymeric foam into a strongly hydrophobic oil absorbent. The excellent absorbents capacity of melamine foam is now turning into an excellent hydrophobic oil absorbent[73]. Another type of sponge is polyurethane (PU) foam which is widely used cost effective sorbent because of its high thermal and oxidation stability, and mechanical performance [74]. Furthermore, some studies shown that PU foams having tailored wettability (superhydrophobicity and

superoleophilicity) represents an effective way to design promising material for oil/water separation[75].

Melamine resin, a thermosetting polymer, is used to make melamine foam[76]. During the processing, a reaction of cross-linking takes place. Melamine resin is colorless, clear, and stable when heated in boiling water[77]. All the resin's properties are self-extinguishing as well as arc-resistant and mechanically sound. By adding blowing agents and other elements to the melamine resin composition, melamine foam is created[71].

A variety of abrasive cleaner sponges use melamine foam as an active ingredient. Due to its superior sound absorption, thermal insulation, and low weight, it is also widely utilized in bullet trains as the primary sound and thermal insulation material.

An excellent substrate for further treatment to produce materials with tailored surface wettability, melamine foams are well-known 3D porous materials that are inexpensive and easy to come by being able to employ recycled items makes them an excellent choice for oil absorption due to their high elasticity and mechanical durability[78][79].

Polyurethane foams include sponge designed for everyday use in addition to more sophisticated synthetic foams, are noted for their high polar and unipolar liquid sorption capabilities[80]. A whole host of water, oil, and their combinations can be absorbed by commercial sponges, which makes them a popular cleaning tool for many industries.

By virtue of their balanced wettability, these sponges don't preferentially absorb any of the components mentioned above. The wettability of foams can be considerably altered by introducing chemical or physical changes to the foam's surface or bulk. As a result of these processes, foams are wettable enough to effectively separate oil from water.

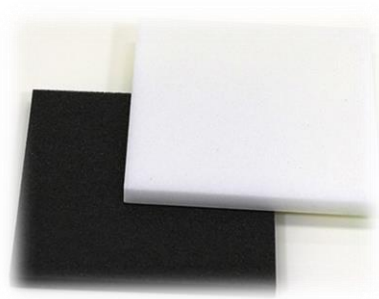
MA and PU foams can be made for both sorts of separations, depending on the treatment[81], [82]. Oil and organic solvents may be constantly, efficiently, and rapidly

separated from water using the improved foam, making it useful for oil/water separation. Flame retardant POS@HNTs covered polyurethane foam (PUF) self-extinguishes and inhibits melting pieces from starting further fires. POS@HNTs-coated foam has a lot of potential for large-scale oil spillage and oil-water separation[83].

2.4 Polyolefin based foams

Unlike polyurethane foams, polyolefin foams can modify their properties by changing the polymer, although the two technologies are extremely different[84]. Open-cell polyolefin foams can be produced post-manufacturing from closed-cell polyolefin foams[85]. The crosslinking and non-crosslinking methods for the foams are distinct[86]. When heated above the polymer's melting point, crosslinked foams retain their basic foam structure, making them perfect for shaping foam sheet into shaped products. Most polyolefin foam materials require extra processing once they have been manufactured[87].

Even while there has long been a wide range of polyolefin products available for foam manufacturing, metallocene catalyst-produced polyolefins have recently been introduced to further expand this range[88]. Polymers with improved qualities such as increased tensile strength, elongation, and flexibility are now possible thanks to these catalysts. Foams based on metallocene-catalyzed polymers have been introduced by some manufacturers, and they claim considerable advantages in terms of properties. Metallocene polymers, according to reports, are more difficult to create and so enhance the rates of foam manufacturing. When it comes to blowing agents for polyolefin foam, azodicarbonamide (ADC) is one of the most commonly used chemicals, as well as a variety of liquids, gases, and gases (for instance CO₂ or N₂)[89], [90].



2.5 Materials for oil sorbent based on the chemical composition

2.5.1 Natural organic and inorganic sorbents

Other carbon-based products to include are peat moss, hay, straw, sawdust, ground corncobs, and feathers[91]. Organic sorbents have an adsorption capability ranging from three to fifteen times their weight in oil, depending on their composition[92]. Once organic sorbents absorb both water and oil at the same time, they may sink[93]. The loose particles in many organic sorbents, like as sawdust, make them difficult to collect once they have been sprinkled over the water[94]. Empty barrels linked to sorbent bales of hay can help reduce the sinking issue, as can the use of floating devices like this, as well as the use of nets to contain loose particles.

On the other hands, the natural inorganic sorbents are a mixture of sand, volcanic ash, sandstone, clay, vermiculite, glass wool, and perlite. They can absorb oil up to a factor of four to twenty times their own weight. Both inorganic and organic sorbents can be found in big quantities at a reasonable price. On the surface of the water, these sorbents aren't used[95].

2.5.2 Synthetic sorbents

Polyurethane, polyethylene, and polypropylene are man-made materials that adsorb liquids onto their surfaces and are similar to plastics[96]. When liquids enter the structure of a cross-linked polymer or rubber, they are absorbed into its solid structure, resulting in an increase in volume. Over 70 times their own weight in oil, most synthetic sorbents can be absorbent



Figure 1: Different types of oil sorbent, such as rolls, pillow, granules, and pads

2.5.3 Carbon and carbon nano tube-based sorbent

Numerous oil sorbent materials have been produced in recent years. Carbon materials, with their high oil absorption capability and environmental tolerance, have been identified as the best options for superhydrophobic and superoleophilic surfaces[97].

With their superior absorption, selectivity, chemical resistance, and remarkable recyclability, superhydrophobic and superoleophilic materials have showed promise in oil spill recovery. The best option is to use absorbents based on carbon because they offer a large surface area, excellent mechanical properties, low density, chemical inertness, nontoxicity, and a high porosity size. All these processes have been investigated using carbon aerogels as well as graphene/carbon nanotube (CNTs) coated sponges, forest-like structures made of CNTs, graphene foams, porous nanoparticle-coated sponges, and carbon aerogels themselves[98]

The oil-water separation and gas adsorption industries are two of the most promising applications of carbon nanotubes. This is due to their strong mechanical property, quick sorption rates, high sorbent ability as well as their ability to be modified to meet specific needs.

2.5.4 Graphene and graphite-based sorbent

Graphene-based materials have received a lot of attention in the oil spill cleaning field because of their hydrophobicity, huge specific surface area, and exceptional chemical, thermal, and mechanical resilience[99]. Mechanical exfoliation, chemical vapors

deposition, graphene oxide reduction, carbon dioxide reduction, and carbon nanotube slicing are all methods for producing graphene.

Additionally, exfoliated graphite has shown promise in oil spill cleanup due to its ability to swiftly absorb heavy oil that is slickening on the surface of the water.

Carbon-based sorbents have absorption capacities ranging from 3 to 913 times their own weight. Through the vacuum pumping technique, some sorbents can follow the continuous absorption/removal process. Carbon nanofibers/ foam composite, carbon soot sponge carbonaceous nanoparticles modified polyurethane foam, and hollow carbon beads have all been used to separate water and oil[100].

2.5.5 Polymeric sorbents

Polymeric sorbents of various forms have been created to remove toxins from the surroundings. It is well-known that the sorption effectiveness and selectivity of functional groups depends on the kind of functional group and the physical properties of the matrix[101].

Polymer-based blends with improved surface functioning, biodegradability, and ease of retrieval and renewal have recently appeared in comparison to conventional sorbents used for oil removal[102][103]. Absorbents, ion-exchange resins, and chromatography applications can all benefit from the large variety of synthetic, nonionic polymers. Styrene divinyl benzene copolymers and acrylic acid esters-divinyl benzene copolymers are common building blocks for commercially accessible resins in bead form. Polymer copolymers can be found in various polarities, porosities, and macropore diameters in a variety of configurations[103]. Emulsion polymerization is used to build up porosity in a porous material by dissolving the monomers and acting as a low-swelling agent[104][105]. Polymeric adsorbents are mostly used for water purification. Activated carbon can be mimicked and replaced by macroporous polymeric resins by

attaching different functional groups, and this is especially useful in the food and pharmaceutical industries where color pollution by final product black carbons is a big issue[106], [107].

2.5.6 Oleophilic porous absorbent

Using porous oleophilic materials for oil spill rehabilitation has proven to be the most effective. In order to make up for this, oleophilic porous material would have to be utilized in large quantities, which would have a substantial economic impact. Using these sorbents is complicated and time-consuming due to the difficulty in recovering oil from them. To overcome the aforementioned challenges, we employ external pumping on oleophilic porous material to continually collect oil spills from the water surface at a lofty rate of effectiveness and with least misuse. Since oil sorption capacity is no longer restricted by absorbent substance weight or volume, this new design makes it possible to do both water/oil separation as well as oil collection at the same time during oil spill cleanup. Aerogel polymethylsilsesquioxane (PMS)[108], nanowire membranes[109], carbon sponges[110][111], porous boronnitride[112][113], and functional polymer sponges[114][115] [116] are only some of the porous oleophilic materials that have been proposed as a solution for oil spill cleanup. While oil sorption capacity is an important consideration, it is overshadowed by the heavy material and shipping costs associated with these lightweight but enormous absorbents. Furthermore, in light of the impending scarcity of fossil fuels, oil recovery from absorbents is a crucial procedure. It is possible to extract the porous oleophilic materials oil from them using methods such as squeezing and distillation but these lengthy and inefficient processes, as well as the need for high-priced equipment, hinder their practical and economic implementation[117].

2.5.7 Polyolefin based absorbent

The polymerization process produces polyolefin (which means 'oil-like')[118].

Consumer goods packaged food coverings, and receptacles typically use polyolefins because they're a low-cost polymer. They are chemically and physically great and recycling them is simple. The molecular weight and crystallinity of polyolefins determine whether they are soft elastomers or hard thermoplastics[119]. This is exactly what happens when the polyolefin is exposed to liquid fuels products. They're all petroleum products that have similar solubility properties. In a recent investigation, researchers found that the cross-linked polyolefin elastomer (i-Petrogel) was able to absorb a wide range of solvents and refined oil products. Thermo-degradable polyolefin oil superabsorbent polymer is a newly developed solution for oil spill cleanup[57]. Furthermore, i-Petrogel technology developed by a recent researcher may provide an all-encompassing answer to the problem of combating crude oil spills in open waters, with a significant reduction in the impact on the environment[120].

2.5.8 Recycled waste as sorbent for oil

despite substantial research, sorbents with both high efficiency and recyclability continue to be sought after, particularly those with exceptional sorption activity in a variety of temperature and climatic circumstances. Along with its hydrophobic or oleophilic properties as well as its flexibility, recycled rubber makes a great hydrocarbon absorbent or an excellent oil absorbent[121]. Waste tyre rubber is highly efficient and cost-effective oil absorbent that may be made from recycled rubber. It has the ability to effectively remove organic chemicals from water. For example, tyres crumb rubber can remove xylene and toluene from aqueous solution in 30 minutes. Waste rubber, which is readily available and inexpensive, can be used as an oil absorbent, preventing oil pollution in the maritime environment, which is beneficial to the rubber recycling industry. Carbon monolith is a reusable sorbent for oil–water separation because of its inherent fire resistance. Even more significant is how quickly

this carbon monolith can be produced due of the low-cost, readily available raw material and straightforward synthesis technique. Oils and organic solvents can be absorbed by the graphene aerogel, which is extremely superhydrophobic[103], [122].

Chapter 3: EXPERIMENTAL WORK

3.1 Materials

Materials used in this work and their basic properties are summarized in table 1.

Table 1: Materials used and their basic properties

Materials	Molecular weight (gmol ⁻¹)	Density (g.cm ³)
Melamine foam	Crosslinked material	0.009
Paraffin wax (Qwax): QAPCO, Qatar	Not available, Mostly C33 to C128 alkanes	0.89
Hexane	86.18	0.66
Diesel oil	Not available	0.85
Engine oil (Oto Motiv Dynamic 20W50 SL)	Not available	0.87
Crude oil	Not available	0.99
Dicumyl peroxide	270.37	1.56
Genitron (foaming agent)	98.86	
Xylene	106.2	0.88
Graphene oxide: Aldrich, 4mg/ml, dispersion in H ₂ O		

Sylgrad 184 silicone elastomer	1395	0.97
Polydimethylsiloxane (PDMS)		
Sylgrad 184 silicone elastomer, curing agent		
Distilled water	18	1.0

For an illustration, oils used in this study are shown in figure 2

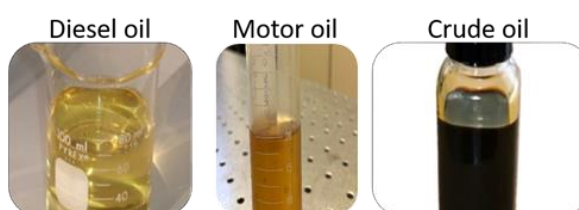


Figure 2: Images of tested oils

3.2 Viscosity of oils

Viscometer is a device used to measure viscosity of fluid. The principle of this device is based upon immersing two sensor within the sample one for the temperature and one for viscosity. Viscosity determination is based on the proportional relationship between the viscous resistance of the sample fluid and the amount of electric current required to drive and maintain the sensor plates at a constant vibration amplitude., The viscosity of the used oils (crude, diesel, and engine) were measured at $21.0 \pm 0.5^\circ\text{C}$ and the results are summarized in table 2.



Figure 3: Viscometer, SV-10 series

Table 2: Viscosity of Diesel, Crude and Engine oil determined at 21°C

Oils	Viscosity (mPa.s)
Diesel oil	3.41
Crude oil	12
Engine oil	493

3.3 Sample preparation

3.3.1 Preparation of Qwax foam

The waste wax (Q_{wax}) was obtained from QAPCO (Qatar). It is a sticky, highly viscous waste product of polymerization process of low-density polyethylene (LDPE) It is a mixture of various alkanes having number of carbons in the range from C33 to C128. The specific density is 0.88 g/cm^3 , melting point $102 \text{ }^\circ\text{C}$, and the specific enthalpy of melting 20 J/g . The very low enthalpy of melting indicates low degree of crystallinity of due to the highly branched chains representing obstacles for the regular folding of chains.

Qwax foams were prepared through crosslinking of Qwax by dicumyl peroxide and foaming by Genitron foaming agent, which is the masterbatch consisting of 40 wt.% 1,1'-azobiscarbamide within LDPE. Various portions of both components were used to

optimize the procedure. The most important point is the determination of suitable content of DCP to obtain sufficiently crosslinked material. The efficiency of crosslinking was characterized by the determination of gel content (Figure 4) – what is insoluble part of crosslinked material forming 3D network and which, unlike sol portion is insoluble in organic solvents and thus cannot be extracted from material. Determination of gel content by extraction is described below. It is seen that at least 9-10 wt.% of DCP is needed to get sufficiently crosslinked structure.

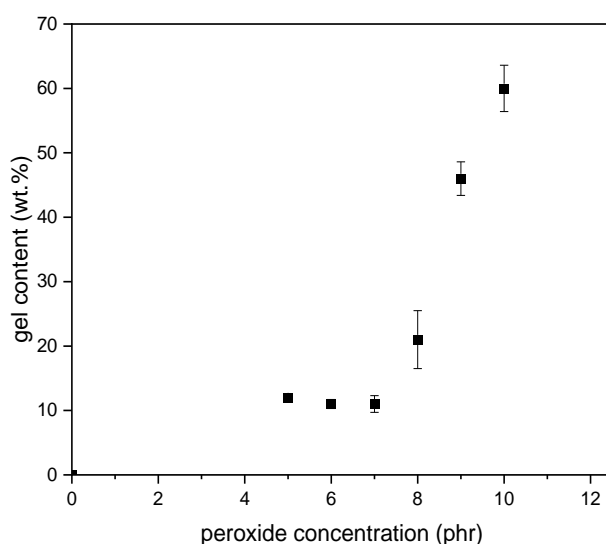


Figure 4: The dependence of gel content in crosslinked Qwax on peroxide concentration

In the final procedure, Qwax was molten at 140 °C in a beaker using magnetic stirrer. Then blowing agent Genitron (Genitron AC2, Schering Polymer Additives, England) – 10 phr, and a cross-linking agent (dicumyl peroxide, SIGMA ALDRICH, USA)-10 phr were added.. The mixture was stirred for 10 minutes until homogeneous compound was obtained. The liquid mixture was poured into the cylinder-shaped mold and inserted to

mounting press and heated at 180 °C for 10 min. During this time DCP and Genitron was decomposed leading to crosslinking of material and formation of gaseous products within a bulk material. Then the form was removed from the press what lead to the expansion of gasses and foaming of material. Finally, the foams were put into vacuum oven at 50 °C overnight to release residual gaseous products from a material.

Efficiency of cross-linking was determined gravimetrically in terms of the insoluble portion (gel) after 24 h extraction of the samples in boiling xylene. Xylene was changed every 6 h.

Table 3: Preparation of Qwax foam according to the following ratios

Qwax amount (g)	Genitron, foaming agent amount (g)	Dicumyl peroxide amount (g)
18	0.9	1.8

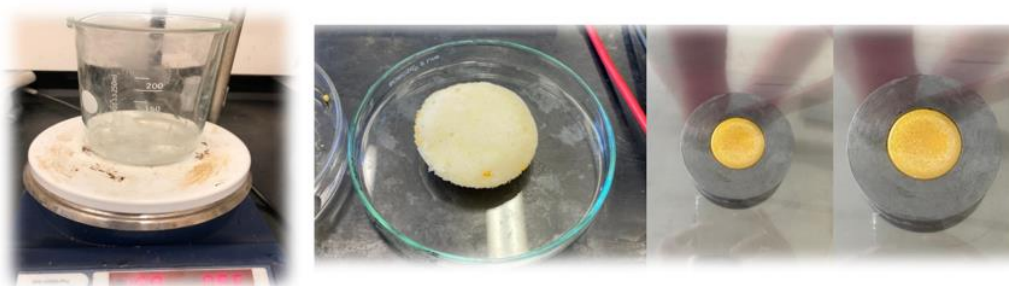
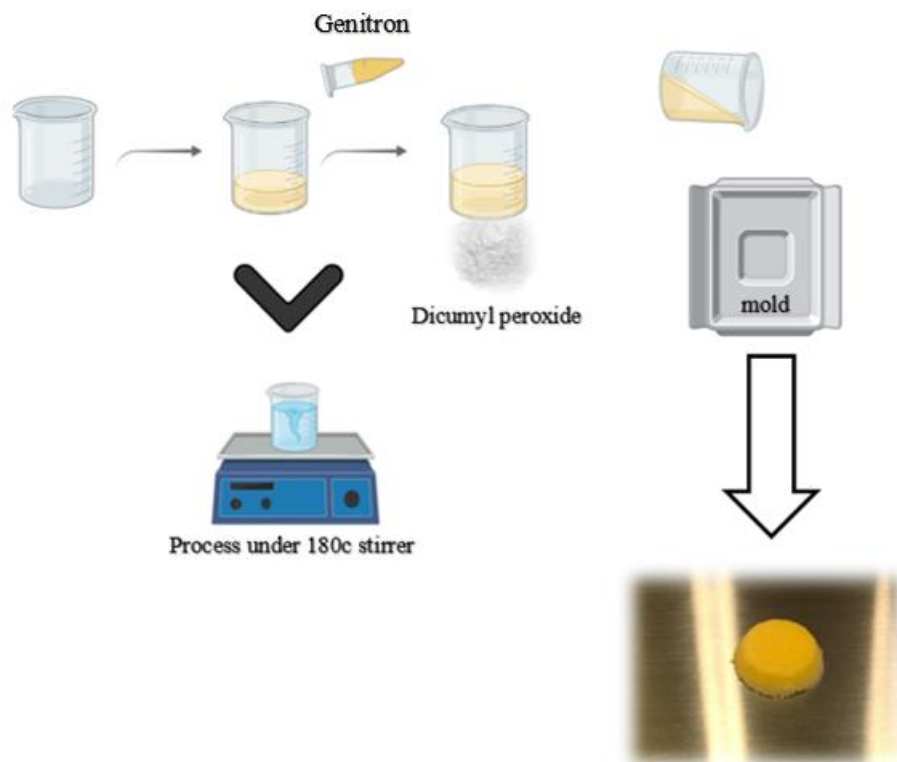


Figure 5: Preparation of Qwax foam using hot plate and mounting press

3.3.2 Determination of gel content in crosslinked samples

3 packs for each sample were prepared by sealing an amount of 0.5g of the sample in a labeled mesh.

All samples were immersed in a flask containing xylene as shown in figure 6.

After that, the flask is placed in a condenser set up. The heater was adjusted to the xylene boiling point and left for 24hr. Finally, the samples were removed from the flask

and kept for another 24hr to dry.

The Equation (1) was used to obtain the gel%.

gel content(%) =

$$\frac{\text{weight after extraction} - (\text{weight before extraction} - \text{sample weight})}{\text{sample weight}} \times 100\% \quad \text{Eq. (1)}$$

The gel content was about 72 wt.%.

Both Genitron and dicumylperoxide are common additives used in processing of polyethylene including crosslinking and foaming. The preparation of a foam from low molecular paraffins in this way is an original procedure (including optimized parameters for processing mentioned above). As for gel content, such are melamine or polyurethane foams) or high molecular polyethylene have gel content close to 100%. This is not possible for crosslinked low molecular waxes, where an efficiency of crosslinking is lower even at high peroxide content.

Porosity of foam was estimated from densities of foam (0.41 g.cm³) and initial Qwax (0.8 g.cm³) by Equation (2):

$$\varphi_{pore} = 1 - \frac{\text{density of foam}}{\text{density of Qwax}} \times 100\% \quad \text{Eq. (2)}$$

Table 4: Selected properties of Qwax foam

Sample	Genitron, foaming agent amount (wt.%)	Dicumyl peroxide amount (wt.%)	Density, g.cm³	Porosity, vol.%	Gel content. wt.%
Foamed Qwax	5	10	0.41	54/59*	72±7

* The value of 54 % was determined from density measurement, and the value of

59% from CT analysis.



Figure 6: Extraction experiment using xylene

3.3.3 Preparation of melamine foam treated with graphene oxide

1cm³ of melamine foam was immersed into graphene oxide solution 4% for 6 hours. After that melamine foams were squeezed to release water and let dry in vacuum oven at 90 °C overnight[123]. Secondly, foams were fully immersed in 5% ascorbic acid at 80 °C for 1 hour. Then foam was gently squeezed and washed in pure water and insert it in vacuum oven at 80 °C till it dry. This step was done to reduce graphene oxide to graphene. Subsequently, the foams were immersed to 2% Sylgacure 183 of ration 10/1 in dichloromethane and dry in vacuum oven. This step was performed to permanently fix graphene onto foam surface. PDMS form 3D network due to presence of crosslinker part in PDMS mixture that ensure embedment of graphene to melamine structure. Moreover, hydrophobic character of PDMS ensure attraction of PDMS network to graphene moieties[124]. The graphene forms π - π stacking interaction with melamine structures and importantly graphene is embedded in PDMS 3D network which ensure crosslinking and prevent leaching of graphene[125]. Investigation of stability of graphene in structure was not performed since it is expected that graphene is stable for proposed application similarly as was reported in previous studies[126], [127]. The modified foam exhibited significantly increased resistance to water uptake (superhydrophobicity).



Figure 7: Preparation of melamine foam treated with graphene oxide

3.4 Characterization techniques

3.4.1 Surface wettability

Wettability of solid surfaces is commonly characterized by measurement of contact angles of droplets of various liquids deposited on the surface. Dependently on the magnitude of a contact angle, surfaces can be either hydrophobic or hydrophilic, as shown in figure 8.

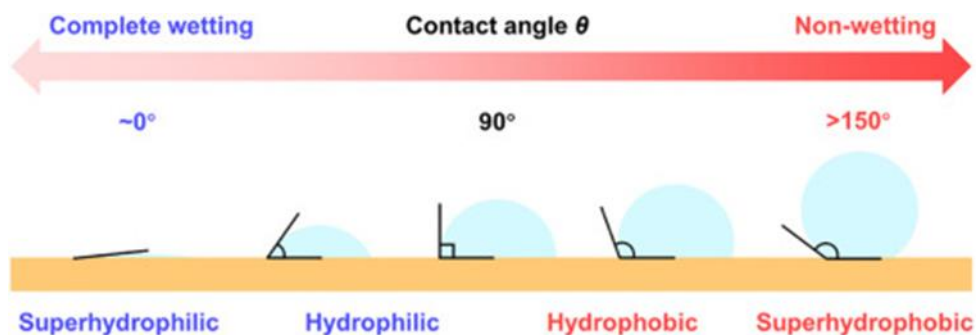


Figure 8: Different contact angle on a solid surface, representing the interaction

The changes in hydrophobicity and oleophilicity of Qwax, polyurethane and melamine foams were evaluated by static contact angle measurements. Surface energy evaluation system (OCA35, DataPhysics, Germany) employed for this purpose was equipped with CCD camera. Three different oils (crude, engine, and diesel) were used for testing the oleophilicity and ultra-pure water for testing the hydrophobicity, to evaluate surface of the contact angle. A droplet of $3 \mu\text{l}$ from each testing oil was dispensed on the sample at ambient air conditions, under water and under diesel oil conditions. The contact angle was calculated approximately after 3 seconds after droplet deposition to allow thermodynamic equilibrium between the liquid and the sample surface to be reached. At least four independent measurements were taken at different positions on each sample and the average contact angle value of oil and water were reported. The total surface free energy and its polar and dispersive components were evaluated using Owens Wendt Rabel Kaelble model. A substance is considered a hydrophobic if the angle is above 90° and if the angle is 150° and above it considers as superhydrophobic. On the other hand, if the angle is below 90° in this case it is hydrophilic and super hydrophilic if contact angle is close to 0° .

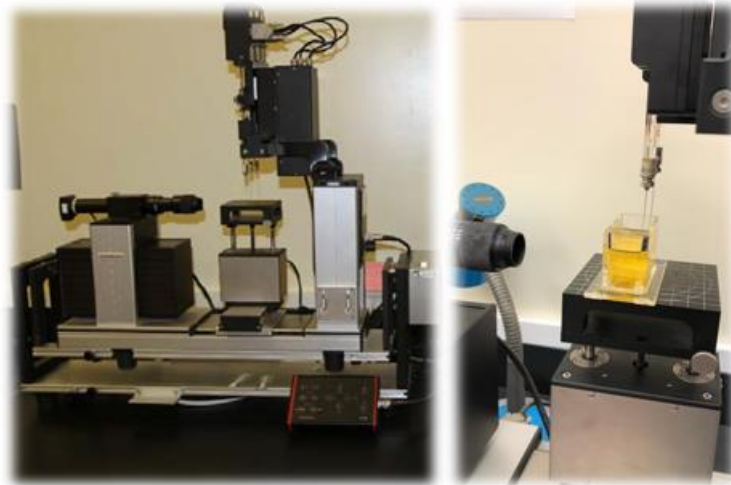


Figure 9: Contact angle goniometer, OCA system, and contact angle measurement under diesel oil condition

3.4.2 Surface Morphology Analysis

The surface morphology of foams was studied using scanning electron microscopy (SEM). SEM microscopy (Nova NanoSEM 450, FEI, USA) is a microscope that produce images using electrons instead of light, which have much shorter wavelength than visible light and it will give more resolution to the 2D image of the analyzed surface. The components of the electron microscope are, electron gun that is produce electrons, electromagnetic lenses are used to focus the electrons and the detector is sensitive to electrons instead of light. Electrons can interact with a sample in several ways the most important are backscattered and secondary electrons. When an electron bean strikes a sample some of the electrons are absorbed, other electrons are backscattered, and some sample electrons can be ejected as secondary electrons. However, if the numbers of electrons that strike the sample is not equal to the numbers of electrons that leave the sample, then the sample will build up a charge this is called charging and it is negatively affect the quality of the image. To prevent charging many SEM samples are coated with a thin layer of metal such as, gold. Finally, most of the SEM image are produced by collecting a secondary electron. The voltage capability

ranging from 200 V to 30 kV and the foam samples required a treatment with a thin layer of gold particles to increase the interaction between the sample and the beam.

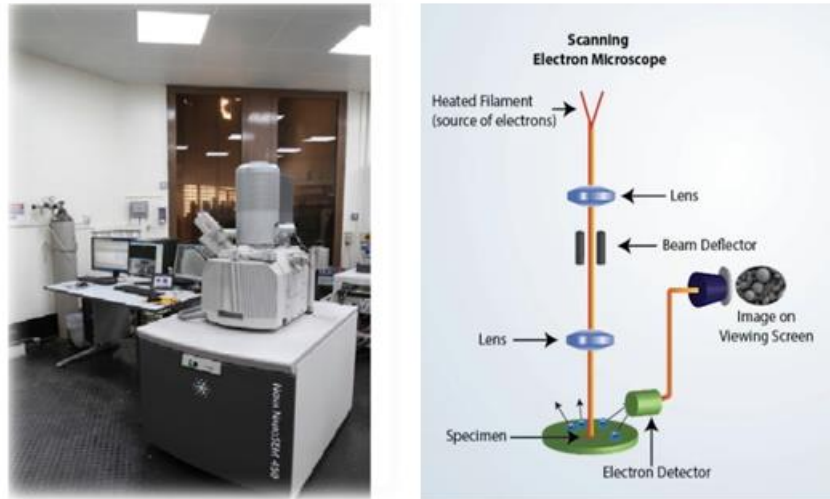


Figure 10: SEM device, and simplified illustration of the SEM mechanism

3.4.3 Thermogravimetric analysis (TGA)

Thermogravimetric analyzer (TGA) measures the weight loss as a function of temperature. The TGA instrument consist of a sample pan. The temperature in the furnace increasing with constant rate. The temperature ranging was from 30 °C to 700 °C, with a constant temperature increase at a rate of 10 °C per minute. The aim is to record the maximum temperature at which the foam samples can withstand before degradation.



Figure 11: Thermogravimetric analyzer (TGA)

3.4.4 Porosity analysis, CT analysis

The porosity of sample was investigated at the cut disk (dimensions) using computer micro-tomography (CT) on the SkyScan Unit (model 1174, Bruker, New York, NY, USA). Device was equipped with an X-ray power source (20–50 kV and maximum power 40 W) and X-ray detector (Bruker, New York, NY, USA). The CCD 1.3 Mpix unit was coupled to a scintillator by a lens with 1:6 zoom range. Projection images were taken at angular increment of 0.3° at a tube voltage of 31 kV and current of $529 \mu\text{A}$. Duration of exposure was set to 10 s without the use of filter. 3D reconstructions were created via preinstalled CT image analysis software v1.16.4.1, Bruker, New York, NY, USA).

Chapter 4: RESULTS AND DISCUSSION

In this chapter the morphology, sorption kinetics, absorption capacity, and multiplied use of both Qwax foam and melamine foam treated with graphene will be discussed.

4.1 Qwax foam

4.1.1 Morphological characterization (SEM image) of Qwax foam

Figure 12 Shows the SEM images of Qwax foam, the SEM images show uniform pore distribution across the Qwax foam sample as seen in figure 12 (a). The average pore size was calculated through imageJ software and found to be 500 μ m. The pores have some defects in their structure, and they behave as open pores, as discussed below.

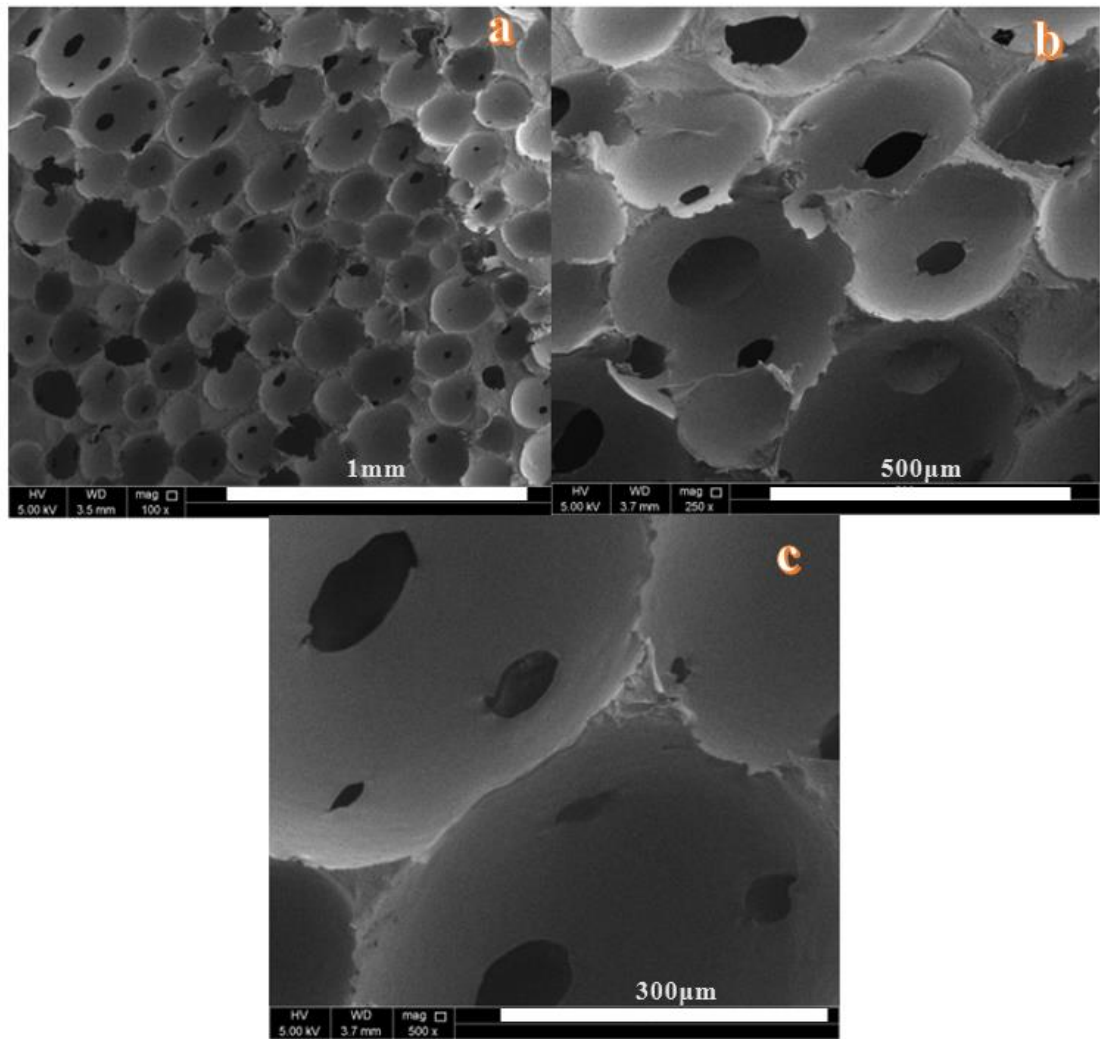


Figure 12: SEM image for Qwax foam

4.1.2 Thermal stability of Qwax foam

Thermal stability of both neat Qwax and the foams was tested by TGA, and degradation curves are shown in Figure 13. It is seen that both degradation curves are almost identical indicating that crosslinking has no influence on thermal stability of foams. Both materials are stable up to 360°C without any weight lost. TGA also indicated some residues within a foam structure originated by decomposition of both DCP and Genitron, which did not release a foam during preparation. However, all these residues released the material after drying in the oven.

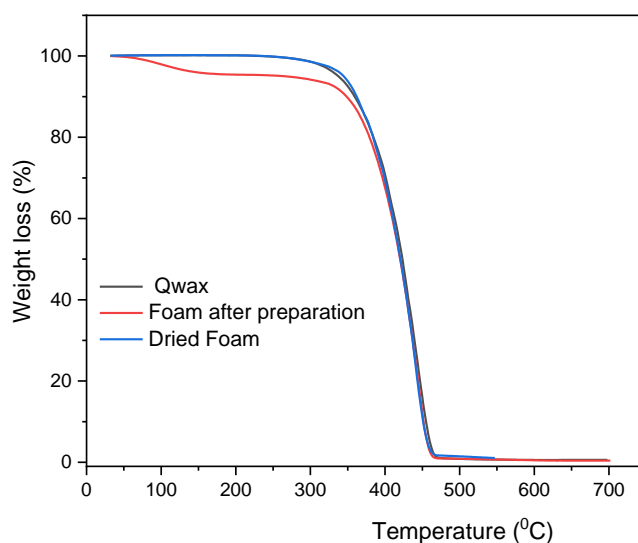


Figure 13: TGA curve for neat Qwax and Qwax foam; shows polymer degradation

4.1.3 Surface wettability (contact angle) of Qwax foam

Oil and water absorption is very crucial in the separation process, because in the presence of both components which are in contact with sorbent, only one component should rapidly diffuse into the sorbent. One of the important properties for oil water separation system is the surface wettability by polar and unipolar liquids, mostly characterized by the contact angle measurement for various polar and upolar liquids. The contact angle is strongly dependent not only on the inherent chemical composition of the surface but also on the surface roughness and overall morphology of the specimen.[128]–[130] Indeed, the contact angle for various liquids is different if measured in air and under liquid. The Qwax foam were tested through the measurement of contact angles of crude oil and water in air, the contact angle of oil under water, and the contact angle of water under oil (Figure 14). The hydrophobic character of foam was observed under both air and oil as the contact angle values of water are 114° and 128°, respectively. On the other hand, super oleophilicity was observed for Qwax foam under both air and water as the contact angle values where 0° (or better said they were

not measurable due to fast sucking of oil into the tested sample), what is a consequence of inherent, nonpolar character of paraffin compounds and surface roughness. Surface wettability of foam by water and crude oil is therefore very suitable for oil/water separation. In our case it is oil, whereas water sorption should be negligible (less than 0.5 wt.% after 24 hours of immersion in distilled water), what is crucial for practical applicability for a removal of free oil from water surface.

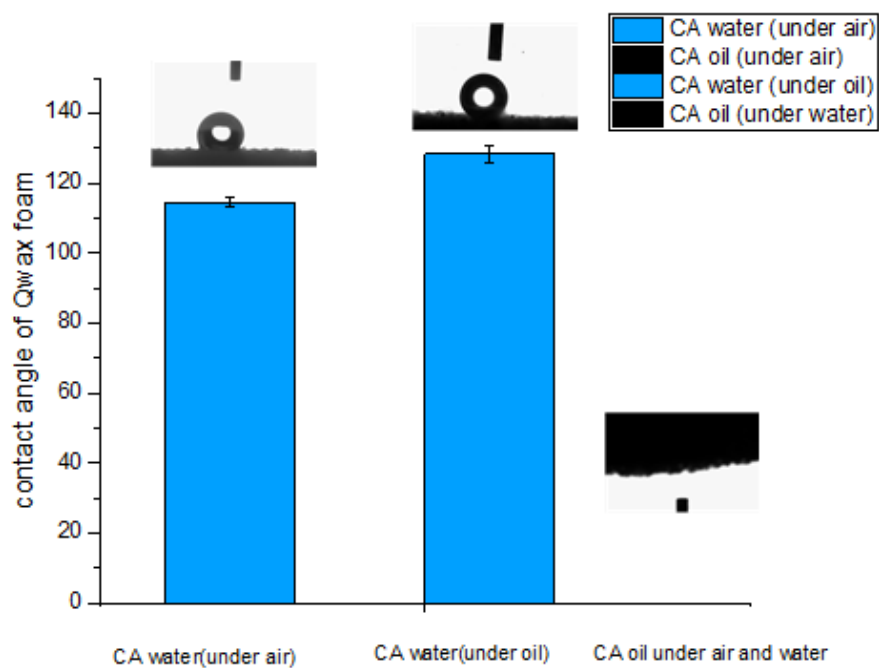


Figure 14: Water and oil contact angle values for Qwax foam

4.1.4 CT analysis for Qwax foam

Internal Foam Structure Investigation

This is non-contact method avoiding a deformation of the pores after cutting/breaking as usually occurs in the case of samples for SEM investigation. The pores' content determined by CT was found to be of 58.9 vol.%. The main difference between SEM and CT analysis is that SEM has small representative area, and pores content cannot be determined.

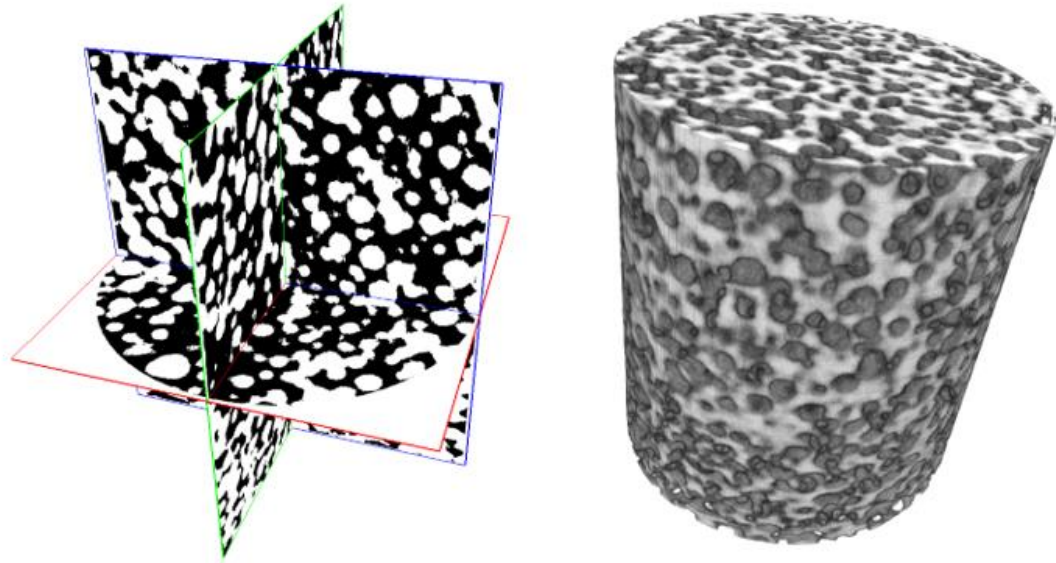


Figure 15: Space cross sections and 3D model of the foam sample Q-Wax. Size of sample 5,5 mm (diameter), 6 mm (height)

Table 5: Results from 3D image analysis of Qwax foams

Total analyzed volume	139,9 mm ³
Foam volume in analyzed volume	57,5 mm ³
Volume of open pores	82,4 mm ³
Volume of closed pores	0,001 mm ³
Open porosity (percent)	58,9 %
Closed porosity (percent)	0,002 %

4.1.5 Kinetics of absorption of Qwax foam

The dependences of the absorption capacity of Qwax foam (S_w) on time of sorption are shown in Figure 16. The experimental data are compared with some selected models as it is discussed below.

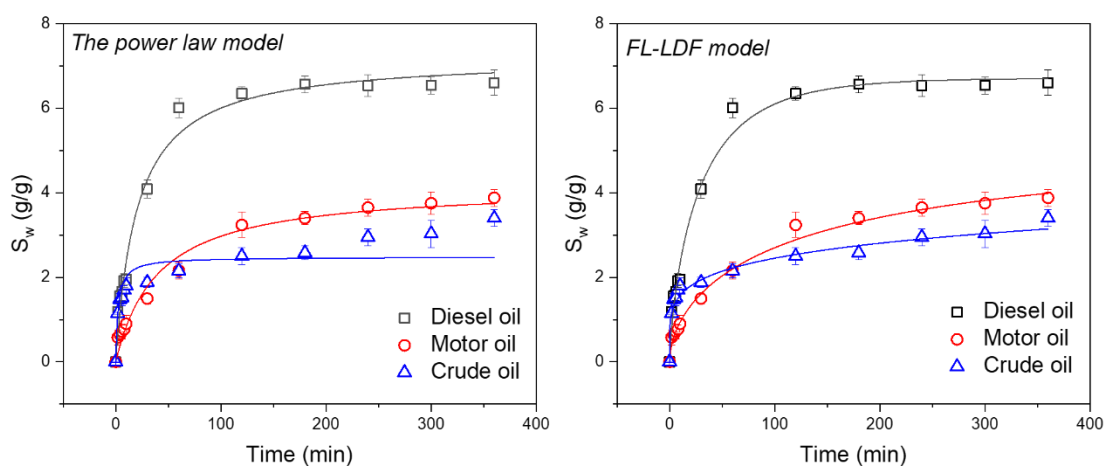


Figure 16: Absorption capacity (S_w) of foam for diesel, motor and crude oil.

The mass of absorbed oils was determined in selected intervals up to 360 minutes of the foam immersion into oils. It is evident from the Figure 16 that the sorption is the fastest at short times in all cases, approximately up to 10-15 minutes after the immersion, and then the penetration of oils into foam is significantly decelerated. The fastest sorption rate was observed for diesel oil, followed by crude oil, and motor oil, what is in line with increasing dynamic viscosities of the liquids. The rate of sorption (v_s) can be easily quantified from the initial slope (tangent) of the experimental curves. The values of v_s are 0.97, 0.93, and 0.51 [$\text{g/g}\cdot\text{min}^{-1}$] for diesel, crude and motor oil. The mass of maximum absorbed liquid per the mass of sorbent was determined arbitrarily after six hours of sorption, and following values were found: 6.6, 3.9, and 3.4 g/g for diesel, motor, and crude oil, respectively. The absorption was accomplished with volumetric changes of samples due to swelling. The initial volumes of testing foams increased in 138%, 30%, and 68% for diesel, motor, and crude oil, respectively.

Experimental data were firstly described by a developed model which called ‘fractal like linear driving force (FL-LDF)’ model[131] (Eq.2) by sorption of liquids (e.g., oils) by porous materials considering following physical aspects of the process: (i)

“absorption” not “adsorption”, (ii) maximum capacity of absorbent, (iii) physical meaning of the rate coefficient and (iv) a presence of different pores for absorption.

$$(2) \quad S_w(t) = S_{w,max}[1 - \exp(-D't^\alpha)]$$

Where S_w [g/g] is the mass of absorbed liquid per the mass of sorbent, $S_{w,max}$ [g/g] is the mass of maximum absorbed liquid per the mass of sorbent, D' [time $^{-\alpha}$] is the mass transfer coefficient, t [s, min] is time of the experiment duration, and α [-] is dimensionless fractal constant ($0 < \alpha \leq 1$). The comparison of results with FL-LDF model is shown in Figure x, and the parameters D' , and α are summarized in Table 6. It is evident that the model fit all the data with high accuracy confirming its - at least mathematical suitability for a description of experimental results.

Table 6: Parameters of FL-LDF, and power law models

Models/Parameters	Diesel oil	Motor oil	Crude oil
$S_w(t) = S_{w,max}(1 - \exp(-D't^\alpha))$			
$S_{w,max}$ [g/g]	6.7 (0.1)	4.9 (0.9)	3.5 (0.9)
D' [min $^{-1}$]	0.076 (0.007)	0.056 (0.008)	0.25 (0.06)
α [-]	0.75 (0.04)	0.58 (0.06)	0.22 (0.08)
R^2	0.99341	0.99695	0.9943
$S_w(t) = kt^n$			
k [(g/g). min $^{-n}$]	1.10 (0.05)	0.37 (0.03)	1.00 (0.02)
n [-]	0.33 (0.01)	0.41 (0.02)	0.19 (0.01)
R^2	0.99331	0.99349	0.97055

The second model used for the description of experimental data is the generalized non-Fickian diffusional model, originally introduced by Ritger and Peppas[132], [133] for

the interpretation of a non-Fickian release of drugs from moderately swelling polymeric systems.

$$\frac{M_t}{M_\infty} = kt^n$$

(3)

In the original papers, M_t , and M_∞ are mass concentrations of a released species at time t , and time approaching infinity, k is a constant involving characteristics of the network (medium) and the species, and n is diffusional exponent. In general, it is considered that if $n=1/2$, the model characterizes Fickian diffusion, however, very rigorously, it is important to point out that parameter n not necessarily must be exactly equal to $1/2$, even if diffusion is purely Fickian, because this parameter also depends on geometry of the system. Ritger and Peppas shown that in case of pure Fickian release of molecules from the media of different geometries, the exponent n had the limiting values of 0.50, 0.45 and 0.43 for release from slabs, cylinders, and spheres, respectively.

Fickian diffusion runs in homogeneous systems without a presence of boundaries, such are pores, swollen and dry regions, regions with different physical states (glassy, rubber). However, the penetration of oil into Qwax foam is far from Fickian diffusion, as it is indicated by values n , which are significantly lower than 0.5. Sorption data of foams for different oils were fitted by Eq. (3), where the term $\frac{M_t}{M_\infty}$ was replaced by the term $S_w(t)$.

The real process involves: i) diffusion of oil into the empty pores filled with air, ii.) diffusion of oil into bulk material (matrix), and iii.) the process is accomplished by volumetric change of the sorbent during sorption. The very high rate of sorption in the first stage (10 minutes of immersion) is probably caused by a penetration of oil into the

pores, which are interconnected each other due to cracks in the walls. This insures fast filling of interconnected pores. At the same time, but slower, oil diffuses into the solid Qwax matrix. If all available pores are filled, only diffusion into the bulk polymer can proceed.

4.1.6 Reusability of Qwax foam

The multiply use of sorbents in general is desirable property of all sorbents, regardless the type of sorbent recovery. Foamy sorbents are frequently recovered by simple mechanical squeezing.[134] Reusability of Qwax foam was tested for absorption of crude oil. Data recorded in this experiment were: the mass of foam after immersion, the mass of foam after squeezing of oil out, mass of squeezed oil, dimensions of foam before and after squeezing. The calculated parameters are i.) the mass of trapped oil /mass neat foam (m_{trapped}/m_0) , ii.) the mass of released oil/mass of neat foam (m_{released}/m_0), iii.) the total mass of absorbed oil/mass neat foam(m_{total}/m_0), iv.) the volume of trapped oil /volume of neat foam (V_{trapped}/V_0), v.) the volume of released oil/volume of neat foam (V_{released}/V_0), vi.) the total volume of absorbed oil/volume neat foam (V_{total}/V_0). The volume of the neat foam was 8 cm^3 (2cm x2 cm x 2cm). More cycles were not realized because the foam has started to lose its mechanical integrity.

Table 7: The parameters characterizing sorption ability of the foam during four sorption/desorption cycles

Sorption parameters	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Average
m_{trapped}/m_0	0.87	1.74	1.71	1.68	1.5 (0.4)
m_{released}/m_0	1.18	1.79	1.24	1.76	1.5 (0.3)
m_{total}/m_0	2.05	3.53	2.95	3.44	3.1 (0.7)
V_{released}/V_0	0.48	0.74	0.51	0.63	0.6 (0.1)
V_{trapped}/V_0	0.35	0.72	0.71	0.69	0.6 (0.1)
V_{total}/V_0	0.83	1.76	1.22	1.32	1.3 (0.4)

The results summarized in table 7 indicate:

Some portion of the oil is irreversibly trapped in the foam and cannot be released by the simple squeezing. Obviously more oil would be released by applying higher forces, however, it would damage the foam. The amount of permanently trapped oil does not significantly change during multiply cycling and remains roughly at the same level as after the first sorption step.

The amount of the released oil does not depend much on the number of squeezing steps, and the average mass of the released oil 1.5 ± 0.3 g/g. It is also seen that approximately one half of the absorbed oil can be released by squeezing, and one half is permanently retained.

The amounts of absorbed oil, as well as the releasing and retaining portions can be expressed in both weight fractions (mass of oil/mass of neat foam), and volume fractions (cm^3/cm^3). The total amount of absorbed crude oil in the weight fractions is $S_w = 3.0 \pm 0.7$ g/g, what is quite low value if compared with data for foamy, highly porous materials reported in literature.[135] Many papers relating to the study of the sorption ability of porous materials refer data for S_w parameter in the range from tens

to hundreds g/g.[135] This may apparently indicate little sorption ability of the Qwax foams in a comparison with those data. However, the situation looks quite different if the comparison is performed for volume of absorbed oil versus volume of the foams. Total volume of absorbed oil per volume of neat foam is $0.83 \text{ cm}^3/\text{cm}^3$ in the first step, and the next sorption cycles lead to the values over unit (the average is $1.3 \pm 0.4 \text{ cm}^3/\text{cm}^3$).

4.2 Neat melamine (ME) and polyurethane (PU) foams compared to Qwax foam

The commercial ME and PU foams are a feasible candidate for the separation applications due to their availability, low cost, high porosity, and excellent sorption capacity for both water and oil phases. In this paragraph we have investigated the sorption ability of untreated ME and PU foam for sorption of crude oil, and water to compare it to Qwax foam.

4.2.1 Comparison of multiply sorption ability for melamine (ME), polyurethane (PU) and Qwax foam.

MA and PU foams, the sorption experiment was realized at the same conditions as for sorption of Qwax foam. Sorption ability of untreated melamine (MA) and polyurethane (PU) foams was tested using common sponges for daily use in kitchens for cleaning. The cubes with dimensions of $2 \times 2 \times 2 \text{ cm}$ were cut and immersed into both crude oil and water for three hours at room temperature. After three hours, the weight of the foams has been recorded.

SEM micrographs of MA and PU foams are in Figure 17 demonstrating high porosity of both foams.

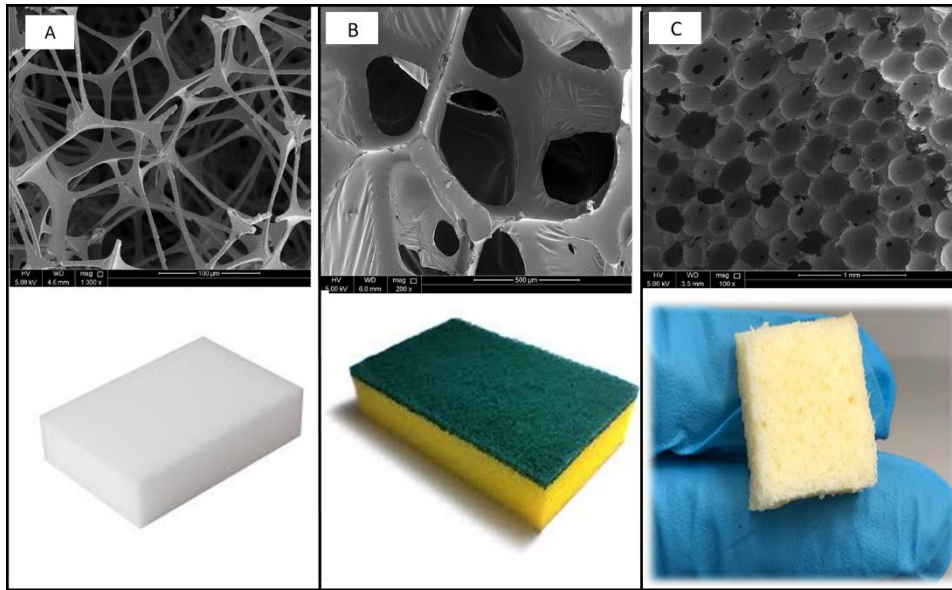


Figure 17: Photographs and SEM micrographs of MA (A), PU (B), and Qwax (C) foams used for the sorption test.

As shown below in figure 18 PU foam and MA foam absorbed around 1ml and 7ml of water. In this case the absorption is not a time dependent since the amount of the absorbed water is almost the same per time interval.

In figure 19 the amount of absorbed oil by PU foam is higher compared to the amount of absorbed water in figure 18. Also, as it is seen in figure 19 the amount of absorbed oil increases over time.

In addition, figure 18 shows that ME foam has higher sorption capacity of water compared to PU foam. figure 19 it demonstrates that ME foam has higher sorption capacity of oil compared to PU foam.

Table 8: Sorption capacity of neat PU and ME foam

	Time (s)								
	0	30	60	90	120	150	180	210	240
	mass of absorbed crude oil (g/g)								
neat ME foam	37.98	39.98	39.48	40.48	40.98	41.48	41.98	39.98	
neat PU foam	12.95	14.76	16.76	19.05	20.33	21.24	22	22.71	
	mass of absorbed water (g/g)								
neat ME foam	62.75	64.25	65.63	66.63	67.25	68	68.63	68.88	
neat PU foam	2.05	2.76	2.95	3.19	3.48	3.43	3.38	3.86	

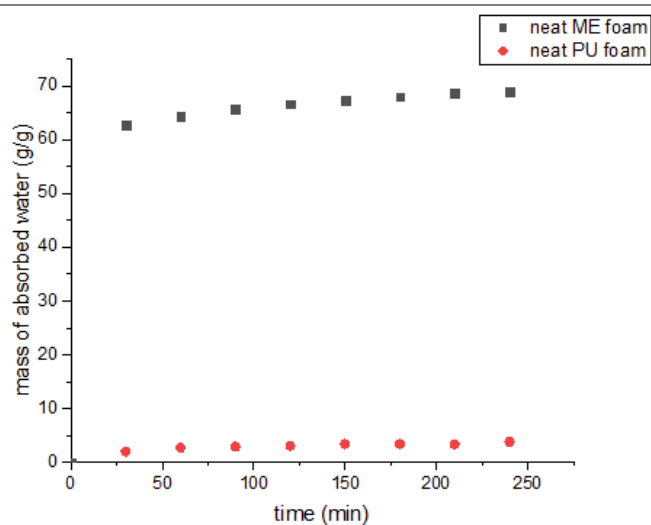


Figure 18: Mass of absorbed water for both melamine and polyurethane foams

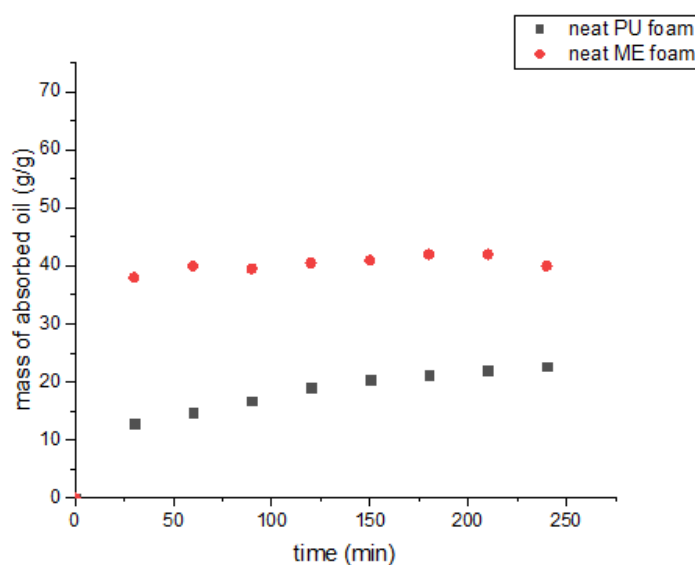


Figure 19: Mass of absorbed crude oil for both foams melamine and polyurethane

Table 9 compare the sorption abilities of MA, PU, and Qwax foam. As for the most used parameter, S_w , MA foam shows the best performance having sorption ability of 59 g/g, followed by PU foam (23 g/g), and Qwax has sorption capacity only 3.1 g/g. The situation changes significantly if the volumes of absorbed oil are related to the volume of neat foams. In this case, the highest performance has Qwax foam with S_v equals to 1.3 cm³/cm³, then PU foam (0.69 cm³/cm³), and the least value was found for MA foam (0.59 cm³/cm³). It is seen that neither PU nor MA foams did not reach full saturation by crude oil, even after a long-time immersion, which is probably caused by blocking of pores.

The comparison of sorption abilities of MA, PU, and Qwax foam is summarized in Table 9.

Table 9: The parameters characterizing sorption ability of MA, PU and Qwax foam

Foam	m_{total}/m_0	$m_{trapped}/m_0$	$m_{released}/m_0$	V_{total}/V_0	$V_{trapped}/V_0$	$V_{released}/V_0$
MA	59 (2)	10.0 (0.5)	49 (2)	0.59 (0.02)	0.10 (0.01)	0.49 (0.02)
PU	23 (1)	2.7 (0.3)	20 (1)	0.69 (0.03)	0.08 (0.01)	0.61 (0.04)
Qwax	3.1 (0.7)	1.5 (0.4)	1.5 (0.3)	1.3 (0.4)	0.6 (0.1)	0.62 (0.09)

Table 10: Experimentally sorption parameters for neat ME foam in water

Mass of water absorbed(g)	6.6
Volume of water absorbed(ml)	6.6
Mass of water/mass of foam(g/g)	82.5
Volume of water/volume of foam(ml/cm ³)	0.95
mass of trapped water/mass of foam (g/g)	12.13
volume of trapped water/volume of foam(ml/cm ³)	0.12
mass of foam (g)	0.08
mass of trapped water after squeezing (g)	0.97

Table 11: Experimentally sorption parameters for neat PU foam in water

Mass of water absorbed(g)	1.05
Volume of water absorbed(ml)	1.05
Mass of water/mass of foam(g/g)	5
Volume of water/volume of foam(ml/cm ³)	0.37
mass of trapped water/mass of foam (g/g)	3.43
volume of trapped water/volume of foam(ml/cm ³)	0.09
mass of foam (g)	0.21
mass of trapped water after squeezing (g)	0.72

Neat PU foam was tested through the measurement of contact angles of oil and water as shown in figure 20. The hydrophobic character of foam is clearly observed under both air and oil as the contact angle values are 115° and 100°. On the other hand, neat ME foam under air and under water are super hydrophilic and oleophilic as the contact angle values were 0°.

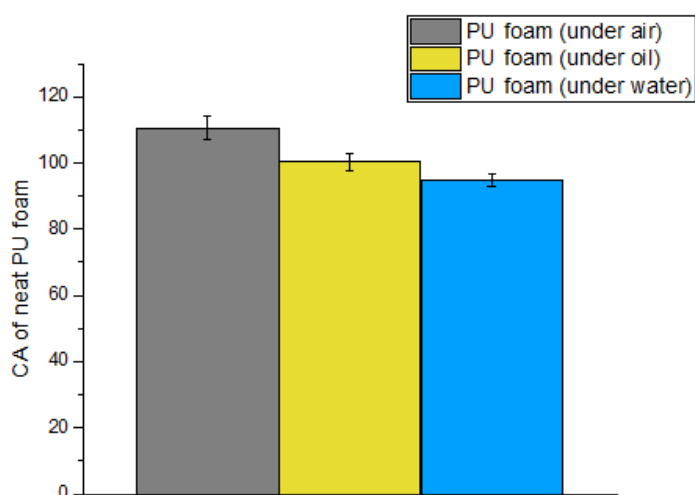


Figure 20: Water contact angle on neat PU foam under air, oil, and oil contact angle under water

It can be concluded that both ME and PU foams have high sorption ability for crude oil and can be used in many repeating cycles. PU foam, unlike ME foam is more hydrophobic, and does not absorb such amount of water as ME foam, especially in short

times of sorption. From this reason, further use of ME foams requires additional treatment to enhance its hydrophobicity.

4.3 Melamine foam treated with graphene

Commercial melamine foam, commonly used for cleaning was modified by graphene oxide to enhance oleophilicity of material and, particularly reduce its hydrophilicity. This type of treatment is to prevent water uptake and it increased the ability of foam to remain afloat. The target of this is to enhance the sorption capability of oils and to increased resistance to water uptake (superhydrophobicity).

4.3.1 Morphological characterization (SEM image) of neat ME foam and ME foam treated with graphene

SEM images in figure 21 show the morphology of the untreated ME foam, which confirm porous structure with pore size of few hundred microns. Figure 22 shows SEM images of modified foam by graphene. There is clearly visible some particles, which should be graphene particles reduced from graphite oxide.

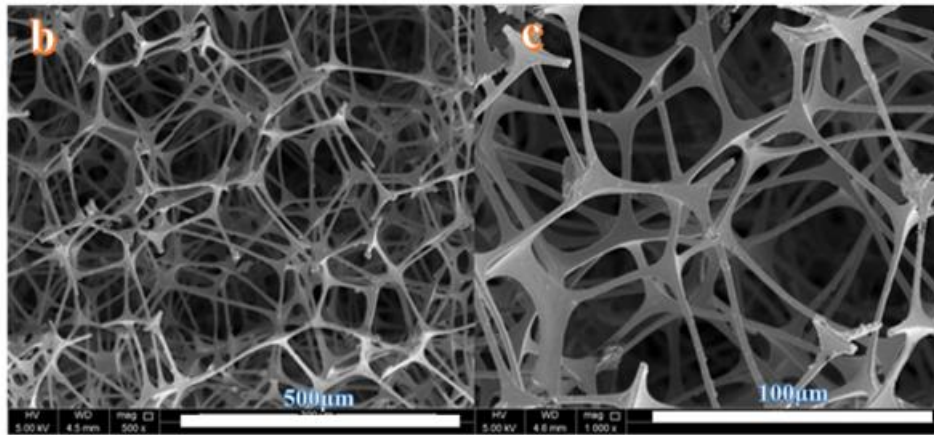


Figure 21: SEM image for neat ME foam

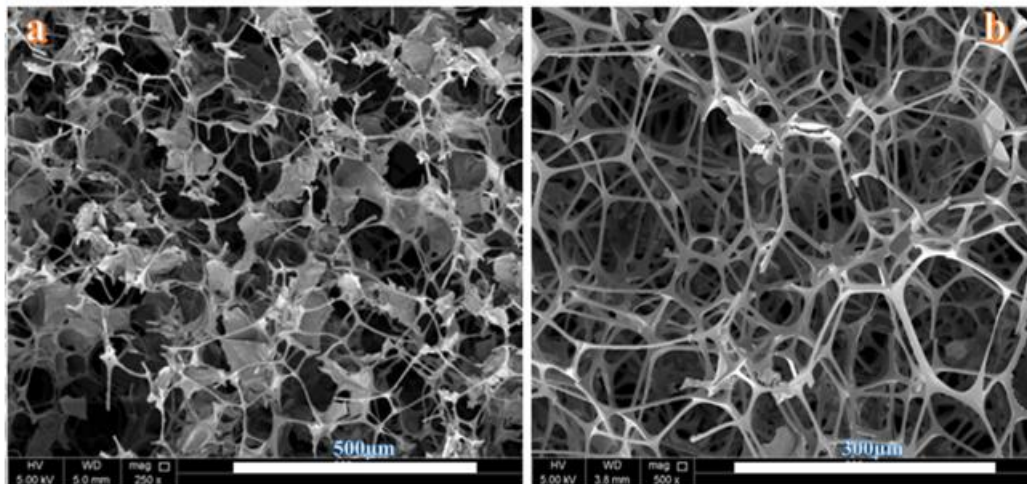


Figure 22: SEM image for ME foam treated with graphene

4.3.2 Surface wettability (contact angle) of neat ME foam and ME foam treated with graphene

The water and oil contact angle for the neat melamine foam under air and water were measured and results are summarized in figure 23. After the enhancement using graphene the water contact angle increased and the melamine foam turned into hydrophobic with a contact angle of 132° under air and 130° under oil.

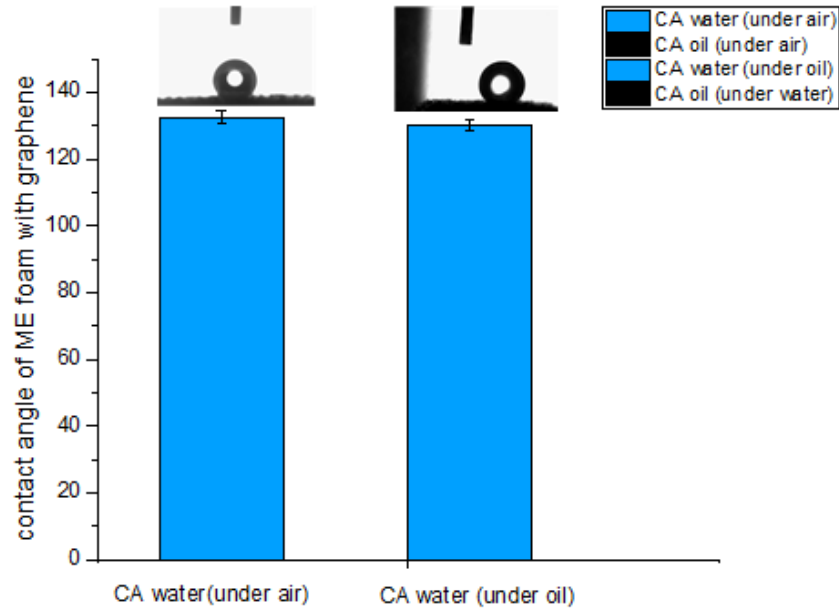


Figure 23: Water and oil contact angle values for ME foam treated with graphene

4.3.3 Sorption kinetics and oil absorption capacity of ME foam treated with graphene

Kinetics and oil absorption capacity was studied using water and three different oils crude, engine, and diesel. Figure 24 and table 12 shows the sorption ability of neat ME foam and as seen it have good sorption ability for oils.

Hydrophilic character was observed for neat ME foam as seen in table 12 as sorption ability is 66.5g/g. After the treatment with graphene the foam started to be float instead of being sunk and it changes to a hydrophobic character as the sorption ability of water become 2.2g/g when the foam was floating in water and 5.4g/g when the foam was immersed in water. In addition, figure 25 and table 13 shows an enhancement in the oil absorption capacity after the treatment with graphene.

In figure 25 it is demonstrating that oil absorption capacity varies with many parameters such as, density of oils, viscosity of oils, time, and amount/area of the foam immersion.

In this case the absorption time and mass of the modified foam were kept constant and

the main factor affecting the absorption performance was the viscosity of oils.

Table 12: Sorption capacity of neat ME foam

	Time (s)								
	0	30	60	90	120	150	180	210	240
	mass of absorbed oil (g/g)								
neat ME foam in crude oil	37.98	39.98	39.48	40.48	40.98	41.48	41.98	39.98	
neat ME foam in diesel oil	37.25	37.96	38.15	38.64	38.2	38.95	38.83	37.74	
neat ME foam in motor oil	27.36	28.72	29.56	30.89	32.47	34.86	37.72	37.96	
	mass of absorbed water (g/g)								
neat ME foam	62.75	64.25	65.63	66.63	67.25	68	68.63	68.88	

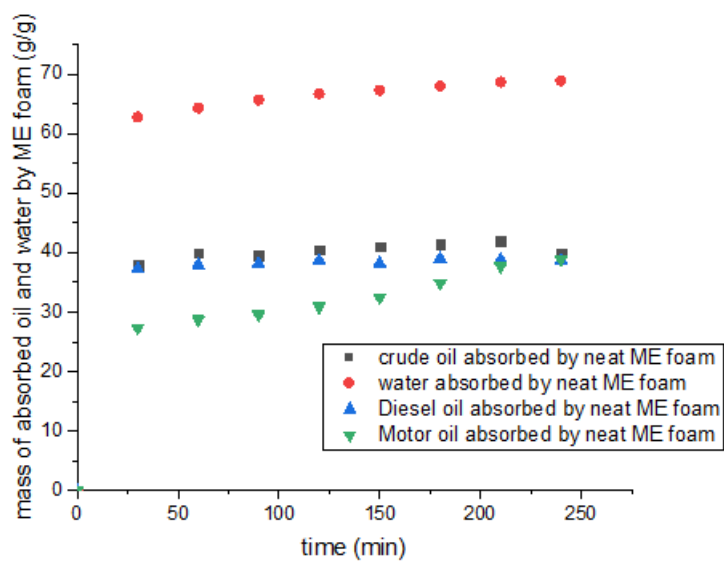


Figure 24: Mass of absorbed oil and water for neat ME foam

Table 13: Sorption capacity g/g of ME foam with graphene (G) in crude oil, engine oil, diesel oil, and water

Time (min)	2	4	6	8	10	60	120	180	240	300	after squeeze
ME+G in CO (g/g)	32.5	34	33	32.5	35.5	42.5	43	42.5	41.5	42	6.9
ME+G in EO (g/g)	18	25.5	28	29.5	28.5	32.5	33.5	36	36.5	37	7.9
ME+G in DO (g/g)	41	40	40.5	38	40	39.5	40.5	41	41.5	42	6.5
ME float on water (g/g)	2	2	1.5	1.4	2.4	3	2.4	3	2.5	2	0.01
ME immersed in water (g/g)	1.5	3	4.5	5.5	5.5	5	6.4	7	6.5	7	2

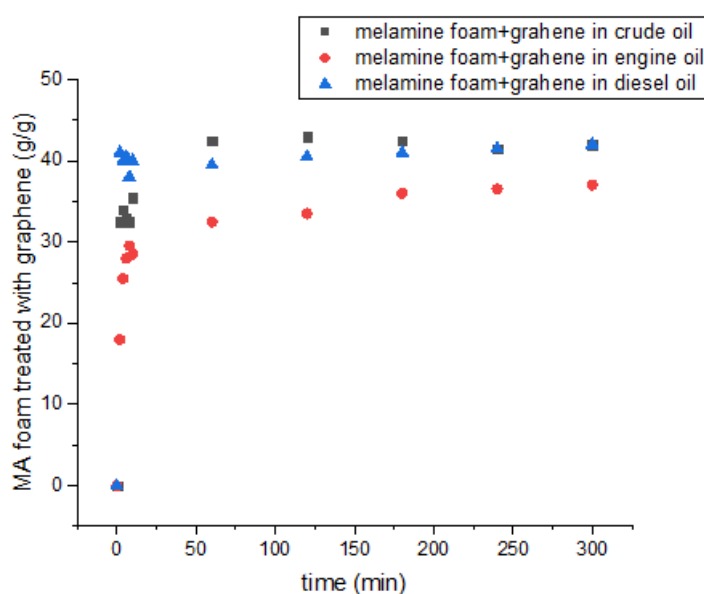


Figure 25: Mass of absorbed oil and water for ME foam treated with graphene

4.3.4 Reproducibility and multiply cycling sorption ability of ME foam treated with graphene

The multiply use of sorbents in general is desirable property of all sorbents, regardless the type of sorbent recovery. Foamy sorbents are frequently recovered by simple mechanical squeezing. For this purpose, the foam was immersed into the crude oil for 3 hours, then oil was squeezed out and the foam was immersed into the oil again,

without any additional cleaning or treatment. This procedure was repeated five times. More cycles were not realized because the foam has started to lose its mechanical integrity. Data recorded in this experiment were: the mass of foam after immersion, the mass of foam after squeezing of oil out, mass of squeezed oil, dimensions of foam before and after squeezing and it is summarized in Table 14, 15 and 16.

Some portion of the oil is irreversibly trapped in the foam and cannot be released by the simple squeezing. Obviously more oil would be released by applying higher forces, however, it would damage the foam. The amount of permanently trapped oil does not significantly change during multiply cycling and remains roughly at the same level as after the first sorption step. The amount of the released oil does not depend much on the number of squeezing steps, and the average mass of the released for crude oil is 45.30 ± 6.09 g/g, for diesel oil is 37.30 ± 1.20 g/g and 36.90 ± 2.58 g/g for engine oil. This is proved as seen in figure 27.

Table 14: Experimentally sorption parameters for ME foam in crude oil

No. of cycles	1	2	3	4	5	AVG	STD
Mass of oil(g)	0.72	1.01	0.95	0.85	1.00	0.91	0.12
Volume of oil(ml)	0.83	1.16	1.09	0.97	1.15	1.04	0.14
Mass of oil/mass of foam(g/g)	36.00	50.50	47.50	42.50	50.00	45.30	6.09
Volume of oil/volume of foam(ml/cm³)	0.83	1.16	1.09	0.97	1.15	1.04	0.14
mass of trapped oil/mass of foam	3.00	4.00	4.00	3.50	1.00	3.10	1.24
volume of trapped oil/volume of foam(ml/cm³)	0.07	0.09	0.09	0.08	0.09	0.08	0.01

Table 15: Experimentally sorption parameters for ME foam in diesel oil

No. of cycles	1	2	3	4	5	AVG	STD
Mass of oil(g)	0.78	0.73	0.76	0.72	0.74	0.75	0.02
Volume of oil(ml)	0.92	0.86	0.89	0.80	0.87	0.87	0.04
Mass of oil/mass of foam(g/g)	39.00	36.50	38.00	36.00	37.00	37.30	1.20
Volume of oil/volume of foam(ml/cm³)	0.92	0.86	0.89	0.85	0.87	0.88	0.03
mass of trapped oil/mass of foam	3.50	3.00	2.50	2.50	2.00	2.70	0.57
volume of trapped oil/volume of foam(ml/cm³)	0.08	0.07	0.06	0.06	0.05	0.06	0.01

Table 16: Experimentally sorption parameters for ME foam in engine oil

No. of cycles	1	2	3	4	5	AVG	STD
Mass of oil(g)	0.65	0.78	0.74	0.77	0.75	0.74	0.05
Volume of oil(ml)	0.66	0.79	0.75	0.78	0.76	0.75	0.05
Mass of oil/mass of foam(g/g)	32.50	39.00	37.00	38.50	37.50	36.90	2.58
Volume of oil/volume of foam(ml/cm³)	0.66	0.79	0.75	0.78	0.76	0.75	0.05
mass of trapped oil/mass of foam	5.50	5.50	5.00	5.00	4.50	5.10	0.42
volume of trapped oil/volume of foam(ml/cm³)	0.11	0.11	0.10	0.10	0.09	0.10	0.01

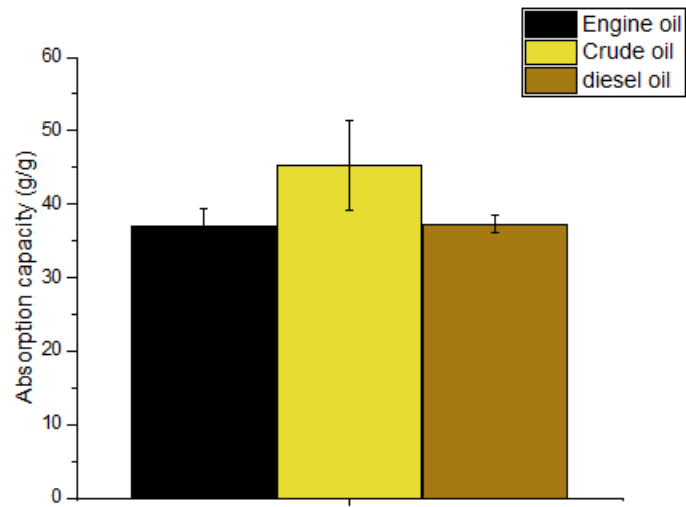


Figure 26: Cyclic foam average absorption capacity for crude, engine, and diesel oils

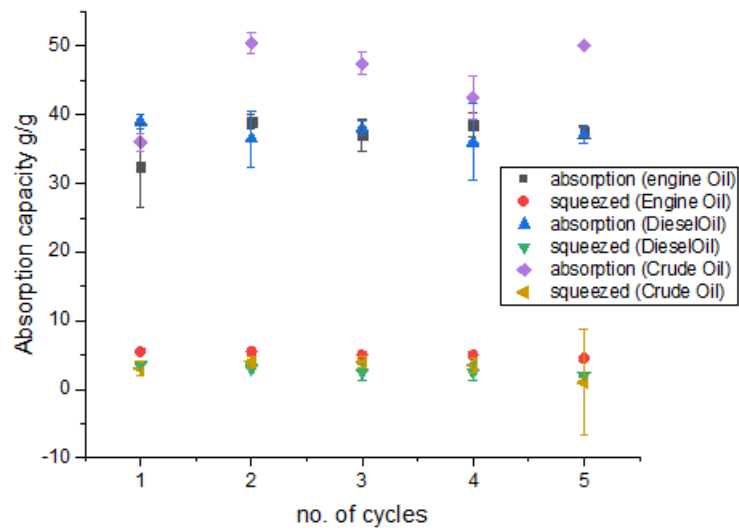


Figure 27: Cyclic ME foam treated with graphene (absorption-squeezing for crude, engine, and diesel oil)

Chapter 5: CONCLUSION

This study was divided into three parts, the first part is the synthesis of Qwax foam from paraffinic waste, its physical characterizations, and testing of sorption ability for different oils. Paraffinic waste product formed during PE synthesis (Q-wax) was used for the preparation of foamy, elastic structures through crosslinking by dicumyl peroxide and foaming by Genitron. The target of this work was the preparation a porous, hydrophobic and hydrophilic material with an appropriately high sorption ability for oil and low sorption of water, suitable for removal of free oil from water surfaces. The porosity of foam determined by computer micro-tomography was found of 58.9 %, and the bulk density of 0.42 g.cm³. The hydrophobic character of foam was observed under both air and oil as the contact angle values of water are 114° and 128°, respectively. On the other hand, super oleophilicity was observed for Qwax foam under both air and water as the contact angle values where 0°. The foams are thermally stable up to 360°C. Sorption ability of the foam were tested using heavy crude oil, diesel oil and engine oil. The absorption capacity of the foam in crude oil is 3.1±0.7 g/g.

The second part was dealt with the absorption ability of water and different oils of untreated polyurethane and melamine foams in multiply cycles. Both foams shown very high and fast sorption for all oil. The difference between melamine and polyurethane foams is in their sorption ability of water. Melamine foam, unlike polyurethane foams absorb water much faster, and therefore has low potential for separation of oil from water.

The third part is a treatment of commercial melamine (ME) foam using graphene. This type of treatment is to prevent water uptake and it increased the ability of foam to remain afloat. The target of this is to enhance the sorption capability of oils and to increased resistance to water uptake (superhydrophobicity). After the enhancement the

hydrophobic character of foam was observed under both air and oil as the contact angle values of water are 132° and 130° , respectively. super oleophilicity was observed for ME foam treated with graphene under both air and water as the contact angle values where 0° . Sorption ability of the foam were tested for ME foam treated with graphene for water and 3 different types of oils (crude, engine, and diesel). Regeneration of foams by squeezing and multiply applicability was tested.

The research future research will be oriented on optimization of porosity with tuned open pores of appropriate size, a reasonable mechanical strength, and mechanical stability in compression to perform more squeezing steps (over hundreds cycles as for MA and PU foams). The core problem seems to be an optimization of a degree of crosslinking. Highly crosslinking density would lead to the significantly higher mechanical strength improving number of working cycles, but a foam will be less swellable as it is common for highly crosslinked polymers.

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