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SEPARATION OF OIL/WATER MIXTURES BY CHEMICALLY MODIFIED MELAMINE FOAMS

BY

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ABSTRACT

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Title: SEPARATION OF OIL/WATER MIXTURES BY CHEMICALLY MODIFIED MELAMINE FOAMS

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Polymeric foams represent suitable porous sorbents for separating various contaminants dispersed in water. One of the most common polymeric foams is melamine (ME) foams, which are particularly suitable for removing oil impurities from water. The commercial ME foams provide facile, low-cost, recyclable, and efficient methods for treating oily water. ME foams are inherently highly oleophilic and hydrophilic. However, for practical reasons, it is suitable to enhance, or at least conserve olephilicity on the one hand, but suppress hydrophobicity on the other hand, and vice versa, to ensure efficient separation of oil/water mixtures.

In this work, a simple modification of ME foams was realized by their immersion in $FeCl_3$ solution. The process, due to the reaction of melamine resin with Fe^{3+} cations, leads to the significant enhancement of hydrophobicity of ME foams (water contact angle $\geq 150°$), maintaining their superolephilic character (oil contact angle ~ 0°).

The modified foams performed excellent separation efficiency for treating of various oily emulsions, synthetic produced water, oil/water mixtures, and showed high sorption ability of free oil.

Two types of oil in water emulsions were prepared and studied in this work, namely emulsions prepared by dispersion of diesel oil in distilled water, and synthetic produced water, which was prepared in such a way to mimic the real produced water by-produced from the petroleum industry. The ME foam purified highly concentrated diesel emulsions up to 1000 ppm of oil component with an efficiency of 94%. Synthetic produced water was also treated successfully by the modified foams with 91% efficiency. Even much higher separation efficiency was demonstrated for separation of o/w mixtures with volume portion of oil up to 60 vol.%., where the separation efficiency was greater than 99%. Finally, the oleophilic foams also exhibited high and fast sorption capability to remove free oils having an oil sorption capacity of 98-112 g/g. The approach explored in this work represents a cost-effective, scalable, and facile method of modifying ME foams, making them a feasible sorbent material for treating different types of oily polluted waters.

DEDICATION

This work is dedicated to

My father: Mohammed Hailan & My mother: Aziza

For their love, patience, faith, prayers, and for all the marvelous things they did, and Allah made me earn its goodness

To my beloved siblings Dr.Yousef, Dr. Amna, and Eng.Ali:

For being my first teachers and my unconditionally loving supporters

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CHAPTER 1: INTRODUCTION

1.1 General background

Oil and gas refining and processing is the backbone of the economy of many countries, especially in the Arab Gulf states. However, the petroleum and gas industry produce vast amounts of wastewater that cannot be disposed into the environment directly as it contains harmful oils and organic contaminants. Therefore, it is essential to treat wastewaters before releasing them into the environment. In detail, the by-product water resulting from the petrochemical, aluminum, steel, and food industry is termed as ‘’ produced water’’ or ‘’ oily wastewater’’. It is becoming an environmental pollutant due to its tremendous volume. For instance, in 2014, the volume of produced water was around 202 billion barrels increasing to 340 billion barrels in 2020 [1]. These huge volumes spotlight the importance of the oil/water separation field as such produced oil threatens the ecosystem.

Indeed, produced oil discharge is not only a serious environmental pollutant, but its danger also exceeds to even economic, energy, and health issues. For example, the complete elimination of water from fuel oil is crucial in ships, airplanes, and automobiles as even small amounts of water can lead to an expulsion that threatens transportation safety [2].

The efficient treatment of oil/water systems depends on the morphology of those mixtures. Generally, oil in water can occur as free oil, mostly floated on the water surface, dispersed, and emulsified depending on the size of the oil droplets in the water. Free oil is the one with the largest droplet size of greater than 150 μm or occurring as a continuous layer, dispersed oil droplets range from 20 μm up to 150 μm, and emulsified oil droplets are smaller than 20 μm. Emulsified o/w mixtures are the most complicated mixtures because their droplets size is very small [3]. Emulsified oil results in huge volumes in the petroleum industry because high amounts of surfactants and other polymeric additives occur in the oil recovered from the by-pass oil process and the oil trapped in porous reservoirs [4]. Demulsification of oily wastewater emulsions is a target surrounded by many challenges associated with very high stability levels and very small oil droplet sizes. Emulsified wastewater is commonly defined as a mixture of oil and water that is highly stabilized by various surfactants, and the average size of the oil droplets is below 20 μm. In another definition, emulsions are mixtures with oil droplets with even smaller scales from 0.1 to 10 μm, associated with the visible light range [5].

Since the separation of oil/water emulsions is challenging, it is fundamental to know the science of emulsions in-depth and explore their efficient separation processes. Conventional methods have been widely used for o/w separation, including centrifuging, gravity separation, ultrasonic separation, and biological treatments via different physical, chemical, and biological-based routes [5–7] [8–11]. However, conventional methods suffer from low efficiency, complexity, and the generation of secondary pollutants. Thus, conventional methods are replaced by membrane technology and sorbent materials.

Membrane technology is used to separate stable o/w emulsion, organic molecules, and dissolved oils by reverse osmosis techniques and size exclusion principle. However, although membrane technology can reach high purification levels, the membrane usually becomes fouled by oil, and needs to be renewed which is a very costly process. In addition to conventional methods and membrane technology, different organic materials (polymers) and inorganic materials were also employed to absorb oil form o/w mixtures selectively. Still, those materials are limited by the low separation efficiency and non-recyclability factor. Besides, those materials ended up being burned or buried under the ground, which is not accepted as it causes toxic gas emissions and very serious ground contamination [12,13]. As an alternate, great attention is paid towards using polymeric foams particularly melamine among other foamy materials including, polyurethane (PU) [14], PDMS, polystyrene [15], polydimethylsiloxane [16], polypropylene [17], and chitin [18]*etc*., because its performance in terms of o/w separation was outstanding compared to other reported foams.

Melamine foams are particularly suitable for different routes of o/w separations. This is because these foams represent a highly porous 3D network (around 98 vol.% of pores), chemical, thermal, and mechanical stability, easy availability, and low cost. Moreover, there are many possibilities for desirably modifying their wettability. The wettability of the foam can be tailored to attain a hydrophilic or hydrophobic surface. Furthermore, melamine foam is associated with very high elasticity enabling it to be re-used for thousands of cycles [19,20]. However, melamine foam is oleophilic and hydrophilic by its nature. Its wettability demands various physical and chemical modifications on its structure to switch it into the super hydrophobicity or superoleophobicity behavior. Many researchers functionalized melamine foam mainly by chemical etching and binding with nanomaterials [21]. However, those techniques are limited by the brittleness, high cost, and the damage they may cause to the environment, especially in the etching technique. [21] For that reason, there is a fundamental need for an environmental-friendly, facile, and scalable functionalization method that provides separating melamine foams with high efficiency and great robustness. In this study, melamine foam was modified by immersion in ferric chloride solution, which led to the creation of superhydrophobic/superoleophilic material. The main effect is switching the foam wettability from being originally a superhydrophilic material into a hydrophobic one. Indeed, this treatment is very efficient, eco-friendly, very simple, and a short-time consuming process. The as-modified foams by this method can separate oil in water emulsions and dispersions of various concentrations with high efficiency and remove free oil from water surfaces with a negligible water intake.

1.2 Research objectives

This research is focused on the efficient separation of oil in water mixtures. The particular interest is in a purification of emulsified (colloidal) o/w mixtures applicable for tertiary treatment of produced water. Indeed, a separation of o/w mixtures with high oil content, as well as sorption of neat oils was investigated as well. The separation of oil from water was realized by modified ME foams. Melamine foams are naturally hydrophilic and oleophilic materials. After treatment through crosslinking by ferric chloride, which forms a metal complex with melamine, the foam wettability turned from hydrophilic to hydrophobic, which is a favorable property for selective separation of various o/w mixtures. The ferric chloride as a modifying agent was chosen due to its high efficiency, low cost, and nontoxicity. The efficiency of the treated foams for separating various oily wastewater emulsions and dispersions has been tested at different oil concentrations and conditions.

The objectives of this thesis can be summarized as follows:

i.) Preparation and characterization of superoleophilic/superhydrophobic foams by modification of commercial ME foams through immersion in $FeCl_3$ solution

ii.) Separation of oil /water emulsions. The initial tests were performed using diesel oil as a contaminant, and the synthetic produced water mimicking real produced water was used.

iii.) Separation of highly concentrated oil in water mixtures (up to 60 vol.% of diesel oil content)

CHAPTER 2: LITERATURE SURVEY

2.1 Melamine foams

Melamine foam is a lightweight thermoset sponge with a porous 3D crosslinked networked structure that was successfully developed in the 1990s. Melamine foams are preferred over other foamy materials such as polyethylene, polypropylene, and polyurethane because the crosslinking degree in the melamine resin is the highest, along with higher cold resistance and heat stability. Due to the heat insulation feature associated with melamine foam caused by its rich nitrogen content, it is commonly used as a flame retardant in upholstered furniture, and up to this date, no adverse effects have been reported due to exposure to melamine when used as flame retardant which confirms that melamine is toxicologically safe. However, melamine resin (melamine sponge) is commonly referred to as melamine. The fabrication of melamine resin is based on the processing of melamine monomers. The decomposition of urea achieves the synthesis of melamine monomer. The synthesis of melamine monomer is carried out by two main methods: (i) liquid phase reaction, without catalyst under high pressure, and (ii) gas-phase reaction, with catalyst under low-pressure [22]. In either reaction, urea is decomposed into ammonia, and cyanic acid condenses to form a melamine monomer. Following that, the monomer is polymerized, crosslinked, and finally foamed to convert melamine monomer into melamine resin.

Melamine has many various advantageous features. For example, ME has sound absorption ability. Also, it has thermal insulation properties and strong temperature resistance up to 240°C. ME retains its properties over a wide temperature range and remains flexibly even at -200°C. Moreover, ME foams has a great resistance for abrasion and chemicals (organic solvents). The properties mentioned above are selected for the o/w separation process as it is feasible for such application [22]. Melamine foam, lightweight with its 3D connected fibrous structure, enables it to absorb water or oil with high capacity depending on the modification. Its elasticity ensures that it is a durable and recyclable technique. Indeed, its low cost and availability confirm that it is the most cost-efficient technique among other oil/water separation technologies.

2.2 Emulsions

In general, an emulsion is a colloidal system formed by two immiscible liquids. In the framework of this thesis, emulsions are created by either diesel or crude oil dispersed in water with and without surfactants. Emulsions prepared without surfactant were produced using intensive ultrasonication, ensuring sufficient homogenization of the mixtures. Despite that, according to the classical physical chemistry of colloids, the upper size of the dispersed phase is in the range of 0.5-1 μm, it is frequently referred to in literature that stable emulsified oil has a particle size below 20 μm [21].

Emulsified oil is the most challenging type to treat due to the very small droplets, and it is the most harmful type [23,24]. Indeed, the main reason behind the high stability of wastewater emulsions is the presence of surfactants, also called emulsifiers, which can be presented in wastewaters in large amounts.

Surfactants are chemicals that create self-assembled clusters called micelles when added to two immiscible liquids. The chemical structure of surfactant includes two different functional groups within the same molecule. Amphiphilic surfactants contain two main functional groups which are: (i) hydrophobic group, mostly long alkyl chain of around 8-22 carbon atoms, and (ii) hydrophilic group, which has an affinity towards water. This unique chemical structure enables surfactants to mix two liquids that do not mix naturally. This is because when surfactants are added to the oil/water mixture, the hydrophobic tail of the surfactant binds with non-polar oil droplets.

In contrast, the hydrophilic head of the molecule binds to the water molecule. With the growing number of oil droplets, the surfactant molecules attached to the oil droplet through the tail coalesce tighter, forming what is called'' micelles'' as shown in figure 1. When the surfactant atoms shield the oil droplet within the micelle, the presence of oil in water becomes more uniform and highly stable for a longer time than the oil/water mixture, which is quickly distinct [21].

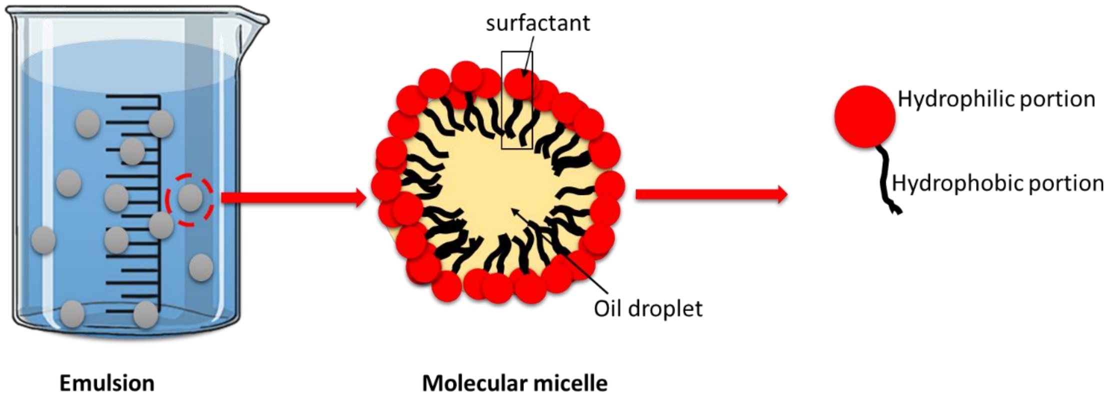


Figure 1. The formation of molecular micelles containing oil droplets shielded by surfactant molecules.

2.3 Surface wettability

Pristine ME foam is naturally oleophilic and hydrophilic. However, this wettability must be switched into the manner where the foam selectively absorbs oil and repel water by enhancing foam's oleophilicity and reducing its hydrophilicity. This can be achieved by applying suitable chemical or physical surface. Surface wettability of any materials is investigated by the contact angle measurements, which are held by dripping polar and non-polar liquids on the material surface. In that system, three main phases exist, including the (i) solid surface, characterized by surface tension, (ii) the surface energy of the liquid, and (iii) the surrounding phase, which is in contact with both former phases, and it is usually air (zero surface energy).

For the case of o/w emulsions and mixtures, the solid phase is represented by the sponge, the liquid phase is represented by the oil, and the third phase is the water (pure or brine). Hence, performing oil contact angle underwater is crucial for determining the sponge wettability towards oil. Considering the situation above, namely the determination of underwater contact angle of oil on a solid surface, the contact angle can be expressed by Equation (1) [25]:

$$\cos\Theta_W = \frac{\gamma_{SW} - \gamma_{SA}}{\gamma_{WA}} \tag{1.1}$$

$$\cos\Theta_O = \frac{\gamma_{SO} - \gamma_{SA}}{\gamma_{OA}} \tag{1.2}$$

$$\cos\Theta_{OW} = \frac{\gamma_{OA}\cos\Theta_O - \gamma_{WA}\cos\Theta_W}{\gamma_{OW}} \tag{1.3}$$

Where γ_{OA}, γ_{OW}, and γ_{WA} reflect the interfaces of oil/air, oil/water, and water/air, respectively. Θ_O, $\Theta_{OW,}$ and Θ_W represents, respectively, the contact angles of oil under air, oil contact angle under water, and water under air. From Eq. 1 it can be concluded that hydrophilic surfaces in air surroundings are also oleophilic in air surrounding because of $\gamma_{OA} << \gamma_{WA}$. Moreover, hydrophilic surfaces in the air are also oleophobic in water, as shown in Eq1.2. [28]. There are different models addressing wettability reported in literature; the oldest one has been developed by Young (1805**)** [27]**.** Wettability of smooth chemically homogeneous solid surface is described by the following equation (Eq. 2):

$$\cos\theta = \frac{(\gamma_{SA} - \gamma_{SL})}{\gamma_{LA}} \tag{2}$$

where γ_{SA}, γ_{SL} and γ_{LA} are the surface free energy of solid/air, solid/ liquid, and liquid/ air. The wettability of rough surfaces is described by Cassie and Baxter model (1944) [28], which postulated that a liquid droplet cannot penetrate through the cavities of the rough surface as those cavities are accumulated by air molecules which leads to a composite interface. The following equation was proposed based on that model (E.q.3):

$$\cos\theta_* = F_{SL}\cos\theta_1 + F_{LA}\cos\theta_2 \tag{3}$$

Where F_{SL} is the fractional area between the solid surface and the liquid droplet, and F_{LA} is the fractional area between the liquid droplet and the air trapped inside the pores of the rough solid surface. θ_1 and θ_2 are, respectively, the contact angle of the liquid droplet in contact with the solid surface and in contact with the air. For the proposed composite interface of this model, the air trapped in the rough surface cavities is non-wetting (θ_2=180°) and $F_{SL}+F_{LA}=1$. Figure 2 summarizes the surface wettability of various interfaces.

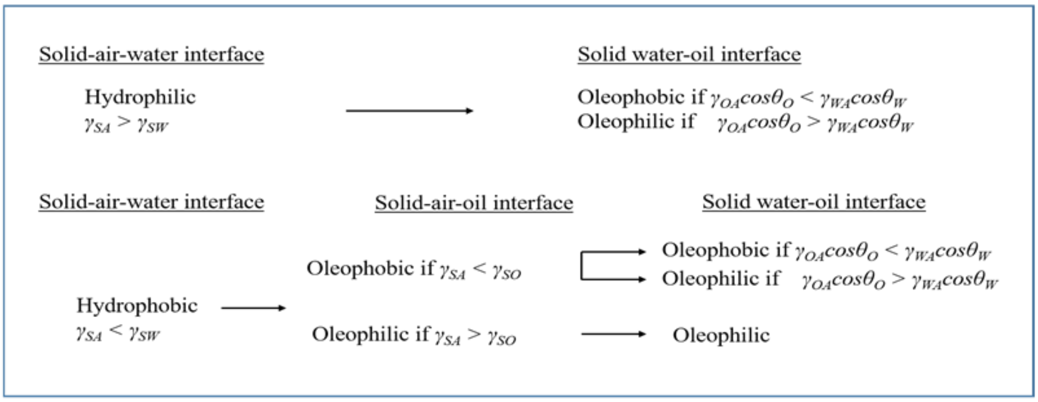


Figure 2. Summary of wettability characteristics of various interfaces.

Indeed, a wettable surface will enable liquid to be absorbed into it through the pores, and the detected contact angle must be less than 90°, whereas, on a non-wettable surface, the liquid droplets will remain on the surface retaining its quasiparticle shape with a high contact angle larger than 90° for phobic materials and even greater than 140° for ‘’super-phobic materials’’ [29]

The surface energy between the solid phase (foam surface) and the liquid that is physically contacting the solid phase, the roughness of the solid phase, and the surface charge are all curial parameters affecting the surface properties and its correlated wettability. The highly stable oxygen-hydrogen covalent bonds of water are the source of the high surface tension of water (72.8 mN/m) [30]. Indeed, the surface tension of oil is much lower than that of water because the strength of hydrocarbon bonds is less. For that reason, separatory polymeric foams must be modified so that their surface energy is in between the surface tensions of water and oil [30–33]. Moreover, melamine foam surface is smooth, but when modifying the foam, creating a rough surface is demanded because it will provide capillary forces for oil to penetrate and travel through the foam while water will be prevented from entering with the help of rough surface [34]. Furthermore, the existence of any charge on the foam surface can enhance or devalue the performance of foams. To clarify, a negatively charged surface such as a foam containing fluorinated ions will repel the water molecule's hydroxyl side, which boosts the surface hydrophobicity [33].

In addition to the surface topography, the internal structure of foam significantly influences its wettability, including the porosity of foam, pore size, and total interconnectivity. Porosity is directly related to the sorption capacity of foam because when the foam is very porous, the gaseous phase volume is high, which increases the available volume for sorbate liquids.

It is well established that the greater the porosity of foams, the higher the oil capacity of the foam becomes. This is clearly because the amount of the gaseous phase in the foam will be higher, thereby the volume of the absorbed oil. The correlation between absorption capacity (AC) and foam's porosity was described by Pinto *et al*. where ρ_f is the foam density and ρ_{oil} oil density (Eq.4) [35]**:**

$$AC = V_f . \frac{\rho_{oil}}{\rho_f} \tag{4}$$

Indeed, the interconnectivity between the pores provides well-connected capillary forces that enhance oil sorption. Moreover, capillary forces, which absorb the oil, depend on the pore diameter. Thus, adjusting the foam’s pores size along with the properties of the oil (surface tension and viscosity) can help the foam to reach its maximum sorption capacity with longer retention times. Moreover, interconnectivity within pores is critical as it allow the liquid to travel and penetrate through the foam and as the pore’s connectivity approaches 100%, the oil intake will be the maximum in very short times.

Nonetheless, foam’s tortuosity influences the sorption rate. For instance, a certain surface tortuosity can establish longer paths for oil until it finally reaches the inner pores thereby decreasing the sorption rate.

2.4 Chemical modifications of melamine foams

Melamine foam is hydrophilic by nature, and to switch its surface wettability into hydrophobicity, a suitable chemical modification must be performed. The methods of modification, conditions and modifying materials are various, and each method has its success and its limitations, but the goal remains to be finding a feasible method that produces the most efficient polymeric foam with high separation efficiency, simple recycling and recovery, good mechanical properties, and a reasonable price. For example, Ruan *et al.* [36] utilized perfluoro-organic materials (1H, 1H, 2H, 2H-perfluorodecanethiol, and dopamine to coat the ME foam surface schematically shown in figure 3. The water contact angle of the coated foam was ~154°, and its sorption capacity was 68-172 g/g. Nonetheless, perfluoro-organic materials are well known to be expensive and toxic, which is not practical for large-scale applications.

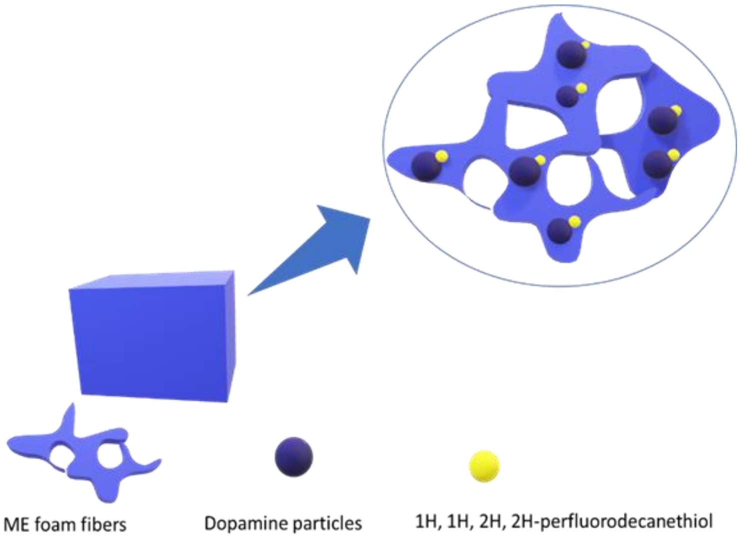


Figure 3. Schematic representation of the modification of ME foam using dopamine and perfluoro-organic materials

Nanomaterials have also been utilized to modify polymeric foams, mainly using microwave/ultrasonic-assisted deposition or via the combination with organic materials. In this regard, Gao *et al.* [37] modified ME foam by combining vinyltrimethoxysilane (VTMS) polymer and silica nanoparticles. The modified foam performed high sorption capacity (60-109 g/g), and the water contact angle was more than150°. However, although the as-fabricated VTMS/silica modified ME foam presented excellent WCA and great sorption capacity, its poor reusability caused by the frequent aggregation of silica nanoparticles devalued its feasibility to be used for large-scale applications.

Carbonization approach has also been tested for the modification of melamine foam. Stolz *et al*. [38] carbonized melamine foam by pyrolysis at 500°-600°C under inert gas for 1h (figure 4). The obtained foams performed high absorption capacity of 90-200 g/g. The water contact angle of the carbonized foams was in the range of 120°-140°. The carbonization process had successfully reduced the surface energy, but, on the counter, it demolished the foam's mechanical properties, which makes it insufficient in terms of reusability and durability.

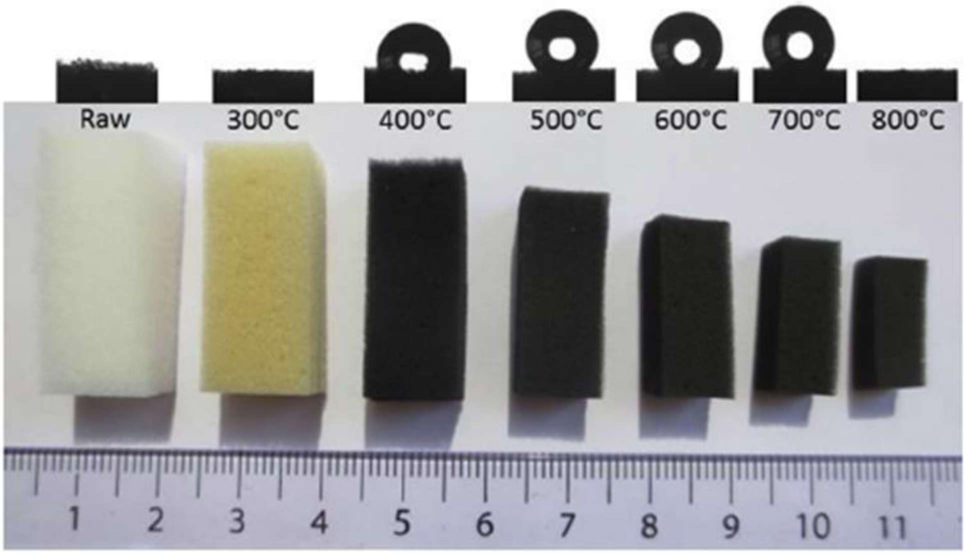


Figure 4. Photographs of pristine and carbonized ME foam (300-800°C) along with their contact angle images. At 300°C and 800°C, the carbonized foams absorbed the water droplets wholly and rapidly.

Indeed, in the literature, variant treatments following different approaches were applied to pristine ME foam and tested for demulsification processes of oil in water emulsions (OW) and water in oil emulsions (WO) with surfactant (SOWE, SWOE) and without surfactant. Table 1 summarizes the recent, most efficient studies.

Table 1: Treating materials developed for modifying ME foams, the resulted WCA (°), corresponding absorption capacity (AC) in g/g, demulsification efficiency (%) and type of utilized emulsion

Treatment	WCA	AC	Efficiency	Emulsion	Ref.
Polybenzoxazine	162°	170	99.9%	SWOE	[39]
Reduced graphene oxide	164°	0.002-5647	95 -97%	OWE	[40]
β-FeOOH NPs	155°	65–136	99.5%	OWE	[41]
Caffeic acid-PEI	150°	-	97%	SOWE	[42]
Dopamine (DA) +PEI	142°	67-177	94%	OWE	[43]
Mg $(OH)_2$	160°	70-190	99.7%	OWE	[44]

Treatment	WCA	AC	Efficiency	Emulsion	Ref.
Co-ZIF-L	-	26–61	98%	OWE	[45]
PDA/ DDT	158°	45–99	77-94%	OWE	[46]
Fe_3O_4 NPs+PVDF-HFP	130°	29-44	-	WOE	[47]
Carbonization + perfluoro-organic materials	158	17–43	-	OWE+SOWE	[48]

However, to this end, the current modification methods suffer from either low efficiency, high cost, toxicity, or brittleness. For that reason, herein, modification technique based on crosslinking ME foam with ferric chloride. This treatment is facile, low coast, and very environmentally friendly.

2.5 Modification by ferric chloride

Various modifying approaches have been reported in the literature, but only a few of those approaches are facile, cheap, reusable/recyclable, and environmentally friendly. Reusability is a key parameter when it comes to modified polymeric foams as the primary purpose standing of choosing them in the field of o/w separation is the fact they are cost-efficient. From an economic point of view, if the polymeric foam is not reusable and must be replaced each time, this method is no longer cost-effective. For this purpose, the method introduced in this work for modifying melamine foams accounts for the recyclability factor and the utilization of environmental materials via the facile procedure.

The approach is based on the crosslinking of the melamine sponge with $FeCl_3$. The transition metal complex induces hydrophobicity. In detail, ME foam is a polymer consisting of the 2,4,5-triamino-s-triazine repeating structural units, which by hence means that the foam is rich in nitrogen content having unpaired electrons in its atom. However, when transition metals are added to the polymeric foam, they reduce the foam polarity, constructed by unpaired electron pairs of a nitrogen atom, forming a coordination metal complex structure (shown in figure 5). It was shown that low concentrations of transition metals are enough to produce superhydrophobic foam [21]. For instance, ME foam modified by only 0.001M $FeCl_3$ was superhydrophobic with a water repellent angle of ≥140°.

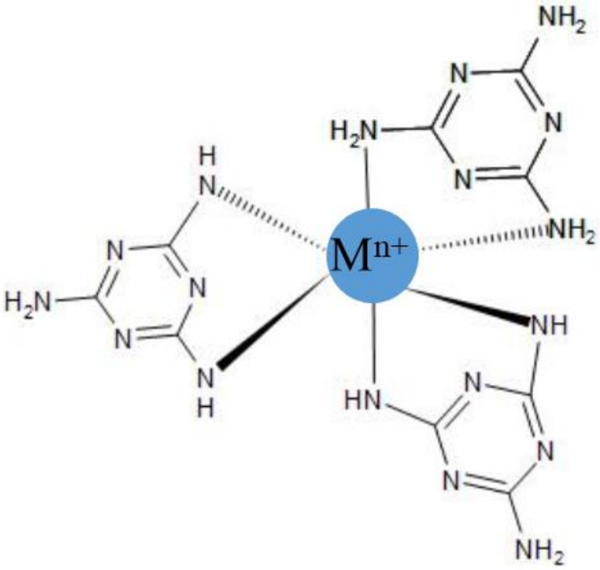


Figure 5. Formation of transition metal complex between the transition metal and ME foam.

2.6 Demulsification

The demulsification process by modified foam begins initially by placing the foams on the surface of the emulsions. Then, emulsion starts to penetrate the foam. In the case of oil in water emulsions, emulsion inter the skeleton of the foam. When it penetrates, oil gets absorbed onto the internal surface of the foam due to lipophilicity. The continuous sorption of emulsion increases the oil content inside the foam, which may promote coalescence between oil droplets forming large particles and saturation of foam by oil phase while the amount of water within the foam decreases until it ultimately repelled out as schematically shown in figure 6 [21].

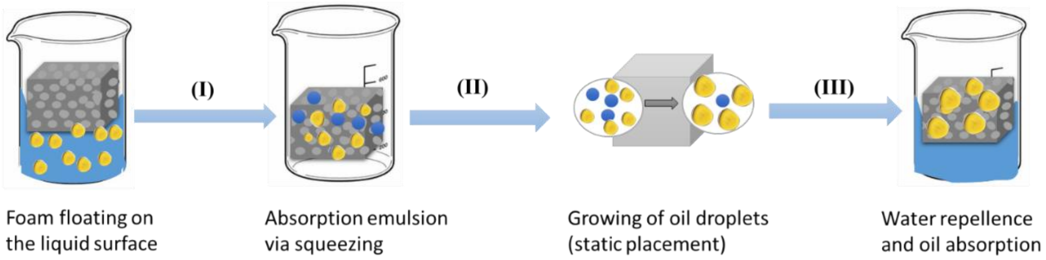


Figure 6. Demulsification by modified ME foams

CHAPTER 3: METHODOLOGY

3.1 Materials

Commercial melamine foams were purchased from LTWHOME. Ferric chloride ($FeCl_3$,97% purity) was purchased from Research-Lab Fine Chem Industries and used for the ME modification as received.

In addition, the following salts were used for the preparation of synthetic produced water: potassium chloride (KCl) (99%) obtained from Sigma-Aldrich, sodium sulfate anhydrous (Na_2O_4) (100%) obtained from VWR chemicals, sodium dodecyl sulfate surfactant ($C_{12}H_{25}NaO_4S$) obtained from Riedel-de Haën, calcium chloride (CaCl) (90%), ammonium chloride (NH_4Cl) (99.5-100.5%), sodium chloride (NaCl) (99.5-100.5%) and magnesium chloride ($MgCl_2$) (95.21%) all obtained from BDH Chemicals Ltd Poole.

3.2 Experimental

3.2.1 ME foam crosslinking with $FeCl_3$

The modified foams were prepared by immersing the foams in ferric chloride solution at four different concentrations (0.001M, 0.005M, 0.01M, and 0.02M) at room temperature for 15 minutes. Then, foams were further washed with distilled water to eliminate untreated $FeCl_3$ residues (figure 7,8).

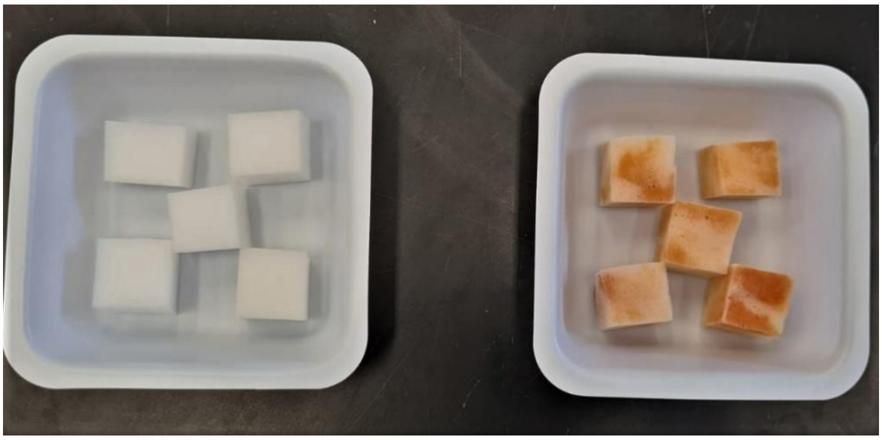


Figure 7: Photoshoot of white pristine ME foams and treated ME foams (0.01M appearing in yellowish color.

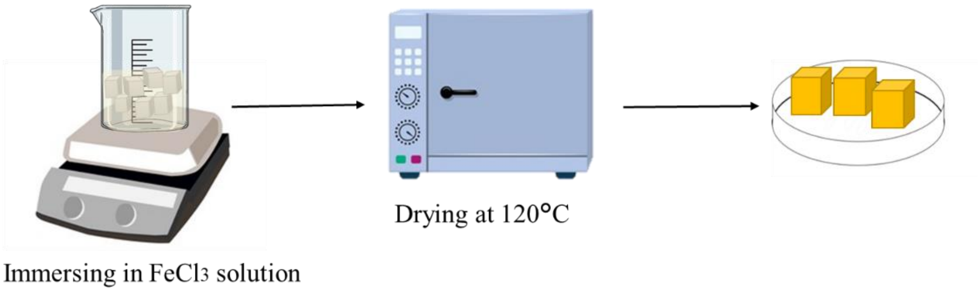


Figure 8. Sketch of the preparation process of modified foams via immersing in $FeCl_3$ solution.

3.2.2 Preparation of emulsions from diesel oil

The first emulsions were prepared using diesel oil as a model oil contaminant dispersed within the water. Different concentrations were prepared by adding an appropriate amount of diesel oil into distilled water. The solution was then sonicated by probe sonicator for 40 min at room temperature.

3.2.3 Preparation of synthetic produced water

The preparation of synthetic produced water (PW) was performed according to Dardor *et al.* [49]. A research team from ConocoPhilips in Qatar has developed this protocol to mimic real, low salinity produced water were added to 1000 ml of distilled water and stirred for 30 minutes, then, to 500 ml of that brine, 0.18 ml of crude oil was added. Following that, the low salinity emulsion was moderately stirred for 30 min and sonicated by a probe sonicator for 30 min. Finally, the synthetic produced water was left in a funnel for 4h to remove the formed thin oil layer, and the rest of the emulsion was then used for further tests. It has to be mentioned here that despite the constant preparation route, the multiply preparation of synthetic water has led to various values of organic carbon content in prepared emulsions, roughly in the range from 170 to 230 ppm.

3.2.4 Sorption experiments

Most of the sorption experiments were done in falcon test tubes of 50 ml. The size of testing foams was arbitrarily chosen at 1.5 x 1.5 x 1.5 cm. The number of testing foams varied from 1 to 7 pieces. Testing foams were inserted into tubes and filled with testing emulsions. Sorption experiments were realized over the selected time periods from 1 to 24 hours at room temperature. The tubes were shaken by a mechanical shaker to suppress the formation of concentration gradients within emulsions during the experiment duration, as shown in figure 9.

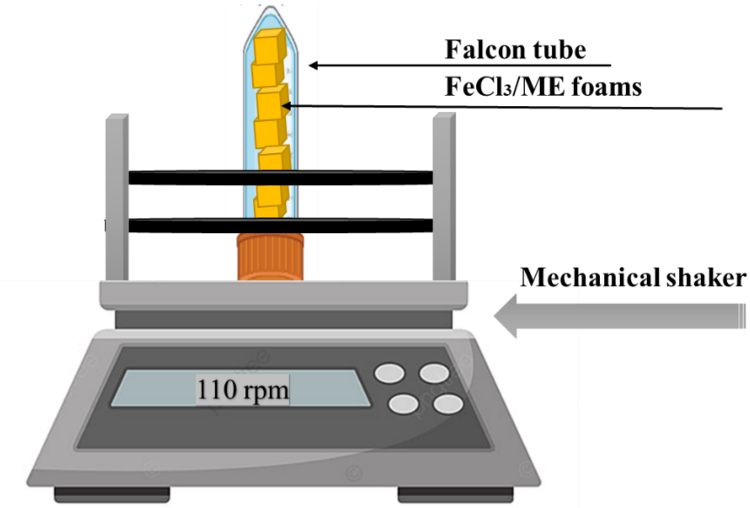


Figure 9. Sketch of the experimental sorption setup

3.2.5 Demulsification experiments

Multiple emulsions of different concentrations were prepared, and sponges were added to those emulsions to demulsify them. In those experiments, the emulsion was prepared, treated foams were added, and mechanically shaken for selected periods. Post that, the foams were taken out of the emulsion and squeezed out to release highly concentrated emulsion while the tube containing the filtrate is oil-free to a certain extent dependently on the foam efficiency (figure 10). However, the filtrate concentration was consistently determined by TOC measurement.

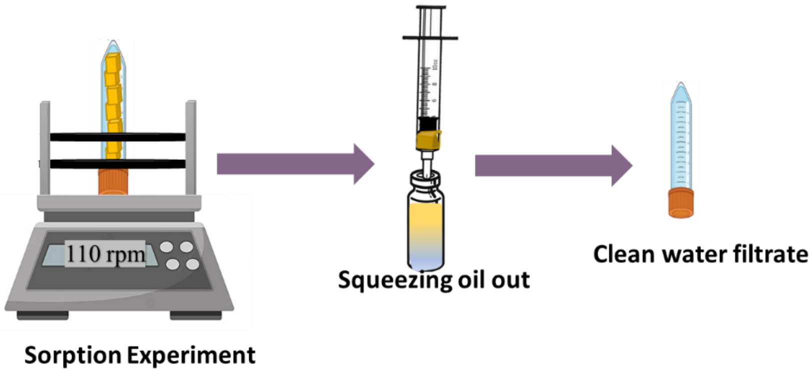


Figure 10. Demulsification experiment set up of modified foams

3.2.6 Sorption/Desorption Cycles tests

Sorption/ desorption cycles were done by immersing the foams in oil for 10 minutes, followed by squeezing out the foam by syringe (figure 11).

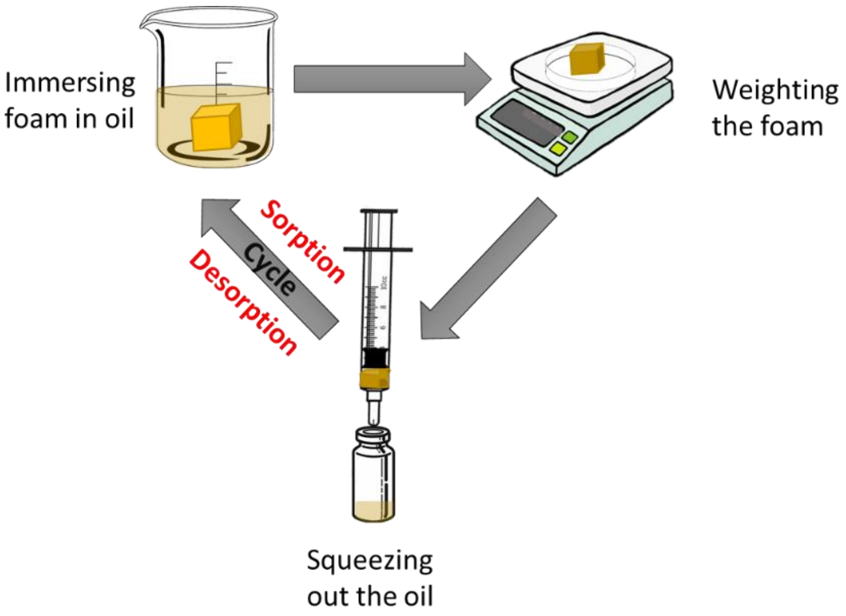


Figure 11.Schematic representation for the sorption/desorption cycles of oil by modified foam to determine its sorption capacity recyclability

3.2.7 Absorption capacity measurements

Modified foams with dimensions of 1.5 x 1.5 x 1.5 cm were used to test the foam's absorption capacity to oils of various densities (diesel, motor, and crude oil). Oil’s sorption capacity was calculated based on the following formula [50]:

$$\text{Absorption capacity (AC)(g/g)} = \frac{m_1 - m_0}{m_0}$$

Where m_0 and m_1 are the foam's initial mass and the foam's mass after absorbing the oil.

3.2.8 Density Measurement

Stock size sponge (3 x 6 x 9 cm) was used for determining the density of the foam by the following formula:

$$\rho(\text{g/cm}^3) = \frac{\text{mass}}{\text{volume}}$$

The density of treated foam was found to be 0.007 g/cm^3.

3.3 Characterization Techniques

3.3.1 Surface morphology analysis and elemental analysis

The morphology of untreated and treated ME foams were analysed by scanning electron microscopy (SEM), (FEI Quanta 200 ESEM, Thermo Fisher Scientific ™, USA) equipped with Energy-dispersive X-ray spectroscopy (EDS) by Secondary electron images with 3 kV and different magnifications. All specimens were sputter-coated with 2 nm gold before the use of the SEM. The unmodified and modified foam with the concentration of 0.01M was observed at different magnifications: 100x, 250x, 500x, and 1000x. The distance between the electron source and the sample surface (working distance, WD) was set within the range of 4.5-6.8 mm. The acceleration voltage was 5.0 kV.

3.3.2 Topography measurement

The topography of the oil droplets in emulsions was characterized by profilometry (The Optical Surface Metrology System Leica DCM8, Mannheim, Germany). This system allows measuring the 3D surface topography of larger surface areas with no limits to the roughness. It contains five objectives with different magnifications (5x, 10x, 20x, 50x, and 100x), allowing for analysis of samples using different-size areas, and a highly sensitive detector (1.4 million pixel resolution) was used for obtaining confocal images.

3.3.3 Composition analysis techniques

Fourier-transform infrared spectroscopy (FTIR) (Spectrum 400, PerkinElmer, USA) was employed to identify chemical shifts caused by ferric chloride binding to the ME foam at the four different concentrations. FTIR spectra were recorded for modified melamine foam surfaces in the wavenumber range of 500-4000 cm $^{-1}$.

3.3.4 Surface wettability investigation

The surface wettability of foams through the contact angles measurements was investigated by System OCA 35 (Dataphysics, Germany). The test was done using three different liquids: ultrapure water, diesel oil, and motor oil. Contact angle measurements were done in the air and under water. The test was done by dripping testing liquid droplets of 3μL volume at a constant flow rate of 2 μL/s on the foam's surface. The droplets were released at different surface areas, and multiple readings were obtained to attain representative average contact angles. Moreover, the surface wettability of foam was determined by different approaches, including oil contact angle under air surrounding, water contact angle under air, and oil contact angle under water surrounding for neat and treated foams.

3.3.5 Characterization of size and surface charge of oily emulsions

All the as-prepared emulsions were always firstly characterized by dynamic light scattering (DLS) and Zeta potential (ZP) measurements.

DLS, also known as quasi-elastic light scattering or photon correlation spectroscopy, was used to determine the colloidal size of the oil droplets in the OWE. ZP, also known as Electrokinetic potential, was used to determine the repulsive force between particles in their charge. The two techniques are evolved in one instrument called the Zetasizer. Malvern labs provided the Zetasizer instrument utilized in this work. Both types of measurements were performed by preparing 12 μl homogenous samples and placing them in disposable glass cuvettes DTS1070 (3 × 3 mm, 5 × 5 mm, or 10 × 10 mm) for the DLS and 2 μl sample using ZS90 cuvette for the ZP. Each measurement was performed in triplets.

3.3.6 Determination of emulsions concentration

The concentration of oil in emulsions which is the amount of oil present in the prepared emulsion was determined frequently using the total organic carbon technique (TOC) provided by Analytikjena. TOC is the amount of carbon in an organic compound commonly used as an indicator of water purity. There is also another different mode in the instrument, including the analysis of total carbon (TC), total inorganic carbon (TIC), and non-purgeable organic carbon (NPOC). The last-mentioned method involves acidifying the sample with phosphoric acid, then purging the sample with a nitrogen carrier gas, and then the amount of organic carbon in liquids is obtained. NPOC mode was mostly used for identification of oil concentration in emulsions.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterization of modified foams

The most significant key parameter in determining the feasibility of any possible o/w separation material is wettability tests, characterized by the contact angle measurements. However, when performing the test, it was found that the pristine foam is superhydrophilic with 0° under the air surrounding. On the other hand, modified foams of all concentrations were superhydrophobic with a similar water contact angle (all above ≥140°). In detail, the WCAs of modified ME foams with the concentration of 0.001M, 0.005M, 0.01M, and 0.02M were 146° ± 2°, 148° ± 4°, 153° ± 2° and 150° ± 4° (figure 12), respectively. Indeed, the water droplets, when released onto the treated foam surface, retained their quasiparticle shape as shown in figure 13. However, the results indicated that even low concentrations of ferric chloride (0.001M) are sufficient enough to produce superhydrophobic foam with superior water-repellent angle of 146°±2°.

Further increase in the concentration, did not lead to a significant enhancement in the WCA; however, a slight increase was detected, and the highest repellent angle was associated with the concentration of 0.01M, so this solution was arbitrarily chosen for further experiments. Moreover, the obtained WCAs were significantly higher than the results reported by Ding *et al*. [50] for the same treatment. In his paper, Ding *et al.* immersed ME foams in $FeCl_3$ solution at different concentrations and the WCA for the 0.001M, 0.005M, 0.01M, and 0.02M were 123° ± 8°, 121° ± 8°, 127° ± 10°, 127°± 9° which are less by at least ~15° than the results reported in this work.

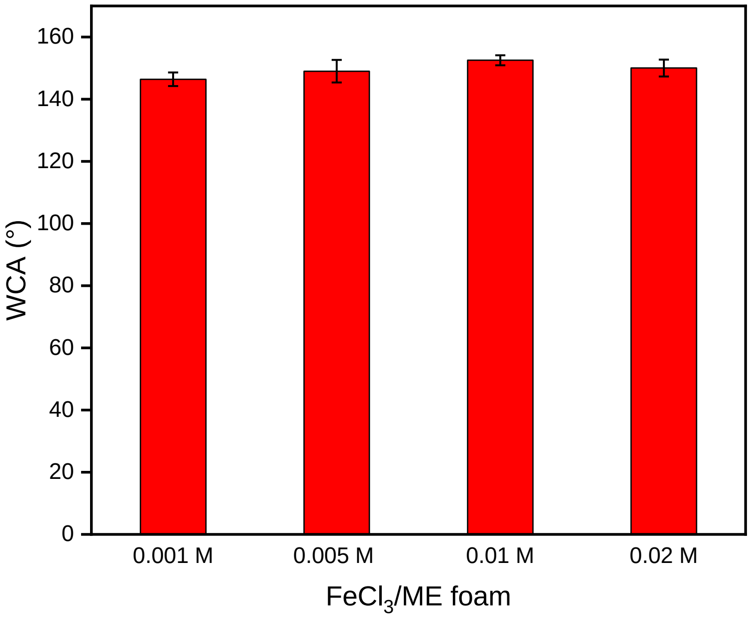


Figure 12. The water contact angles of modified ME foams

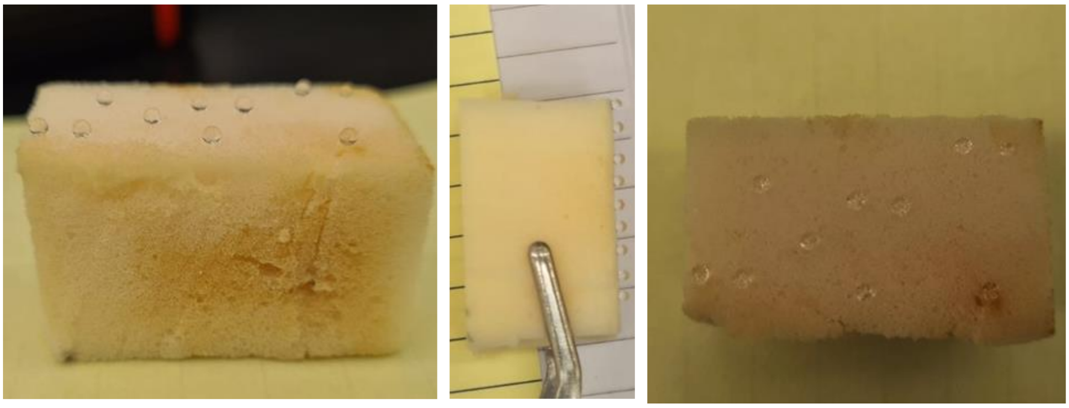


Figure 13.Photoshoots of the water droplets deposited on the surface of the treated foams.

Moreover, for the oil contact angle under air, all foams (pristine and modified) with no exceptions were oleophilic with 0° contact angle. However, for the oil contact (diesel and motor) angle under water surrounding, the pristine foam immediately sank inside the water once placed on its surface due to its hydrophilicity which prevented the oil droplets from penetrating into the foam's skeleton as the skeleton was fully saturated by water. However, for the case of modified foams, the oil droplets were quickly absorbed onto the foam within less than 1s with 0° angle (superoleophilic).

Nonetheless, the morphology of untreated and treated ME foam was investigated using a 2D scanning electron microscope (SEM) at a magnification of 100x, 250x, 500x, and 1000x as shown in figure 14(A-H). The SEM images showed that crosslinking by ferric chloride did not significantly change the morphology of the foam. The foam retained its open cell foamy structure and its smooth fibrous network. Indeed, in figure 14, H, small particles are observed, attributed to aggregated $FeCl_3$ salt particles. However, ferric chloride aggregates can also be beneficial as they provide some source of roughness to the surface. Surface roughening is demanded because it provides capillary forces which prevents liquids from entering the groves of the foam. Metal complex crosslinking lowers the surface energy of the foam and its agglomerated particles, indeed, roughen the foam surface by creating small gaps throughout the surface which prevent water diffusion [51].

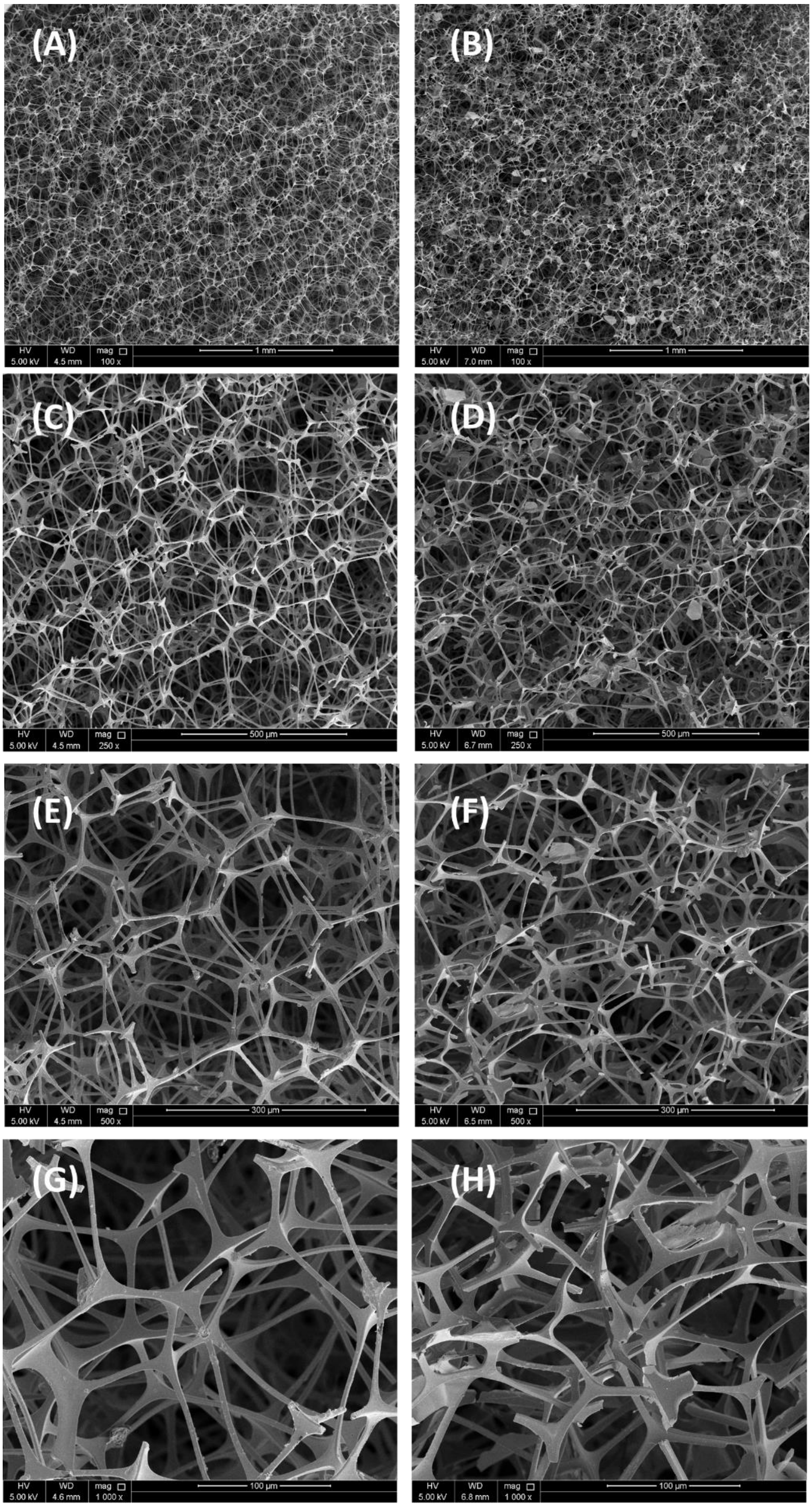
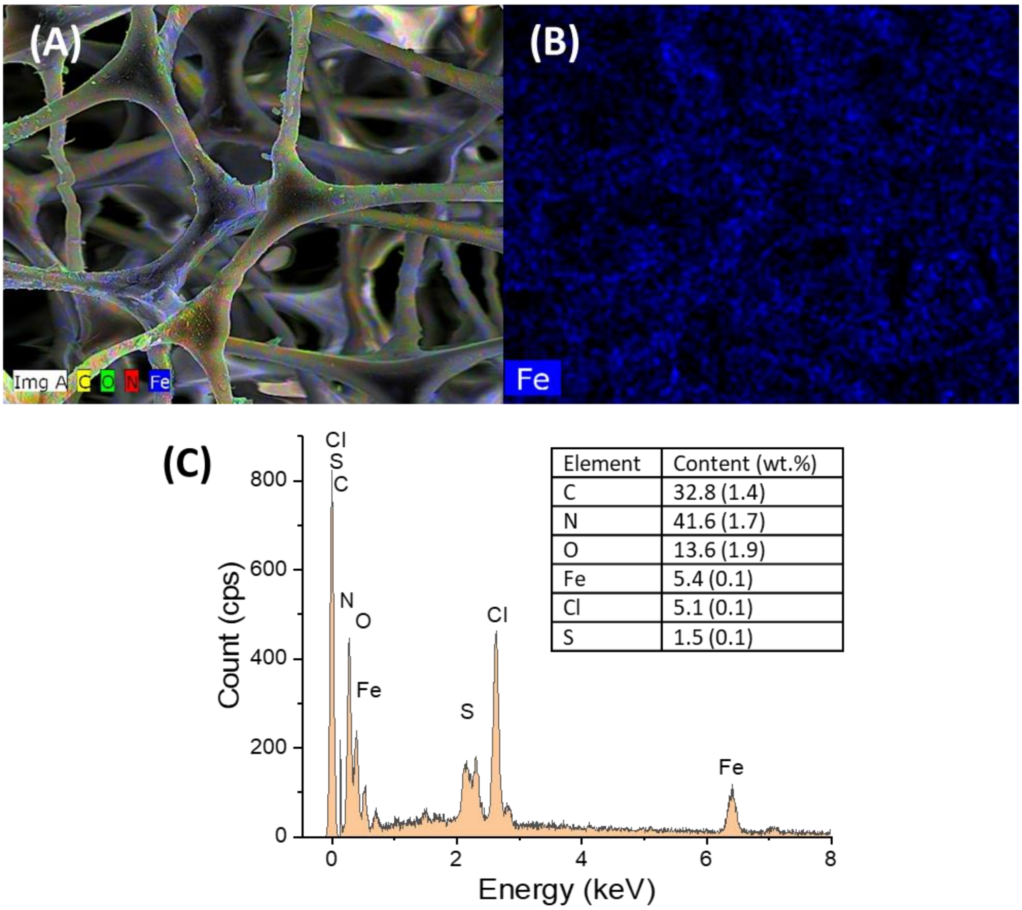


Figure 14.SEM images of prestine foam (A,C,E,G) and treated foam (B,D,F,H) at magnifications of 100x, 250x, 500x and 1000x recpectively

EDS analysis was performed for cross-section of Fe modified melamine foam. Figure 15.A shows EDS mapping of foam where C, O, N and Fe was scanned and shows as different colors. Figure 15.B shows only Fe element where a homogenous distribution of Fe confirming successful modification of melamine foam. Mass analysis (Figure 15.C) of EDS identified several elements, such as C as 32.8 wt.%, N 41.6 wt.%, O 13.6 Fe 5.4 wt.%, Cl 5.1 wt.% and S as 1.5 wt.%. C, N and O elements belongs to melamine foam structure. Fe and Cl belong to $FeCl_3$, which was used to modify pristine melamine. There is Sulphur as impurities most likely from manufacturing process of melamine foam.



Element	Content (wt.%)
C	32.8 (1.4)
N	41.6 (1.7)
O	13.6 (1.9)
Fe	5.4 (0.1)
Cl	5.1 (0.1)
S	1.5 (0.1)

Figure 15. EDS analysis of modified foams

The chemical composition of the foam after modification by ferric chloride solution was investigated using FTIR in the range of 4000 cm^{-1} to 500 cm^{-1}. For the pristine foam, the IR spectrum showed stretching vibration bands at 1542 cm^{-1} and 1329 cm^{-1} which are characterized for the C=N and C-N bands, respectively proving the existence of triazine ring. Indeed, another vibration mode was detected for the C-NH bond at 1468 cm^{-1}. However, after immersing the foam in ferric chloride solution, the vibration modes of the triazine ring, 1542 cm^{-1} and 1329 cm^{-1} shifted to lower wavenumbers of 1539 cm^{-1} and 1326-1328 cm^{-1} receptively. These shifts indicated the formation of coordination bonds between the nitrogen atom of the triazine ring and the metal ion (Fe^{3+}). Indeed, a shift from 1468 cm^{-1} vibration mode into a higher wavenumber of 1471-1472 cm^{-1} was detected, confirming the formation of coordination bonds between the metal ion and the amino Nitrogen atom (figure 16). Indeed, these results agree primarily with what was reported by Ding *et al*. for the 0.05, 0.1, 0.2, and 0.5M $FeCl_3$/ME foams, which showed a shift in the vibration modes of 1542 cm^{-1} and 1329 cm^{-1} into 1539-1541 cm^{-1} and 1321-1327 cm^{-1}, correspondingly. Also, a shift in the 1468 cm^{-1} band into higher wavenumbers (1471-1478 cm^{-1}) was reported in the Ding team’s paper [50].

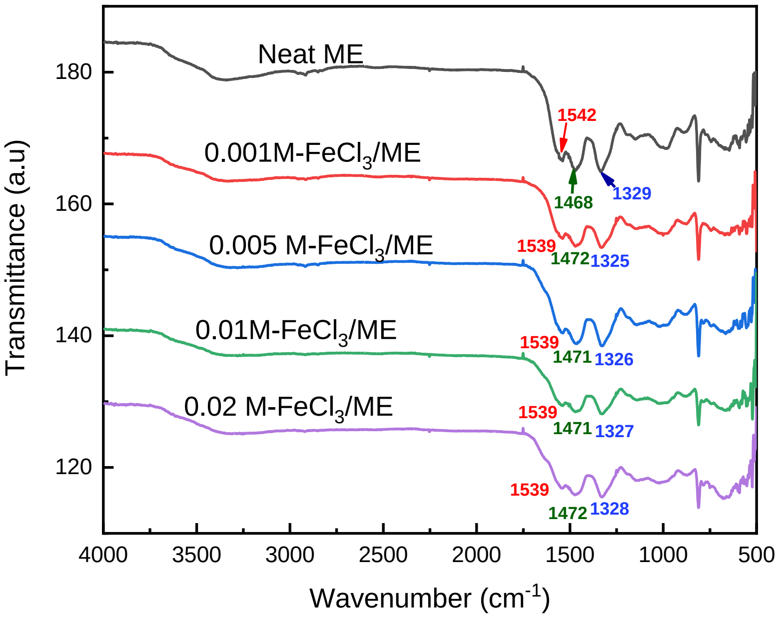


Figure 16. FTIR spectra of the pristine ME foam and treated foams

4.2 Characterization of diesel oil in water emulsions and synthetic produce water emulsions

The size of oil droplets for the as-prepared emulsions was assessed by the DLS. For the case of diesel oil in water emulsions (DOE), the droplet's size of 100, 500, and 1000 ppm DOE were found to be 159 ± 1, 164 ± 2, and 214 ± 3 nm, respectively, which confirm that the particle size for the emulsions is in the emulsified oil range (i.e., ≤ 20 μm). Table 2 and figure 17 represent the average particle size and its corresponding distribution curve.

Table 2. The size of diesel oils droplets in water dispersant of different concentrations obtained by DLS

Emulsion concentration	Average size (nm)
1000 ppm	214±3
500 ppm	164±2
100 ppm	159 ±1

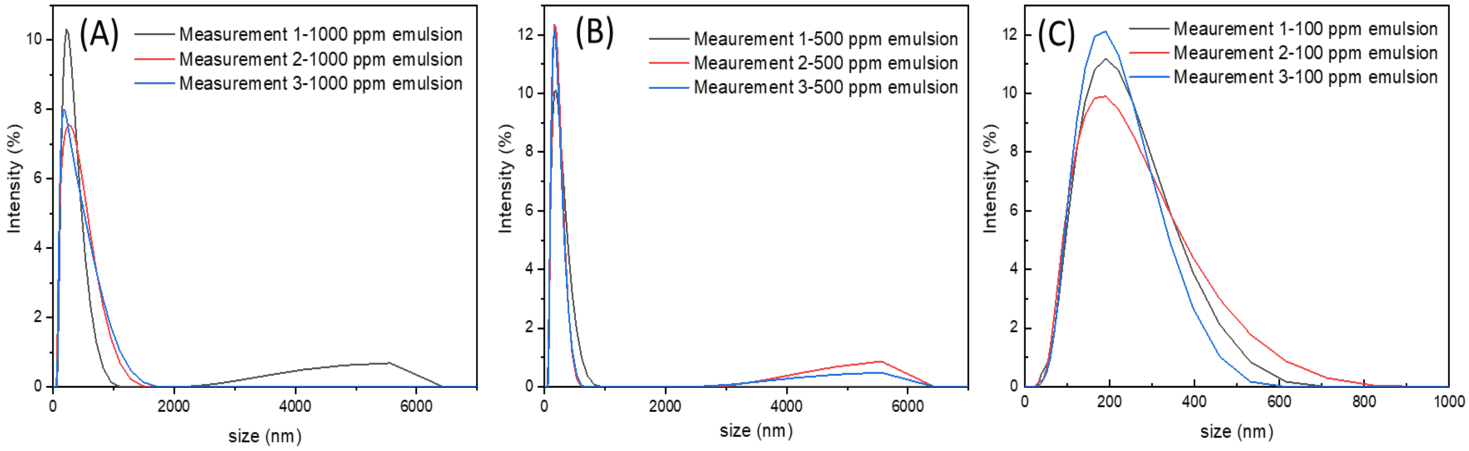


Figure 17. Particle size distribution of (A) 1000 ppm,(B) 500 ppm, and (C) 100 ppm diesel oil emulsion

The size distribution of the crude oil-synthetic produced water (PW) is shown in figure 18. The distribution indicates an average droplet size of 356 ± 16 nm represented by the major peak. The minor peak is related to the presence of some agglomerated oil particles.

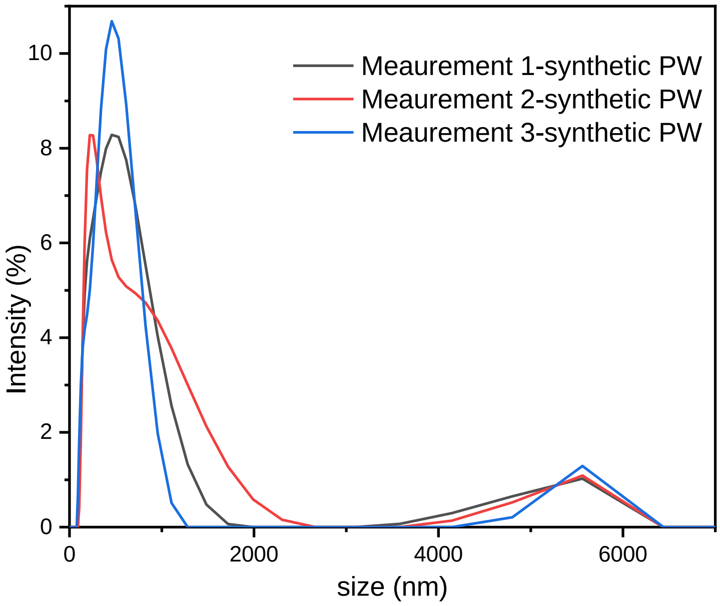


Figure 18. Size distribution of crude oil-synthetic PW by DLS

Microscopic image by profilometry of oil droplets of the PW is shown in Figure 19. It shows droplets ranging from 0.5 to 10 µm. Obtained results are in line with DLS results where oil droplets of various sizes have been observed.

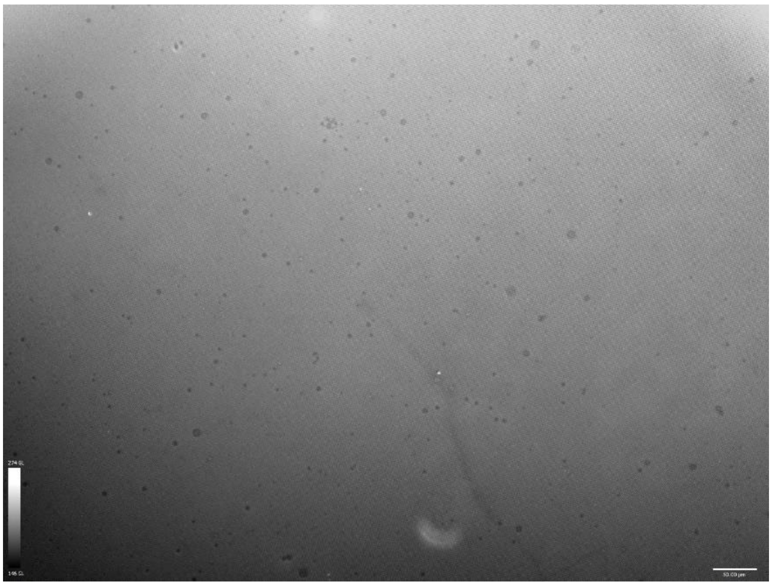


Figure 19.Microscopic image of oil droplets in emulsion. (A bar is 50 µm)

The stability of the DOE was confirmed by the zeta protentional measurement. ZP is frequently used to indicate any colloidal system's stability dependently on the obtained ZP value. Indeed, for the DOE emulsions prepared and utilized in this work of 100, 500 and 1000 ppm concentrations, high ZP values of are -34 and -39 mV were obtained respectively. The high ZP indicated that the as-prepared emulsions are highly stabilized by great repulsive forces between the oil droplets. The source of repulsive forces is the OH^- anions, which are formed by water dissociation and adsorbed onto droplets surface.

Subsequently mean that oil droplets will remain dispersed in the water for longer times until the oil droplets eventually aggregate, and the emulsion will reform the two phases. Indeed, the obtained ZP values were similar (-34 and -39 mV) for the three different concentrations, which indicate that the emulsions are highly stable.

Table 3. Zeta potential data for the oily emulsions

Emulsion	ZP (mV)
1000 ppm	-39.0 ± 1.0
500 ppm	-39.0 ± 0.1
100 ppm	-34.0 ± 0.2

For the PW emulsions, obtained ZP value was -54 mV which indicated extreme stability. The reason behind this very high value is the high ratio of SDS surfactant to oil (5:1). The synthetic PW prepared in this work was done following the exact procedure of Dardor *et al*. However, they did not mention the ZP value of the prepared PW. Still, they investigated the stability of their PW water and found that the crude oil-synthetic PW was stable over 80 days with only 9% decrease in its TOC value.

4.3 Demulsification of oily emulsions

Despite superhydrophobicity of treated ME foams, as discussed about regarding water contact angle measurement, water, as well as diluted emulsion, diffuse into the foams over time. It is due to foam’s great porosity and large pore size. However, opposite to the untreated foams, where water penetrates into the foams immediately, and foams are fully saturated during a few seconds, the diffusion of water into foams is much slower. The liquid sorption capacity of treated modified ME foam (0.01M) was tested for pure water and diesel emulsion (100 ppm) during the same time intervals. Results shown in figure 19 indicated that the foams were already saturated after 60 minutes of immersion in both pure water and emulsion. Obviously, this time depends on the size of testing samples – this value is determined for samples with a size of 1.5 x 1.5 x 1.5 cm. From figure 20 is evident that the sorption capacities of foams for both types of testing liquids are very similar. This is a favorable phenomenon for emulsions', otherwise oily droplets would not be adsorbed onto the internal surface of the foams.

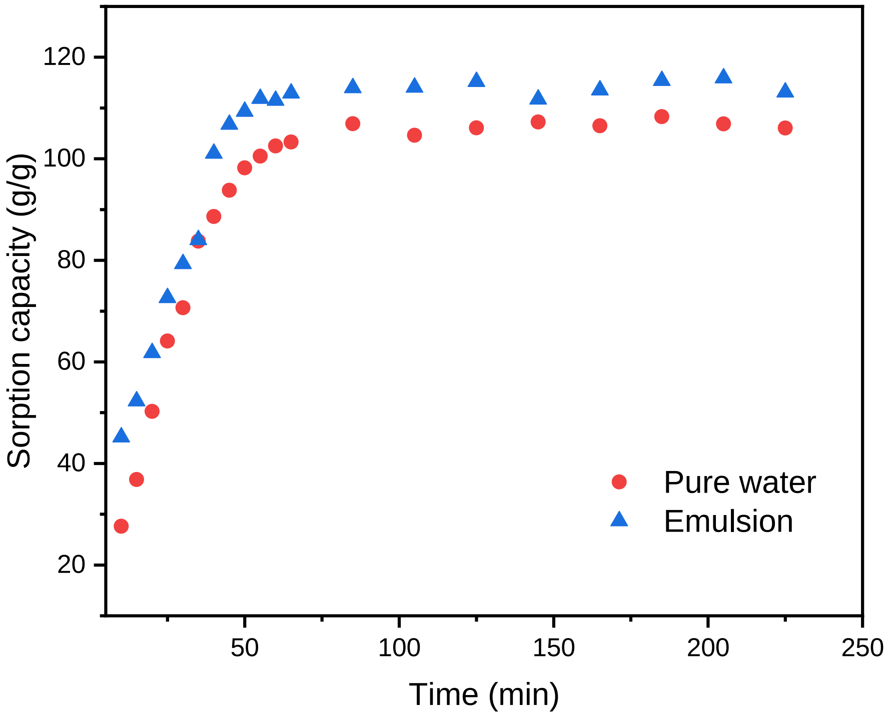


Figure 20. The sorption capacity of treated foam for pure water and emulsion

Separation efficiency of treated ME foam was tested at various conditions and different oil content in emulsions. Here, we must clarify the terminology used in the following text. If the emulsion is referred to as - e.g., 100 ppm emulsion, it means analytical concentration of oil in mg of oil per 1L of distilled water used for the emulsion preparation. Obviously, any oil is a mixture of various hydrocarbons, aromatics, etc., so real carbon content is lower than oil content. In our case, the portion of the carbon in used diesel oil was around 80 wt.% of the total composition, and thus the portion of the carbon in the emulsion is proportionally lower. However, a multiply repetition of emulsions' preparation showed that despite constant conditions used for preparation, the experimentally determined TOC varied case by case.

For this reason, any set of experimental results is always completed by the real TOC value of stock emulsion, determined just before realizing any sorption experiments. The same is true for emulsions with different oil content. Saying X ppm emulsion means that the analytical concentration of oil used for an emulsion preparation was X ppm.

Testing of volume portion of foams

It is generally known that the number of sorbents related to the volume of treated emulsion significantly influences the separation efficiency of used sorbents. Predominantly it is expressed as a mass of sorbent per volume of the treated emulsion. In the case of experiments performed in this study, the mass of foams is not a relevant parameter. More suitable seems to be the relation between the volume of used foams per treated volume of emulsions. In the following text, the volume of foams is given by the number of used foams', as the volume and size of each individual foam were always constant (1.5 x 1.5 x1.5 cm).

Multiple demulsification experiments of 100 ppm diesel oil emulsions at a constant time of 4 h were performed using 1, 3, 5, and 7 modified foams. As expected, it was found that the number of foams enhanced sorption efficiency. According to preformed sorption experiment data, the separation efficiency of 1, 3, 5 and 7 foams were 47 %, 66 %, 80% and 84%, respectively. Hence, increasing the number of foams elevates the resulting efficiency, which is reasonable as it means a higher contact area. The separation efficiency percentage was the highest, with a slight difference in five foams when using seven. Nonetheless, since seven foams performed the highest efficiency, it was then selected for the most sorption experiments.

Comparison of sorption ability of untreated and treated foams

This comparison was realized via performing a sorption experiment of 100 ppm emulsion using five neat ME foams and five treated foams. The whole experiment took 4 h. The separation efficiency of the modified ME foams was confirmed to be superior compared to the pristine foam performance. The separation efficiency of the treated foams was 84%, significantly more than the separation efficiency of pristine ME foam (9%), as indicated by the TOC values summarized in table 4. It was also noticed that the concentration of liquid squeezed out of foams is similar to the concentration in the filtrated liquid.

Table 4. The TOC values of the stock emulsion (100 ppm), the foam's filtrate, and the liquid squeezed out of the foams post the experiment

Liquid	Averaged TOC value (ppm)
Stock emulsion (100 ppm)	67.3 ± 0.1
Treated foam filtrate	11.1 ± 0.1
Neat foam filtrate	61.0 ± 0.2
The liquid squeezed out from the modified foam	13.9 ± 0.1
The liquid squeezed out from the Pristine foam	81.7 ± 0.6

The influence of the duration of sorption experiment (contact time)

The influence of contact time was investigated using 5 treated foams upon varying the shaking time at a constant rate (110 rpm) and tested for 100 ppm emulsion. It was found that the separation efficiency increased upon increasing the sorption time. In detail, at 15, 30, 45, 90, 120 and 180 min the separation efficiency of the five foams were 34%, 36% ,40% ,44% ,65% and 80% respectively as shown in figure 21 and summarized in table 5.

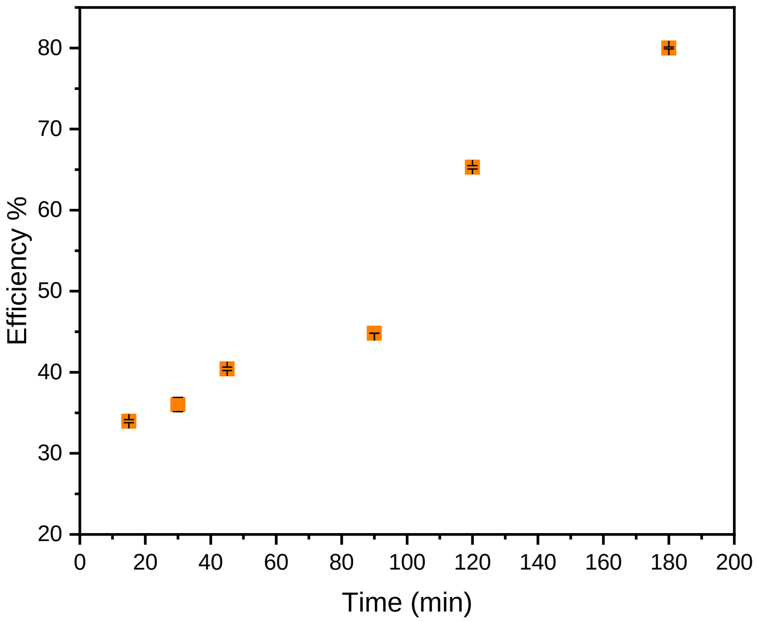


Figure 21. Separation efficiency of treated foams for 100 ppm upon changing time

Table 5.The TOC values of the stock emulsion (100 ppm) and the foam’s filtrate

Liquid	TOC value (ppm)
Stock emulsion	67.7 ± 0.2
15 min-filtrate	44.7 ± 0.2
30 min-filtrate	43.3 ± 0.1
45 min-filtrate	40.4 ± 0.1
90 min-filtrate	44.7 ± 0.2
120 min-filtrate	23.5 ± 0.1
180 min-filtrate	13.0 ± 0.1

The influence of the diesel oil concentration of separation efficiency of treated foams

Various initial concentrations of diesel oil (0, 50, 70, 100, 300, and 1000 ppm) were selected. To maximize the foams’ efficiency, the contact time of the experiment was prolonged up to 24 hours, 7 treated foams were used.

The separation efficiency of the modified ME foams was 86%, 86%, 84%, 92%, 95%, and 94% for the 30-1000 ppm emulsions respectively (figure 22, and table 6). Therefore, it can be confirmed that the performance of the foam is higher for more concentrated emulsions. It can be supposed that at higher concentrations of emulsions, the probability of the coalescence between oil droplets is higher resulting in droplets which are easy to be adsorbed onto the surface.

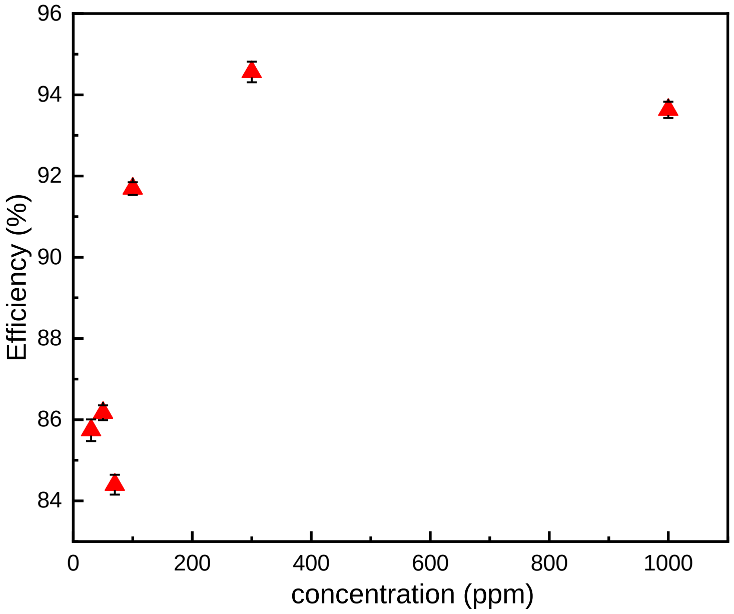


Figure 22. Separation efficiency of treated foams for different concentration of diesel emulsions

Table 6.The TOC values of the stock emulsions (30-100 ppm) and the foam's filtrate

Emulsion	Stock TOC value (ppm)	Filtrate TOC value (ppm)
30 ppm	29.4 ± 0.1	4.1 ± 0.3
50 ppm	52.6 ± 0.4	7.5 ± 0.6
70 ppm	78.2 ± 0.5	12.2 ± 0.7
100 ppm	111.9 ± 1.0	6.1 ± 0.1
300 ppm	185.9 ± 0.4	15.4 ± 0.6
500 ppm	285.6 ± 0.1	35.6 ± 0.2
1000 ppm	552.7 ± 0.1	35.2 ± 0.3

Re-use of treated foams

The recyclability, or better said – re-use of the foams is essential for a practical application. For this reason, it was tested by performing four constrictive cycles of sorption- desorption using 100 ppm emulsion and seven treated foams. The duration of each cycle was 4 h. It was found that the efficiency of the foams dropped in the second cycle by ~20% from 84% efficiency in the first cycle of the foams into 63% in the second cycle (figure 22, table 7). Indeed, the same percentage is valid for the difference between the second and third cycles, but after that, the performance of the sponges remained constant throughout cycles 4 and 5 (38%). The reason behind the drop in efficiency is the fact that the foam skeleton retained some residual oil droplets formed during sorption experiments and was difficult to be extracted by simple squeezing of sponge.

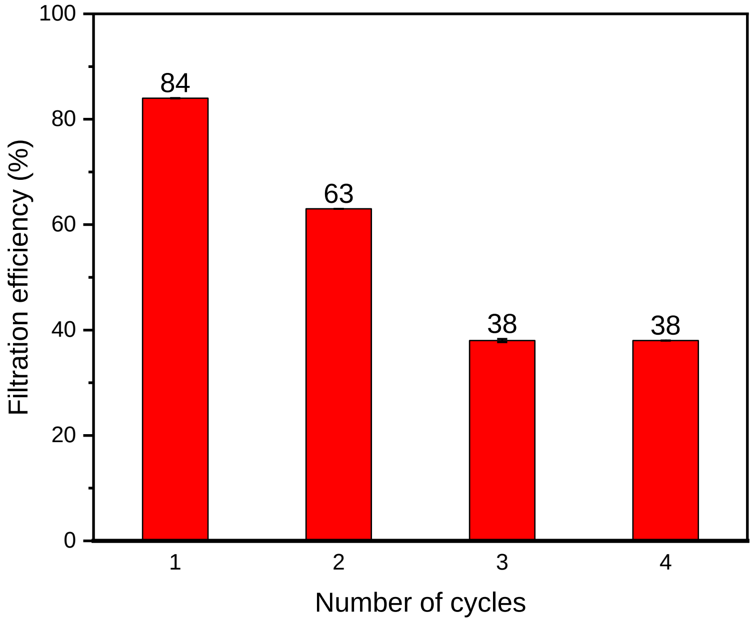


Figure 23. Reusability of treated foam for DOE

Table 7.The TOC values of the 100 ppm stock emulsions and the foam's filtrate upon cyles

Liquid	Stock TOC value (ppm)	Filtrate TOC value (ppm)
Cycle 1	67.2 ± 0.1	11.1 ± 0.1
Cycle 2	73.1 ± 0.1	27.0 ± 0.1
Cycle 3	70.2 ± 0.3	43.6 ± 0.1
Cycle 4	70.2 ± 0.1	42.6 ± 0.2

4.3 Demulsification of synthetic produced water by modified ME foam

Emulsions are one of the most challenging systems in the field of oil/water separation. However, the challenge becomes more elevated for the case of produced water emulsions. Produced water contains hydrocarbons that results during oil and gas extraction from conventional and unconventional resources [49]. Indeed, the challenging part about the PW is that it contains different oils of different densities, mainly crude oil known for its higher density and the presence of high percentage of emulsifiers triggering the extreme stability of the PW. Nevertheless, real PW samples obtained from petroleum industry are not accessible which forced many researchers to attempt mimicking the original PW by synthesizing one in the lab. Many recipes for the synthesis of produced water are published in the literature, but few of those recipes actually mimics the real PW of industry. The recipes varied in the amount and type of oil and surfactant used and the properties of the aqueous phase.

In this work, the protocol of Dardor *et al.* [49] developed by ConocoPhillips in the Qatar team for the synthesis of PW was followed. This protocol was of particular selection among many as it includes vital parameters that exist in the real PW. However, in this work, the synthetic PW was prepared using crude oil instead of commercial oils such as motor oil. These oils may contain chemical additives that can affect the PW's TOC value and exhibit certain analytical properties that do not represent the organics that existed in real PW.

Indeed, the aqueous phase contains salts presented in real PW and not just deionized water or even tap water as these salts affect different properties of the PW, including the partition of the organics into the aqueous phase within the PW. A typical PW sample contains large amounts of surfactants that guarantee its stability for a longer time. In this procedure, the ratio of surfactant to oil is 5:1, which is similar to the ratio of surfactant to oil in real PW. Also, two types of emulsification methods were applied: stirring and sonication to further enhance the PW stability and homogeneity [49].

The effect of volume variation on the performance of foam separation of PW emulsions was investigated by utilizing 1-7 foams, and it was clearly seen that as the number of foams increased, the better the efficiency became. However, a significant difference was noticed between using one foam, two foams, or three foams. The efficiency of one, two, and three foams for emulsification of PW was 62%, 82% and

89% respectively, which means that the number of one or two foams is not sufficient enough for higher separation. However, beyond three foams, the efficiency of the higher number of foams became roughly the same as three-seven foams exhibited separation performance of 89, 90, 90, 90, and 91%, respectively, as indicated by figure 24 and table 8.

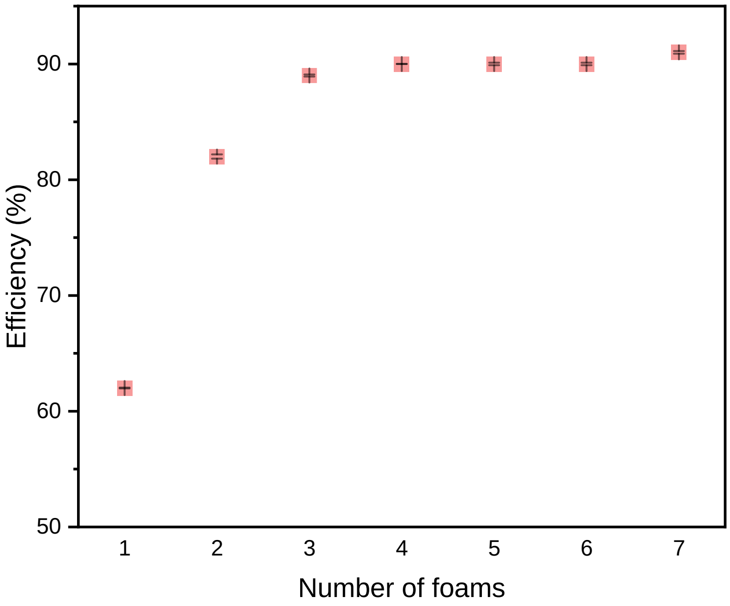


Figure 24. The efficiency of treated foams upon variation of volume

Table 8.The TOC values of the PW emulsion and the foam's filtrate

Liquid	TOC value (ppm)
Stock emulsion	227.9 ± 0.1
One foam filtrate	85.8 ± 0.2
Two foams filtrate	40.8 ± 0.2
Three foams filtrate	24.6 ± 0.1
Four foams filtrate	21.3 ± 0.2
Five foams filtrate	22.8 ± 0.1
Six foams filtrate	21.46±0.13
Seven foams filtrate	20.01±0.33

The effect of mechanical shaking duration of the foams and PW was also investigated. The number of utilized foams was only one foam (1 x 1 x1 cm) with less amount of PW (15 ml). The reason behind minimizing the dimension and the volume of PW is because these parameters were the best fit to allow the foam to be fully immersed by PW in 15 ml common veils. Nonetheless, the results confirmed that longer durations are the best for the foam's system. This is because starting from 20 min and up to 180 min with in between 40, 90 and 100 min intervals, the foams showed low efficiency starting from 15% only and up to 21% at its highest (figure 25, table 9).

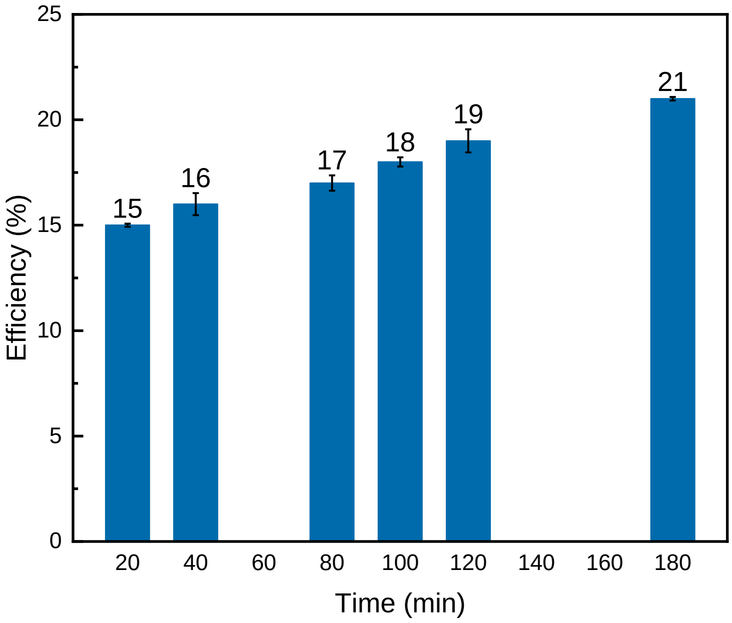


Figure 25.The efficiency of treated foam for demulsification upon time variation

Table 9.The TOC values of the PW emulsion and the foam's filtrate

Liquid	TOC value (ppm)
Stock emulsion	201.9 ± 0.8
20 min filtrate	170.9 ± 0.1
40 min filtrate	167.7 ± 0.5
80 min filtrate	167.5 ± 0.4
100 min filtrate	164.4 ± 0.2
120 min filtrate	163.2 ± 0.5
180 min filtrate	158.4 ± 0.1

At the same conditions and by maximizing the dimension of the foams to 1.5 x 1.5 x 1.5 cm and utilizing 50 ml of PW, demulsification experiment was held for 1, 2, 3, 4, 5, 6, 12 and 24h as shown in figure 26. The separation efficiency was 42%, 64%, 64%, 65%, 70%, 72%, 73% and 90% for 1- 24h respectively, as summarized in table 10.

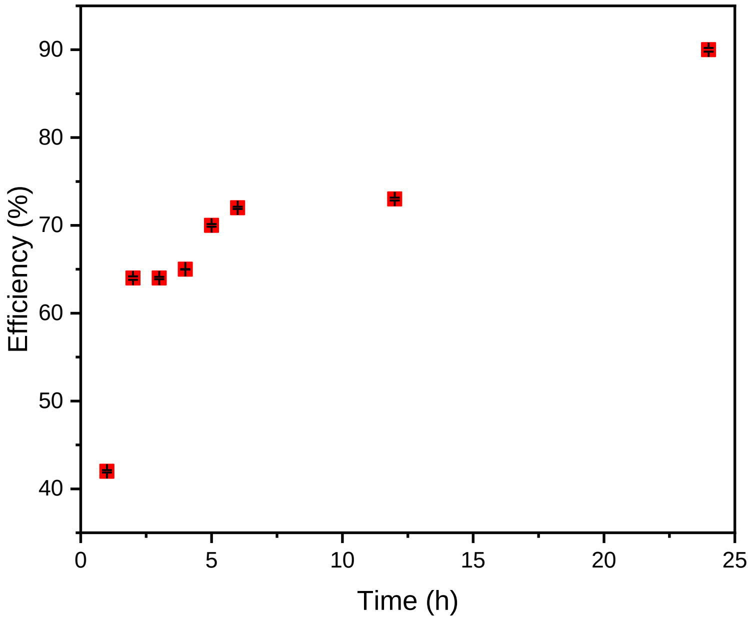


Figure 26. Efficiency of treated foams for demulsification upon time variation

Table 10.The TOC values of the PW emulsion and the foam's filtrate

Liquid	TOC value (ppm)
Stock emulsion	218.8 ± 0.2
1h filtrate	126.3 ± 0.1
2h filtrate	78.9 ± 0.2
3h filtrate	77.6 ± 0.1
4h filtrate	75.6 ± 0.3
5h filtrate	65.2 ± 0.2
6h filtrate	61.5 ± 0.1
12h filtrate	58.6 ± 0.2
24h filtrate	21.3 ± 0.2

The efficiency of foam separation upon varying the PW concentration was investigated at three different concentrations (300, 150, and 100 ppm). The foams were able to demulsify the emulsion with 91%, 84% and 81% efficiency for the 300, 150 and 100 ppm PW emulsions as illustrated in figure 27 and indicated TOC values in table

11. The separation efficiency of the foams is superior, and it is higher for increased concentrations for the previously discussed reason that at higher concentrations, the existence of oil droplets is more and, thus, great probability of oil penetration into the foams.

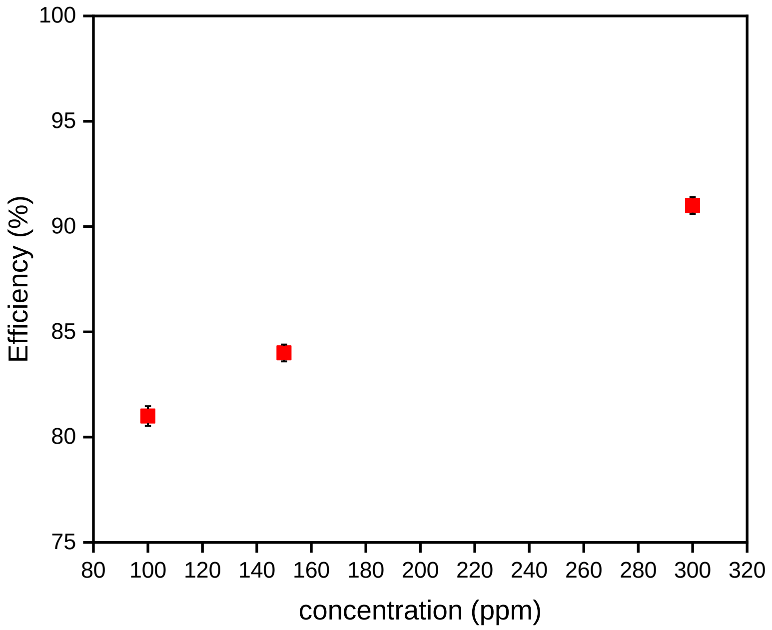


Figure 27. Separation performance of modified ME foam for three different concentrations (300,150 and 100 ppm)

Table 11.The TOC values of the PW emulsions (100,150 and 300 ppm) and the foam's filtrate

Liquid	Stock TOC value (ppm)	Filtrate TOC value (ppm)
100 ppm	93.1 ± 0.5	17.9 ± 0.1
150 ppm	158.0 ± 0.4	24.1 ±0.1
300 ppm	272.9 ± 0.2	20.1±0.3

The reusability of foams for the separation of PW was investigated by performing multiple sorption experiments. The separation efficiency of modified foams throughout six constructive cycles was 91%, 83%, 75%, 74%, 73%, and 72% respectively as shown in figure 28, and table 12. The foam's performance decreased by only 8% from the first to the second and from the second to the third cycles; then, it devalued gradually to its lowest performance at the sixth cycle (72%). Indeed, by the end of the six cycles, the foam's performance was still quite high (72%), indicating that the as-modified foams are highly reusable.

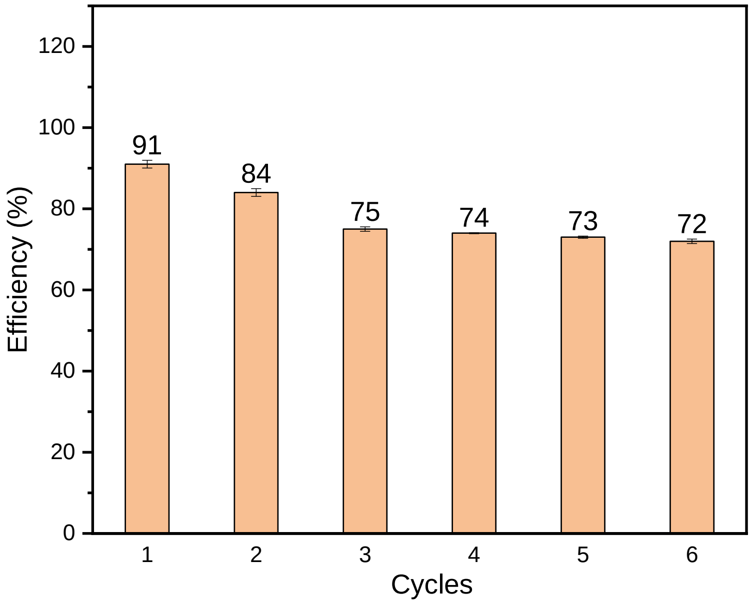


Figure 28. Reusability of treated foams throughout six cycles of PW demulsification

Table 12.The TOC values of the PW stock emulsion and the foam's filtrate upon six cycles

Liquid	Stock TOC value (ppm)	Filtrate TOC value (ppm)
Cycle 1	250.0 ± 0.3	21.9 ± 0.3
Cycle 2	249.7 ± 0.3	40.2 ± 0.1
Cycle 3	249.7 ± 0.3	61.7 ± 0.2
Cycle 4	249.0 ± 0.2	64.5 ± 0.1
Cycle 5	249.0 ± 0.3	65.9 ± 0.2
Cycle 6	249.0 ± 0.2	69.6 ± 0.2

4.4 Separation of oil/water mixtures by modified foams

The modified foams were used to separate oil/water mixtures at three different oils to water portions which were 20/80, 40/60, and 60/40 vol./vol. ratios. The results were overwhelming, the modified foams treated the mixture with high efficiency of 99% for all the mixtures. In figure 29, it is seen that the filtrate of foams is almost transparent, and the liquid squeezed out of the foams is mostly pure oil while the neat foam filtrate is cloudy and contains oil at high concentration, and it is very similar to the squeezed-out liquid of the foam in color what indicates that the foam did not separate oil from water properly. Table 13 summarizes the TOC values and the exact separation efficiency.

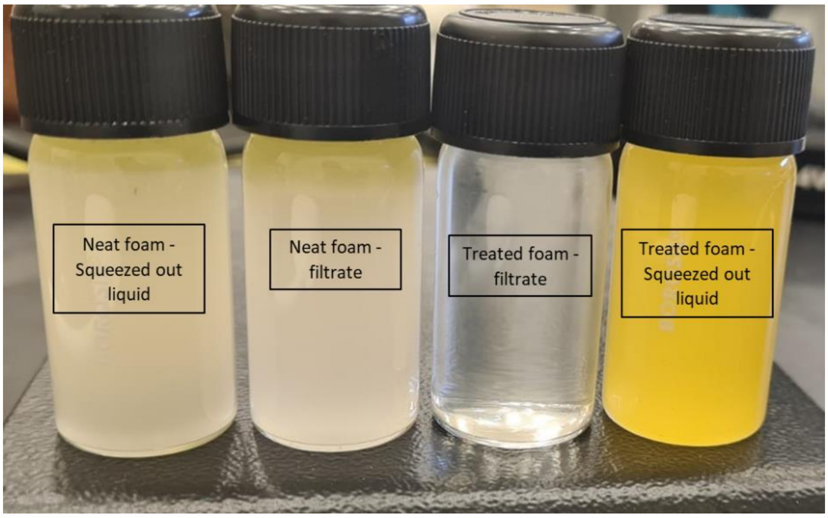


Figure 29.Photograph for the filtrated liquid and the squeezed liquid of neat and treated sponges for the 20/80: oil/water mixture

Table 13. The oil/water mixtures (vol./vol.) filtrates' TOC value by pristine and modified foams

Liquid	Filtrates' TOC value (ppm)	Efficiency (%)
20:80-pristine foams	8188 ± 0.4	95.18
20:80-modified foams	231.3 ± 0.1	99.86
40:60-modified foams	335.8 ± 0.2	99.90
60:40-modified foams	516.9 ± 0.3	99.98

Indeed, the kinetics of modified sponges' ability to separate 20:80 vol/vol.% mixtures separation was investigated for the short periods of 1, 3, 5, 10, 20 and 30 min and for longer periods at 5 and 6 h as shown in table 14. The foams were able to separate o/w mixtures with high efficiency (~99%) even at very short periods such as 30 min. However, the optimum performance is achieved at quit longer durations (6 h) as the measured TOC value for that period was only 235 ppm.

Table 14.The TOC values of the o/w mixtures (20:80) filterates upon time

Time	Filtrates' TOC value (ppm)	Efficiency (%)
1 min	1388.1± 1.8	99.18
3 min	1244.1 ± 2.2	99.27
5 min	414.3 ± 2.4	99.76
10 min	335.9 ± 2.5	99.80
20 min	286.6 ± 2.4	99.83
30 min	272.3 ± 2.0	99.84
5 h	266.1 ± 0.3	99.84
6h	234.7 ± 0.4	99.86

4.5 Sorption of neat oils by modified foams

Throughout the world, around 50 million tons of petroleum and crude oil products are lost during the recovery process. Indeed, 4-6 million tons of that amount ended up floating on the water surface, causing irreparable spills. For this need, organic sorbent materials, including polymeric foams and fibers, are developed for oil sorption from the water surface. However, sorption by polymeric foams is distinguished by the high floatability of foams, low density, and high sorption capacity with respect to petroleum products. Nonetheless, the modified sponges are tested for sorption of three different oils (diesel, crude, and motor oil) with variant oil densities for 15,30,45,60,90, 120,180,240 (4 min),300 (5min), and 600s (10 min), as shown in figure 30 (A-F). In addition to sorption capacity measurement, the recyclability of foam’s sorption capacity was tested by performing 10 cycles of sorption (10 min)/desorption.

Finally, the hydrophobicity of treated foam was confirmed by floating the foam on the water for certain times, followed by measuring the weight intake. The same was performed using neat foam as a reference. The neat foam sink into the water once placed on it while treated foam floated on the surface for 24h.

It is apparent that the difference in sorption capacity of the modified foam and neat foam is negligible, which indicated that immersing by $FeCl_3$ solution did not influence the foam morphology significantly. Indeed, the treated foam absorbed diesel, crude, and motor oil with corresponding sorption capacities of 98,103 and 112 g/g, respectively, reflecting that treated foam's sorption capacity is superior. Moreover, the reason behind the excellent sorption capacity associated with ME foams is their low volume, which is associated with larger pore diameter and open cell structure. However, the differences between sponge sorption capacity for the three different oils vary slightly depending on the sorbate density. When the sorbate density is higher, the flowability of sorbate in the material is higher, and that’s the reason behind the low sorption of diesel compared to motor and crude. Indeed, the sorption capacity of foams increased gradually upon increasing the immersing time in oil until it reached saturation at a maximum time of 240 s (4 min). However, in the motor oil sorption plateau, the modified foam reaches saturation quickly due to its enhanced oleophilic. At the same time, it takes longer for neat foam because it did not sink into the oil directly, and it floated initially on the oil surface due to the difference between oil and foam density. However, with time and gravity, it started to drill down the oil.

Moreover, when the foam is in contact with oil and due to its oleophilic wettability, oil starts to be adsorbed onto the foam internal surface increasingly upon time elevation, and the change in sorption capacity is the fastest at the beginning. Then, the increment becomes less as the fibers become saturated by oil, and any further accumulation of oil will escape the foam pores as excess oil during weighting the foam. However, when testing the recyclability of the modified foams by performing multiple sorption/desorption cycles, the foams retained their high sorption capacity beyond 10 cycles with minor loss of capacity by 3.5% and 6.4% for diesel and crude oil. The desorption step was done via simple squeezing with the support of a syringe, as shown in figure 2. Indeed, the devaluation of capacity upon recycling is the highest in the case of motor oil by 17% decrement; it is believed that the reason is related to the thick consistency of motor oil, which can chock some pores and cells of the foam.

In addition, when the two modified and pristine foams were placed on the water surface, the pristine one sank into the water immediately and reached sorption capacity 118 g/g after 10 min. In contrast, the superhydrophobic modified foam had sorption ability only 1.17 g/g as it remained floating on the surface and did not move down. Furthermore, when the foam was left for more extended times of 3h, 24h, and 72h, it remained hydrophobically floating on the water surface, confirming that ferric chloride treatment is sufficient to produce superhydrophobic foam.

This observation is in contradiction to previous experiments in which foams immersed in water and shaken were fully saturated by water after 60 minutes. It is evident that immersion combined by mechanical forces can overcome surface tension of treated foam what lead to the diffusion of water into foam, unlike a case, if foam freely float on the water surface.

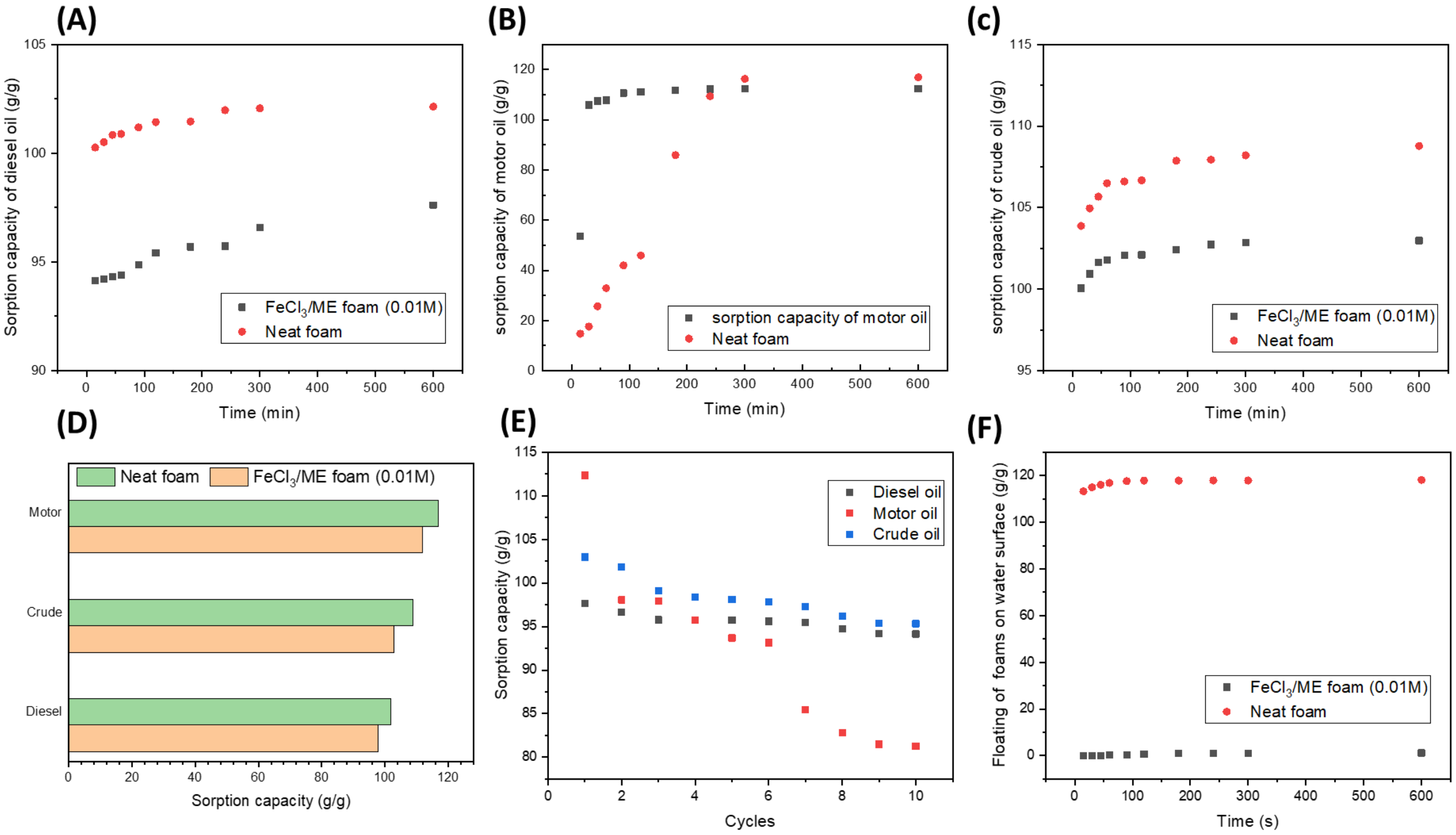


Figure 30.Sorption capacity of $FeCl_3$/ME foam for (A) diesel, (B) motor, and (C) crude oil, a summary of the three oil's sorption (D), the recyclability of sorption capacity of the foam through 10 cycles (E) and the sorption capacity of prestine and modified foam floating on water surface

CHAPTER 5: CONCLUSION & FUTURE WORK

In conclusion, oily wastewater treatment is a challenging area of research, particularly the separation of oily emulsions whose particle size is below 20 µm, and the need for an efficient filtration tool of low price is urgent. For that aim, commercial ME 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. However, in this work, ME foam modification was carried out using a facile, low-cost, and environmentally friendly method via induced metal complex transition.

According to this method, the foams were treated by simple immersion in $FeCl_3$ solution. However, the effect of immersion in $FeCl_3$ on the properties and morphology of the foams was investigated by different characterization techniques including SEM, EDS, FTIR and contact angle measurements.

The modified foams were utilized for o/w separation in three different o/w dispersant including, oily emulsions, PW and o/w mixtures. Successfully, the foams demulsify oily emulsions (1000 ppm) with separation performance of 94%. Similarly, the foams were able to clear very stable synthetic crude oil - PW samples (300 ppm) with high efficiency of 91%. Moreover, the foams proved great reusability as they retained around 72% efficiency throughout six cycles of PW demulsification.

In addition, the foams were used for treating highly concentrated o/w mixtures (20:80, 40:60 and 60:20 vol./vol.) and the performance was superior. The foams efficiently separated the oil from the mixture with very high performance approaching 100% within few minutes.

In addition, the sorption capacity of modified foams for neat oils was excellent. Within few seconds, the foams were fully saturated by the oils with sorption capacity of 98, 103 and 112 g/g for diesel, crude, and motor oil, respectively. Moreover, the sorption capacity of the foams is high enough beyond 10 cycles of sorption / desorption with few devaluations of 4%, 6% and 17% after cycle 10 for diesel, crude, and motor oil respectively.

Apparently, $FeCl_3$/ME foams are very promising for treating three important types of o/w mixtures (emulsions, PW, and mixtures). Still, this approach, as any other approach, has its own limitations. The critical limitation associated with this method is the fact that the foams require long periods (24h) to be fully saturated by the o/w mixtures. Long durations are not practical because rapid demulsification is demanded for the industrial large-scale applications.

However, for the advantages associated with utilizing polymeric foams and for the sake of boosting their performance and resolving the related challenges. Other modification approached are suggested and has been partially started - by our team- to modify ME via copolymers grafting. This approach satisfies the main purpose of it, which is switching the neutral wettability of the foams into oleophilic/ hydrophobic wettability and, furthermore, it boosts this wettability character by significantly roughening the surface. Moreover, an increase in biofouling resistance is also expected using some copolymers (particularly zwitterionic ones), which is an important parameter for cleaning of real waters. In detail, this method is based on surface grafting by N-methacryloyl-4-azidoaniline (AzMA)- methyl methacrylate (MMA) copolymer via free radical polymerization as shown in figure 31. The first monomer can be polymerized in the lab through the other monomer that is commercially available.

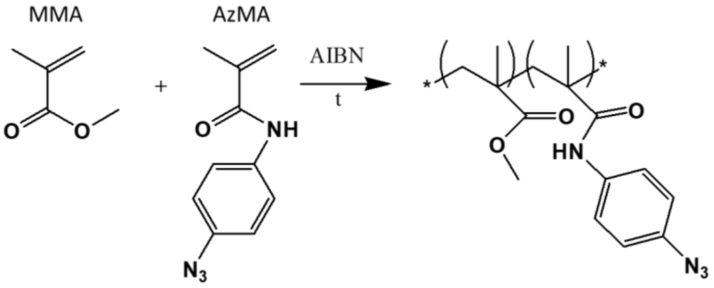


Figure 31.Copolymerization of AzMA and MMA

Indeed, the method is facile and eco-friendly. Synthesis experiments by this patch started already, and superhydrophobic foam was successfully obtained (water repellent angle of ≥140°) with a very rough surface. However, some challenges occurred during grafting by the copolymer, including the low produced yield (only 4%).

REFERENCES

[1] A. A. El-Samak, D. Ponnamma, M. K. Hassan, A. Ammar, S. Adham, M. A. A. Al-Maadeed, and A. Karim, *Designing Flexible and Porous Fibrous Membranes for Oil Water Separation—A Review of Recent Developments*, Https://Doi.Org/10.1080/15583724.2020.1714651 **60**, 671 (2020).

[2] Z. Xue, Y. Cao, N. Liu, L. Feng, and L. Jiang, *Special Wettable Materials for Oil/Water Separation*, Journal of Materials Chemistry A **2**, 2445 (2014).

[3] M. Cheryan and N. Rajagopalan, *Membrane Processing of Oily Streams. Wastewater Treatment and Waste Reduction*, Journal of Membrane Science **151**, 13 (1998).

[4] F. Li, B. Bhushan, Y. Pan, and X. Zhao, *Bioinspired Superoleophobic/Superhydrophilic Functionalized Cotton for Efficient Separation of Immiscible Oil-Water Mixtures and Oil-Water Emulsions*, Journal of Colloid and Interface Science **548**, 123 (2019).

[5] M. Takahashi and K. Sakamoto, *Regulations on Cosmetics*, Cosmetic Science and Technology: Theoretical Principles and Applications 137 (2017).

[6] F. Li, B. Bhushan, Y. Pan, and X. Zhao, *Bioinspired Superoleophobic/Superhydrophilic Functionalized Cotton for Efficient Separation of Immiscible Oil-Water Mixtures and Oil-Water Emulsions*, Journal of Colloid and Interface Science **548**, 123 (2019).

[7] P. Sobolciak, A. Popelka, A. Tanvir, M. A. Al-Maadeed, S. Adham, and I. Krupa, *Materials and Technologies for the Tertiary Treatment of Produced Water Contaminated by Oil Impurities through Nonfibrous Deep-Bed Media: A Review*, Water 2020, Vol. 12, Page 3419 **12**, 3419 (2020).

[8] *Oil Spill Data - Naoc*, https://www.eni.com/en_NG/health-safety-

environment/environment/oil-spill-data.page.

[9] T. R. Jerry, W. K. Lawrence, H. Yung-Tse, and K. Hung Li, *Potable Water Aeration*, in *Advanced Physicochemical Treatment Processes* (Humana Press, 2006), pp. 1–45.

[10] J. S. Eow and M. Ghadiri, *Electrostatic Enhancement of Coalescence of Water Droplets in Oil: A Review of the Technology*, Chemical Engineering Journal **85**, 357 (2002).

[11] Y. Suzuki and T. Maruyama, *Removal of Emulsified Oil from Water by Coagulation and Foam Separation*, Separation Science and Technology **40**, 3407 (2005).

[12] A. Y. Hosny, *Separating Oil from Oil-Water Emulsions by Electroflotation Technique*, Separations Technology **6**, 9 (1996).

[13] A. A. Al-Shamrani, A. James, and H. Xiao, *Destabilisation of Oil–Water Emulsions and Separation by Dissolved Air Flotation*, Water Research **36**, 1503 (2002).

[14] L. Wu, L. Li, B. Li, J. Zhang, and A. Wang, *Magnetic, Durable, and Superhydrophobic Polyurethane@Fe3O4@SiO2@Fluoropolymer Sponges for Selective Oil Absorption and Oil/Water Separation*, ACS Applied Materials and Interfaces **7**, 4936 (2015).

[15] N. Chen and Q. Pan, *Versatile Fabrication of Ultralight Magnetic Foams and Application for Oil-Water Separation*, ACS Nano **7**, 6875 (2013).

[16] M. Khosravi and S. Azizian, *Synthesis of a Novel Highly Oleophilic and Highly Hydrophobic Sponge for Rapid Oil Spill Cleanup*, ACS Applied Materials and Interfaces **7**, 25326 (2015).

[17] D. Ponnamma, S. S. Nair, H. Parangusan, M. K. Hassan, S. Adham, A. Karim,

and M. A. A. Al-Maadeed, *White Graphene-Cobalt Oxide Hybrid Filler Reinforced Polystyrene Nanofibers for Selective Oil Absorption*, Polymers 2020, Vol. 12, Page 4 **12**, 4 (2019).

[18] Y. Luo, X. Wang, R. Zhang, M. Singh, A. Ammar, D. Cousins, M. K. Hassan, D. Ponnamma, S. Adham, M. A. A. Al-Maadeed, and A. Karim, *Vertically Oriented Nanoporous Block Copolymer Membranes for Oil/Water Separation and Filtration*, Soft Matter **16**, 9648 (2020).

[19] X. Zhang, D. Liu, Y. Ma, J. Nie, and G. Sui, *Super-Hydrophobic Graphene Coated Polyurethane (GN@PU) Sponge with Great Oil-Water Separation Performance,* Applied Surface Science **422**, 116 (2017).

[20] X. Chen, J. A. Weibel, and S. V. Garimella, *Continuous Oil–Water Separation Using Polydimethylsiloxane-Functionalized Melamine Sponge*, Industrial and Engineering Chemistry Research **55**, 3596 (2016).

[21] S. M. Hailan, D. Ponnamma, and I. Krupa, *The Separation of Oil/Water Mixtures by Modified Melamine and Polyurethane Foams: A Review*, Polymers 2021, Vol. 13, Page 4142 **13**, 4142 (2021).

[22] K. E. Eseller, I. H. Boyaci, B. Sezer, G. Bilge, and H. Berberoglu, *Food Science Application*, Laser-Induced Breakdown Spectroscopy 347 (2020).

[23] C. A. Dyke and C. R. Bartels, *Removal of Organics from Offshore Produced Waters Using Nanofiltration Membrane Technology*, Environmental Progress **9**, 183 (1990).

[24] L. Han, H. Bi, X. Xie, S. Su, P. Mao, and L. Sun, *Superhydrophobic Graphene-Coated Sponge with Microcavities for High Efficiency Oil-in-Water Emulsion Separation*, Nanoscale **12**, 17812 (2020).

[25] N. K. Adam and G. Jessop, *CCL. - Angles of Contact and Polarity of Solid*

Surfaces, Journal of the Chemical Society, Transactions **127**, 1863 (1925).

[26] J. Yong, F. Chen, Q. Yang, J. Huo, and X. Hou, *Superoleophobic Surfaces*, Chemical Society Reviews **46**, 4168 (2017).

[27] N. Valipour M., F. C. Birjandi, and J. Sargolzaei, *Super-Non-Wettable Surfaces: A Review*, Colloids and Surfaces A: Physicochemical and Engineering Aspects.

[28] C. Chen, D. Weng, A. Mahmood, S. Chen, and J. Wang, *Separation Mechanism and Construction of Surfaces with Special Wettability for Oil/Water Separation*, ACS Applied Materials & Interfaces **11**, 11006 (2019).

[29] J. Pinto, A. Athanassiou, and D. Fragouli, *Surface Modification of Polymeric Foams for Oil Spills Remediation*, Journal of Environmental Management **206**, 872 (2018).

[30] H. Zhou, H. Wang, H. Niu, and T. Lin, *Recent Progress in Durable and Self-Healing Super-Nonwettable Fabrics*, Advanced Materials Interfaces.

[31] P. Gupta and B. Kandasubramanian, *Directional Fluid Gating by Janus Membranes with Heterogeneous Wetting Properties for Selective Oil–Water Separation*, ACS Applied Materials and Interfaces **9**, 19102 (2017).

[32] R. Arora and K. Balasubramanian, *Hierarchically Porous PVDF/Nano-SiC Foam for Distant Oil-Spill Cleanups,* RSC Advances **4**, 53761 (2014).

[33] K. V. Udayakumar, P. M. Gore, and B. Kandasubramanian, *Foamed Materials for Oil-Water Separation,* Chemical Engineering Journal Advances **5**, 100076 (2021).

[34] J. Pinto, A. Athanassiou, and D. Fragouli, *Effect of the Porous Structure of Polymer Foams on the Remediation of Oil Spills*, Journal of Physics D: Applied Physics **49**, 145601 (2016).

[35] J. Pinto, J. A. Heredia-Guerrero, A. Athanassiou, and D. Fragouli, *Reusable*

Nanocomposite-Coated Polyurethane Foams for the Remediation of Oil Spills, International Journal of Environmental Science and Technology 2017 14:10 **14**, 2055 (2017).

[36] C. Ruan, K. Ai, X. Li, and L. Lu, *A Superhydrophobic Sponge with Excellent Absorbency and Flame Retardancy*, Angewandte Chemie International Edition **53**, 5556 (2014).

[37] H. Gao, P. Sun, Y. Zhang, X. Zeng, D. Wang, Y. Zhang, W. Wang, and J. Wu, *A Two-Step Hydrophobic Fabrication of Melamine Sponge for Oil Absorption and Oil/Water Separation*, Surface and Coatings Technology **339**, 147 (2018).

[38] A. Stolz, S. Le Floch, L. Reinert, S. M. M. Ramos, J. Tuaillon-Combes, Y. Soneda, P. Chaudet, D. Baillis, N. Blanchard, L. Duclaux, and A. San-Miguel, *Melamine-Derived Carbon Sponges for Oil-Water Separation*, Carbon **107**, 198 (2016).

[39] D. D. Ejeta, C. F. Wang, C. H. Lin, S. W. Kuo, J. K. Chen, H. C. Tsai, W. S. Hung, C. C. Hu, and J. Y. Lai, *Preparation of a Main-Chain-Type Polybenzoxazine-Modified Melamine Sponge via Non-Solvent-Induced Phase Inversion for Oil Absorption and Very-High-Flux Separation of Water-in-Oil Emulsions*, Separation and Purification Technology **263**, 118387 (2021).

[40] R. M. G. Ahmed, B. Anis, and A. S. G. Khalil, *Facile Surface Treatment and Decoration of Graphene-Based 3D Polymeric Sponges for High Performance Separation of Heavy Oil-in-Water Emulsions*, Journal of Environmental Chemical Engineering **9**, 105087 (2021).

[41] G. Chen, Y. Cao, L. Ke, X. Ye, X. Huang, and B. Shi, *Plant Polyphenols as Multifunctional Platforms to Fabricate Three-Dimensional Superhydrophobic Foams for Oil/Water and Emulsion Separation*, Industrial and Engineering

Chemistry Research **57**, 16442 (2018).

[42] R. Krishnamoorthi, R. Anbazhagan, H. C. Tsai, C. F. Wang, and J. Y. Lai, *Preparation of Caffeic Acid-Polyethyleneimine Modified Sponge for Emulsion Separation and Dye Adsorption*, Journal of the Taiwan Institute of Chemical Engineers **118**, 325 (2021).

[43] W. Liu, X. Huang, K. Peng, Y. Xiong, J. Zhang, L. Lu, J. Liu, and S. Li, *PDA-PEI Copolymerized Highly Hydrophobic Sponge for Oil-in-Water Emulsion Separation via Oil Adsorption and Water Filtration*, Surface and Coatings Technology **406**, 126743 (2021).

[44] S. Liu, Q. Zhang, L. Fan, R. Wang, M. Yang, and Y. Zhou, *3D Superhydrophobic Sponge Coated with Magnesium Hydroxide for Effective Oil/Water Mixture and Emulsion Separation*, Industrial and Engineering Chemistry Research **59**, 11713 (2020).

[45] M. Cao, Y. Feng, Q. Chen, P. Zhang, S. Guo, and J. Yao, *Flexible Co-ZIF-L@melamine Sponge with Underwater Superoleophobicity for Water/Oil Separation*, Materials Chemistry and Physics **241**, 122385 (2020).

[46] J. Wang, H. Wang, and G. Geng, *Highly Efficient Oil-in-Water Emulsion and Oil Layer/Water Mixture Separation Based on Durably Superhydrophobic Sponge Prepared via a Facile Route*, Marine Pollution Bulletin **127**, 108 (2018).

[47] J. Li, M. Tenjimbayashi, N. S. Zacharia, and S. Shiratori, *One-Step Dipping Fabrication of Fe3O4/PVDF-HFP Composite 3D Porous Sponge for Magnetically Controllable Oil-Water Separation*, ACS Sustainable Chemistry and Engineering **6**, 10706 (2018).

[48] J. Wang and Y. Zheng, *Oil/Water Mixtures and Emulsions Separation of Stearic Acid-Functionalized Sponge Fabricated via a Facile One-Step Coating Method*,

Separation and Purification Technology **181**, 183 (2017).

[49] D. Dardor, M. Al-Maas, J. Minier-Matar, A. Janson, R. Sharma, M. K. Hassan, M. A. A. Al-Maadeed, and S. Adham, *Protocol for Preparing Synthetic Solutions Mimicking Produced Water from Oil and Gas Operations*, ACS Omega **6**, 6881 (2021).

[50] Y. Ding, W. Xu, Y. Yu, H. Hou, and Z. Zhu, *One-Step Preparation of Highly Hydrophobic and Oleophilic Melamine Sponges via Metal-Ion-Induced Wettability Transition*, ACS Applied Materials and Interfaces **10**, 6652 (2018).

[51] C. Te Hsieh, J. M. Chen, R. R. Kuo, T. Sen Lin, and C. F. Wu, *Influence of Surface Roughness on Water- and Oil-Repellent Surfaces Coated with Nanoparticles*, Applied Surface Science **240**, 318 (2005).