QATAR UNIVERSITY

COLLEGE OF ARTS AND SCIENCES

DESIGNING OF POLYETHYLENE-BASED MATERIAL MODIFIED BY PLASMA DISCHARGE FOR WATER/OIL SEPARATION.

BY

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ABSTRACT

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Produced water (PW) from petrochemical industries is one of the largest wastewaters generated in Qatar. Soluble and insoluble oil contaminants occur in this water and must be removed if water will be used or discharged into the land or sea. Adsorption is a common procedure used in the industry for a wastewater treatment and oily components removal. It is a simple, cost effective process. Currently there are many available natural and synthetic, particularly polymeric adsorbents. Polyolefins are pure hydrocarbon polymers, which due to an appropriate sorption efficiency of low-molecular weight hydrocarbons can be used as suitable sorbents. However, polyolefins' based sorbents are commercially used only for removal of free oil. In this work, we have investigated a potential use of polyethylene as a filtration media in tertiary filtration of emulsified oil/water mixtures with respect to key parameters determining their adsorption ability. Polyethylene powders of various size and physical treatment were used. Emulsion formed from distilled water and commercial Diesel oil (DO) with a concentration below 200 ppm was used as a model of PW. The emulsions were prepared without emulsifier, and emulsification was insured by ultrasonication. The relationships between the sorption properties and surface composition and morphology of modified and unmodified PE powders were evaluated. Characterizations include the neat oil sorption, and sorption from emulsions, scanning electron microscopy, and profilometry. The PE adsorbents were further characterized by Brunauer-Emmett Teller surface area analysis, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were employed in order to characterize the porosity, crystallinity and chemical composition of PE, respectively. Sorption experiments were carried out as a function of different weight dosage, initial oil concentrations, and contact time to obtain the optimum conditions for the adsorption process. The results showed that LDPE powder, at a dosage of 3 g treated with plasma, using initial oil concentration of 100 ppm and 720 min of contact time presented the most suitable conditions for the adsorption of oil from emulsified DO. The adsorption process renders LDPE a suitable adsorbent for the removal of oil from diluted oil emulsions with an oil removal efficiency exceeding 93.5%. Equilibrium studies have been carried out to determine the sorption capacity of LDPE for the adsorption of oil from diluted DO emulsions using the optimum conditions. Langmuir and Freundlich adsorption models were applied to describe the experimental isotherms. Equilibrium data were fitted very well with the Freundlich model. The pseudo first- and second-order kinetic models were used to describe the kinetic data and the rate constants of sorption were evaluated. The experimental data were fitted well with the pseudo-second-order kinetic model. The study confirmed the feasibility of using oil adsorbents based on plasma treated PE powders as potential adsorbents media for the removal of oil contaminants from PW.

DEDICATION

I dedicate the accomplishment of this research work to my parents who regular prayers are my archangel, and to my dear siblings and close friends for the boundless love and care.

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LIST OF ABBREVIATIONS

AC	Activated Carbon
AFM	Atomic Force Microscopy
BET	Brunauer-Emmet-Teller
BOD	Biochemical Oxygen Demand
COD	Chemical oxygen demand
CPI	Corrugated-plate interceptor
DAF	Dissolved air flotation
DLS	Dynamic light scattering
DO	Diesel oil
DO	Dissolved oxygen
DSC	Differential Scanning Calorimetry
DVB	Divinylbenze
EDS	Energy-dispersive spectroscopy
EDX	Energy-dispersive X-ray spectroscopy
EPA	Environmental Protection Agency
FTIR	Fourier-transform infrared spectroscopy
HDPE	High density polyethylene
LDPE	Low density polyethylene
MAA	Methacrylic Acid
MF	Microfiltration
NDIR	Non-dispersive infrared detector
O&G	Oil and grease

PA	Polyamide
PAN	Polyacrylonitrile
PE	Polyethylene
PET	Polyethylene terephthalate
PH	Potential of Hydrogen
PMMA	Poly(methyl methacrylate)
POME	Palm oil mill effluent
PP	Polypropylene
PPIs	Parallel-plate interceptors
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PW	Produced water
RF	Radio frequency
SEM	Scanning Electron Microscopy
TCs	Total carbons
TIC	Total inorganic carbons
TOC	Total Organic Carbon
TOF SIMS	Time of flight - Secondary ion mass spectroscopy
TP	Total phosphorus

TSS	Total suspended solids
UF	Ultrafiltration
UHMWPE	Ultra-high molecular weight polyethylene
UV	Ultraviolet spectroscopy
VORWs	Vegetable oil refinery wastewaters
XPS	X-ray photoelectron spectroscopy

CHAPTER 1: INTRODUCTION

1.1 General Background

Water is a major source for survival on the planet [1]. Approximately 60 to 70 % of the land is covered by water, and water sources such as lakes, wetlands, rivers, reservoirs and watercourses provide us with fresh water, its conservation is therefore a priority, not just for humans, but for all other life forms too [2, 3]. Growth in industrial production and urbanization, which started with the industrial revolution in the 18th century and accelerated dramatically over the last decades, introduced tremendous and more sophisticated changes in the manufacturing processes, science and living conditions of populations [4]. Most of the growth and progress observed over the past decades have led to the rise of multiple environmental consequences related to overexploitation and insufficient waste disposal. Among these, contamination of water resources has been one of the most distressing. Essentially, five main water contamination sources are found from domestic activities such as cleaning or cooking, agricultural pollutants, sewage run-off from septic tanks, rainwater and industrial wastewater [3, 5, 6]. Industrial wastewater contamination is a by-product of industrial or commercial activities induced by the disposal of hazardous toxins and contaminates into water, rendering it ineligible for consumption and for other purposes. Huge amount of oily polluted water comes from both oil and gas industry. The processes of oil and gas exploration and production require a large quantity of water [7]. Therefore, as a bi-product of oil and gas discovery the oil and gas sector had a massive amount of wastewater to deal with. This wastewater is known as produced water (PW).

PW is one of the largest wastewater and oil-related source of contamination produce. These large volumes of water are estimated to be over 437 million barrels per day [8]. Soluble and insoluble oil contaminants including highly toxic elements, hydrocarbons, heavy metals and some chemical additives are presented in this water [8-11]. Consequently, PW discharge may cause serious air, soil and groundwater pollution. A key issue for the sustainable development of the oil and gas fields is the effective management of PW. Many approaches have been investigated for the management of PW, including recycling, re-injection and disposal in the environment, and they all require an appropriate treatment process before reuse. Nevertheless, the expense of treating PW to the allowable discharge limit is becoming increasingly costly due to strict environmental regulations. Technologies for the treatment of processed water can generally be divided into two categories: conventional and advanced treatment technologies [12]. Conventional techniques such as hydro-cyclones and skimmers typically act as a primary separation technique to eliminate non-dissolved components, where the content of the exit effluent in water is generally about 150 – 50 mg / l oil in water concentration [13]. Nonetheless, as the size dissolved components decreases, removal with conventional techniques becomes more challenging. Accordingly, at this stage more sophisticated and advanced technologies are required. These selective technologies includes membrane filtration or advanced oxidation processes (AOPs), and adsorption. Adsorption technique is a common procedure used in the industry for a wastewater treatment as a polishing step. It is simple, cost effective, relatively less generation of sludge, and it can be easily regenerated [14]. Consequently, adsorption is widely implemented for tertiary treatment. Currently, adsorption is used by companies all over the world, such as Siemens, as a polishing stage for the treatment of water before discharge [15].

Currently there are many available and low cost adsorbents such as natural materials, biomass and byproducts. The criteria for selecting novel adsorbents for removing oils from water are based on multiple factors, including adsorption capacity and rate, adsorbent cost, recyclability, high porosity, and the surface hydrophobicity [16]. Within Qatar and internationally, the primary adsorbent used in the oil & gas industry for PW treatment is a “walnut shell media”. Small pieces of crushed walnut shells are loaded into vertical cylindrical vessels with usually 48–66 inch bed depth [17, 18], also referred to as a media filter [19]. Walnut shell media excels by its affinity to remove oil from PW in tertiary filtration applications [20]. Furthermore, Walnut shells are relatively light in weight and characterized as strong with high elastic modulus. In compare with some other synthetic materials such as polymers, the affinity of Walnut shells to oils expressed by an oil affinity quotient (oil retention per unit of volume media) is less. As shown in Figure 1, the oil affinity quotient (g/g) of walnut shells to kerosene is only 0.033 g/g in compare with 0.212 g/g for polyvinyl chloride polymer [17]. It is even less in water environment, while oil droplets can be repelled from the walnut shells since they are coated by water film. However, this is suitable for backwashing process and easy extraction of attached oil from filtration media. As of late, polymeric adsorbents such as polyvinyl chloride, polyurethane, nylon polystyrene, or vinyl chloride-vinyl acetate copolymer have risen as another class of adsorbent materials for effective PW treatment in specific form such as powdered, shredded, chopped, disintegrated, ground or granular ones as well [21].

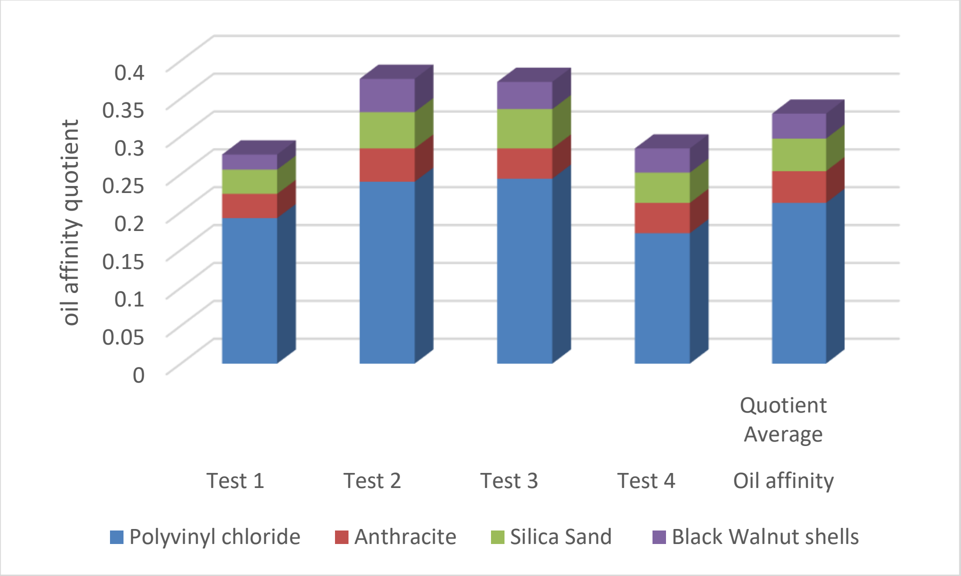

Figure 1. Oil affinity of different materials [17].

Referring to earlier reports, polyolefins are pure hydrocarbon polymers with high sorption efficiency for low-molecular weight hydrocarbons present in the water [22]. However, only a few studies are reported in literature on the use of polymer-based media for tertiary treatment [22-24]. As reported from previous studies the crosslinked polymer, which are prepared by a polymerization of a monomer having as a core moiety there of an alkyl (meth)acrylate the alkyl group [25] can be utilized as a swellable absorbent of oil. The oil material absorbing consists of particles (sorbent) with an average aspect ratio of about 5 to about 500 with an average particle diameter range 10 µm-1 mm [26]. Nowadays, the most available commercial oil sorbents used for free moil removal from water surfaces are made of polyethylene (PE) and polypropylene in the form of mats, excelled by a fast adsorption and high sorption capacity [27]. Despite this, there is lack of comprehensive and complex study focused on the use of these polymeric materials; as a filtration media in tertiary filtration with respect to key parameters determining their adsorption ability. These parameters include the specific surface area [28], porosity [29], oleophilicity [30], roughness [31] and internal morphology, such as molecular weight [32], crystallinity [33, 34] and degree of branching [35]. These parameters can be effectively altered *via* a suitable surface modification. In response to this issue, surface modification through plasma treatment in the respect of the surface and chemical changes has been implemented in this thesis. Plasma treatment represents one of the most powerful tool for surface modification of polymeric surfaces and it is frequently used in many polymer-oriented industry applications [36]. Plasma treatment is powerful tool, frequently used in plastic industry for a modification of surface properties of polymers which changes not only surface topology but also modifies their chemical character. Treatment by plasma in air/oxygen atmosphere leads to the attachment of polar functional groups such are various carboxyl and hydroxyl groups, which not only increases polarity of those surface, but also enables further chemical reactions with other low and high molecular species. This enables a modification of surfaces by various compounds and functional groups, giving them desirable functionality. Because all the changes are realized only on the surface (or in very thin top layer), the original physical character of materials is unchanged. Moreover, all these modifications are realized on the final, solid product, which is very desirable technological route [37, 38].

1.2 Objectives of the research

This research focuses on an investigation and development of an advanced oil sorption PE-based media applicable in tertiary filtration with impact on high oil affinity/retention, efficiency, regeneration, backwashing and lifespan aspects in water environment. The theoretical analysis is dealt with the adsorption kinetics of oil sorption on surfaces of treated and untreated PE powders. In more details, main objectives of this thesis are summarized as follow:

1. Preparation and characterization of untreated and the plasma treated PE grade samples.
2. A comprehensive study of plasma treatment on the surface morphology, chemical composition, and wettability of PE samples.
3. Preparation of model PW with concentration of DO within the range of 75-200 mg / L that is suitable feed for a tertiary system.
4. Investigation of PE media to remove DO from oil/water emulsions.
5. Investigation of adsorption isotherms and kinetics of sorption selected emulsions for treated and untreated PE surfaces.

CHAPTER 2: LITERATURE SURVEY

This chapter provides general background about the PW treatment, types and sources of Oil & Grease (O&G) as class of pollutants in the PW. It explains the treatment methods of PW with O&G. Moreover, it reveals the various stages in PW treatment; primary, secondary, and tertiary treatment. Furthermore, the attention was paid to an overview of what has been done in previous work related to treatment of PW with O&G by adsorption. It establish the achievements and weakness reported in previous studies. It reveals in general the types and characteristics of adsorbents and in polymers specifically. In addition, the development of oil adsorption properties using plasma treatment and description of the industrial methods for tertiary treatment of PW is discussed.

2.1 PW Treatment

Due to the large population growth and the development of life on all levels, demand for clean water has increased. This generated the need for the discovery and use of technologies to treat the PW. As mentioned earlier, PW is byproducts generated from offshore and onshore wells in oil and gas production and exploration. The quality, form and concentration of contaminants such as heavy metals, salt and oil hydrocarbons that present in PW significantly varies based on their source [39]. The direct usage or disposal of PW with high organic content to water bodies is deemed to be a biological hazard that could harm the marine environment strongly by increasing the algal growth and decreasing the amount of dissolved oxygen [40, 41]. Hence, the advancement of methods and technologies of PW treatment is therefore important to the environmental concerns of PW handling and disposal [32, 41]. PW treatment seeks to eliminate pollutants in order to comply with end-user needs. The key pollutants in the PW are conventional (toxic) pollutants such as total suspended solids (TSS), fecal coliform, biochemical oxygen demand (BOD_5), pH and O&G, and nonconventional pollutant such as chemical oxygen demand (COD), ammonia and sulfide [42, 43]. Among these pollutants, O&G is considered to be the most complex pollutants to eliminate and main parameters for the disposal of PW [10, 42].

2.2 The O&G class of pollutants in the PW (types, sources)

O&G is a class of organic constituents that are characterized by a very low water affinity [4]. O&G include fatty acids, hydrocarbons, soaps, lipids, and waxes [10]. They are hydrophobic in nature because of their non-polar characteristics [44]. Rhee et al. [45] perceive O&G" one of the toughest wastewater contaminants to be removed in PW". As most substances in this class are relatively poor in biodegradation, hence uncontrolled discharge to the environment can lead to great damage to the biosphere of the plant [46]. Even the thinnest oil layer can affect marine life by reducing light penetration between air and water and prevent the transfer of oxygen from the atmosphere into water. [47]. Generally, oil is not water-soluble, so oil-phase behavior is variable from case to case in oily wastewater [48, 49]. The chemical analysis process, particularly the solvent used for aqueous phase extraction (namely hexane), typically determines allocation of pollutants to the O&G group. O&G substances can be classified into two major groups, which vary in origin and chemical composition. The first group composed of mineral provenance, namely of petroleum based hydrocarbons (now referred to as 'nonpolar materials'), while the second It of biological origin (animal or vegetable), and consists primarily of triglycerides, such as fatty acids and glycerin esters [48, 50]. Interestingly, biologically derived oils behave like nonpolar molecules that is due to Wide non-polar fatty acid hydrocarbon tails regulating triglycerides, given the carbon-oxygen bonds of slightly polar glycerol that control the polarity of triglycerides [51]. Hence, both groups can be determined as a whole or as just the non-polar material. Furthermore, regardless of the chemical classification, O&G in PW may be studied with regard to their physical characteristics, which are important for right treatment strategy. The degree of dispersion and stability of oil droplets in water will affect can impact will impact the separation readiness and the resources needed to achieve the goal of treatment. Below, Patterson [45] describes four more O&G groups, which were subsequently completed by Rhee et al. [6] by assigning each group a droplet-size range as summarized in Table 1. As illustrated in the table, the oil-water mixture is classified as free oil mixture when the droplets-size is greater than or equal (≥) to 150 microns, dispersed oil mixture as the mixture droplets size is ranging between 20 and 150 microns. While, oil-water mixture with droplet sizes smaller than 20 microns and 5 microns are classified as an emulsified oil and soluble or dissolved oil mixture, respectively [44].

Table 1. The Physical classification of O&G droplets [4]

Physical class	Diameter range	Description
Free oil	150 > µm	Droplets that rise quickly to the surface in quiescent conditions, due to imbalance of forces caused by the differential density between oil and water.
Dispersed oil	20-150 µm	Droplets stabilized by electric charges and other inter-particle forces
Emulsified oil	< 20 µm	Droplets stabilized by the chemical action of surface active agents
Soluble or “dissolved “ oil	< 5µm	Dissolved or very finely dispersed droplets
“Oil-wet solids”		Suspended solids with oil adhered to their surface

The O&G is present in PW, but not at elevated concentrations. It originates from several sources. O&G entry into the municipal wastewater treatment plant is limited to household activities, i.e. cooking and cleaning [51]. The O&G content in an untreated domestic wastewater was reported to vary in between 50 to 150 mg/l [52]. Furthermore, a research by Stenstrom et al.[53] found that O&G, comprising leached hydrocarbons from motor vehicles and related activities such as parking lots and gas stations, rarely exceeded a few milligrams per liter in storm waters. Nevertheless, concentrations of O&G can approach a few dozen grams per liter. This results mainly from the industrial processes producing oily wastewater from which three predominant activities are identified as representing diverse realities. A variety of food manufacturing industries i.e. dairy, slaughterhouses and meat processing industries are renowned for generating O&G effluents [54-56]. In addition to that, VO production and refining that originate from sources such as sunflower, cottonseed, soybean and rapeseed [57], often dump huge amounts of oily wastewater known as VO refinery wastewaters (VORWs) [57, 58]. Furthermore, due to its high O&G concentrations (4000 to 6000 mg / l), oil extraction processes in most oil mills and mill effluents such as palm oil mill effluent (POME) can be labeled as oily wastewater [59]. O&G also comes from industries that manufacture non-vegetable oil, such as stainless steel, machinery, oil refining, metal cuts and metals preceding , and the textiles industry [60]. Furthermore, metalworking and finishing wastewater that results from using in coolers and lubricants used to cool work pieces and machine tools, minimize friction and rubbing of tools and dies and improve the surface quality, it generates O&G in the emulsified form with concentrations which could approach dozens of grams per liter [6, 61]. Table 2 below describes various types of wastewater characterized in the literature, According to their

O&G quality and discharge rates [6].

Table 2. Amount produced and O&G characteristics and legislation for different sources of oily wastewaters reported in the literature [4]

Source of wastewater	Amount produced	O&G (mg L^{-1})	Limit of O&G discharge in country	Reference
Oil and gas PW	>300 x 10^6 barrels d^{-1}, World	Natural gas: 2.3–60 Oilfield: 2–565	30 mg L^{-1} (daily), 50 mg L^{-1} (instantaneous), Australia; 29 mg L^{-1} (monthly), 42 mg L^{-1} (daily), U.S.A.; 10 mg L^{-1}, China; 40 mg L^{-1}, North-East Atlantic	[62]
Petroleum refinery effluent	33.6 x 10^6 barrels d^{-1} (minimum), World	1.1–3000	10 mg L^{-1}, China; 23 mg L^{-1}, Brazil	[11]
Metalworking fluids	2 x 10^9 L y^{-1}, World	20–200,000	17 mg L^{-1} (monthly), 35 mg L^{-1} (daily), U.S.A.	[63, 64]
POME	30 x 109 kg y^{-1} (2004), 44 x10^9 kg y^{-1} (2008), Malaysia (about 40% of world production)	4000–8000	50 mg L^{-1}, Malaysia	[52, 65-68]
VORW	-	480–7782	10 mg L^{-1}, India; 15 mg L^{-1}, Portugal	[57, 58, 69]

2.3 Treatment of PW with O&G

Treatment of wastewater is described as the process of extracting various forms of contaminants from water in order to produce a valuable effluent, which can be recovered under water. Oily wastewater production has risen in recent years as a result of rapid industrial development in oil and gas, dairy, petrochemical and pharmaceutical industries. Therefore, the removal of these pollutants represents always big challenge involving the combination of various treatment technologies based on the demands on the treated water [45]. Discharging oily water into the environment has adverse effects on aquatic life and agriculture. Since, disposing oily water with high O&G content into water bodies contribute to oil layer formation, which contributes to major pollution issues, including light penetration reduction, photosynthesis and elevated consumption of amount of dissolved oxygen (DO) by microorganisms [46]. Besides its ecological effect, O&G impacts conventional wastewater treatment facility activities, prevents Biological development in activated sludge reactors and causes pumps and piping to be blocked and fouled [45]. Stams and Oude [70] have stated that, the O&G effects in wastewater steam include physical blocks in drain, pump, screen and distributor arms, leads to an increase in maintenance expenses. Furthermore, the other problems relating to the presence of O&G are decreasing the efficiency of wastewater treatment processes by interfering with aerobic and anaerobic processes via reducing oxygen transfer rates and the transfer of soluble substrates to the bacterial biomass respectively, [53, 71]. O&G is a major concern in the management of wastewater. Due to the heterogeneity of this effluent, the strict law on discharge limits were laid down by government legislation. The permissible amounts of O&G in discharge effluents differ from country to country. US EPA limit the concentration of O&G in the effluent to a daily maximum of 42 mg/L per day and a 29 mg/L per month on average [72]. Australian EPA makes maximum permissible 30 mg / L of petroleum hydrocarbons [73]. Nevertheless, the discharge regulations in South America are stricter. The discharge limit for O&O in Ecuador and Colombia is 15 mg / L. While, in Argentina the discharge limit is only limited to 5 mg / L [73]. In addition, there is strict regulation in the Middle East in which the oil and grease discharge limit is less than 10 mg / L [74]. Thus, removal of O&G in PW needs specific treatment to a level at which the water disposed is not going to disturb the environment negatively. As illustrated in Figure 2 below, the treatment process of wastewater includes three main steps, which are primary, secondary and tertiary treatments depending on the purification level required.

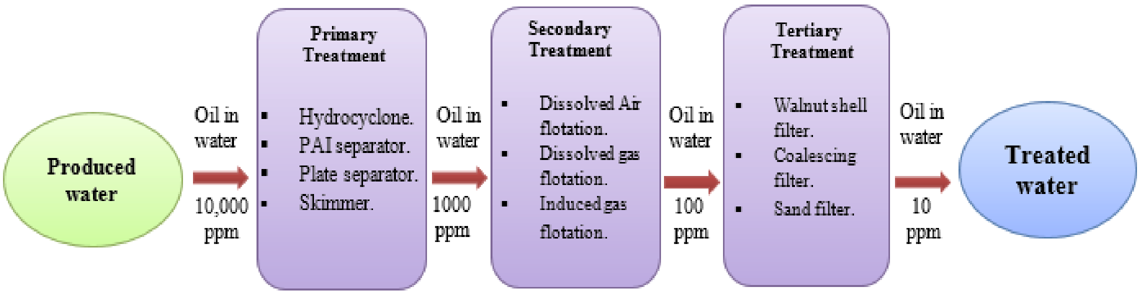

Figure 2 . Water treatment processing stages.

2.3.1 Primary treatment step

The first step in any wastewater treatment process after the collection of various types of wastewater. It is a physical process where most free oil, suspended and settled solids are eliminated followed by sedimentation and chemical additions in the case of wastewater with high content of solids. Also, it involves chemical dosages to reduce the odors, BODs and balance the acidity and basicity of water[75]. Primary treatment gets rid of about 60% of the suspended solid [76]. Primarily all solids are removed by means of gravity, where heavy solids settle at the bottom of tank used. Furthermore, to promote aggregation and ascension of oil droplets three different configurations of gravity separation tanks can be used as primary treatment methods. These methods are namely: traditional American Petroleum Institute (API) separator, parallel-plate interceptors (PPIs) and corrugated-plate interceptor (CPI) [4]. For the treatment of PW with O&G, API separator is dimensioned for removing only free oil (droplets with dimeter > 150 µm) and reducing the O&G concentration down to a value of 100mg L^{-1}[49]. While, PPI and CPI have more sophisticated design than the API separator. By taking the advantage of tilted plates inside these tanks; they can meet the treatment requirements of O&G concentration by removing oil globules (droplets as small as 60 µm) and lower the O&G concentration to value of 50mg L^{-1}[4, 6]. Following the primary treatment, a more homogenous wastewater is obtained, however it still has high-energy molecules that need another treatment step.

2.3.2 Secondary Treatment step

This step aims to separate emulsified form of oily wastewater that is dispersed so finely and cannot be spontaneously separated via buoyancy and gravity forces. The secondary treatment step involves multiple treatment methods, classified as chemical, electrical and physical.

- The chemical treatment method: is the most common treatment used in practice; as it targets the elimination of emulsified droplets of oil via the addition of acids, polymers and chemical coagulants, such as iron and aluminum salts [77]. Nonetheless, this method is less attractive due to the generation of effluents such as sludge, which will be forwarded to biological reactors to be separated. The most commonly chemical treatment methods are coagulation, flocculation and dissolved air flotation (DAF) [78].
- The electrical treatment method: is an electrochemical method that raises the efficiency of coagulation and flotation methods by taking the advantage of the electrochemistry. The only disadvantage for this method is that it produces unrecoverable amounts of dangerous sludge from chemicals or coagulation.
- The physical treatment method: it namely membrane separation method that targets the removal of oil droplets by changing the physical characteristics of wastewater to promote agglomeration and coalescences of droplets. Examples of physical methods, i.e. screening, DAF ,filtration and sedimentation [4].

2.3.3 Tertiary treatment step

The last stage in wastewater treatment process known as the polishing step. It separates all the harmful constituents, nutrients and ultra-small droplets of oil that remained after the primary and secondary treatment steps via using more sophisticated technologies. Primarily, tertiary step focuses on the elimination of all the residual organics and inorganics effluents, heavy metals, total phosphorus (TP), O&G, COD and nitrogen to meet specific discharge or reuse standards [79].

If PW was treated properly, part of the reuse can be in refrigeration systems, process water and feed boiler that involves the manufacturing, agriculture and groundwater recharging applications. Several industrial technologies are used in the tertiary treatment step. These technologies are : distillation, crystallization, evaporation, solvent extraction, oxidation, coagulation, precipitation, electrolysis, electrodialysis, ion exchange, reverse osmosis and adsorption [4]. Table 3: summarize the most commonly implemented industrial technologies to treat the O&G based on their removal percentage, efficiencies and different particle size.

Table 3. Industrial technologies to treat the O&G reported in literature[80].

Technology	Removal efficiencies	Minimum size of particle removal (µm)	O&G removal (%)
Nutshell or walnut shell filters	1-10 ppm free O&G *dependent on particle size and media size	5	95%
Filter media		25-5	95%
Activated carbon filters		0.3	99.97%
Microfiltration (MF) /ultrafiltration (UF)		1 - 2	95.2 – 99 %
Wire Mesh Coalescers		2 -5	98-99%

2.4 Treatment of PW with O&G by adsorption

Treatment of PW is an effective approach for handling such undesirable effluent. As it has the potential to forward it to valuable and harmless product rather than a waste. Nonetheless, the cost of treating the PW to the allowable discharge limit is becoming more and more costly due to the strict environmental regulations. Hence, at this stage the treatment requires advanced and more sophisticated technologies. Among a several technologies, adsorption considered the most effective, widely used technology in tertiary treatment systems as a polishing step for further PW purification [6]. Due to its lower cost, ease of operation, relatively reduced sludge generation, adequate regeneration capacity and higher efficiency at low concentrations, adsorption in the water treatment industry is receiving growing attention [14]. It has also been widely applied recently in new fields such as remediation of groundwater and improved wastewater treatment where it is competing with well-established process technology such as distillation and absorption [81] . In addition to that, in recent studies many authors center their treatment approach on adsorption as a core methodology. Ahmad et al. [82], Al-Malah et al.[83], Dalmacija et al. [51]and Hami et al.[84] all have used the adsorption as treatment of oily effluent as follow up to other processes such as coagulation, sedimentation, activated sludge and DAF [4]. The adsorption columns principle - in particular is about the ability of certain solid materials, generally known as adsorbents, to remove dissolved compounds that has long since existed. As such, the PWs that contain containments, i.e. dissolved organic compounds can be purified by transferring this contaminated water through a column containing these solid materials. Furthermore**,** several materials are identified as O&G adsorbents in the literature. As for illustration, Dalmacija et al.[51] and Hami et al. [84] utilized the activated carbon, in the granular form, as a tertiary stage in refinery of PW with O&G [4]. While, Wang et al. [85] attempted to solve the problem associated with activated carbon by using a fluidized hydrophobic bed of nanogels. However, as the manufacture of these two materials is costly, many authors have turned to the use of natural adsorbents as cheap technology for O&G removal by adsorption. For instance, Ahmed el al. [86] have used chitosan in powder and flake form to investigate the adsorption of residue oil from POME. Whereas, Ngarmkam et al. [65] have used palm shell (natural resource), as a precursor of activated carbons for the treatment of POME. Besides, Alther [87], proposed the use of organoclays as adsorbent for O&G , and he suggested the use of this material as a pretreatment for membrane separation and more sensitive adsorption processes and in primary treatment units as a post treatment such as gravitational separators. Although, the natural adsorbents are easier to dispose after use due to their low specific gravity and they have shown to provide good removal O&G efficiency, they require pretreatments to improve their affinity to oil by themselves. As a response to this issue, Zhou et al. [88], have opted the use of synthetic polymeric adsorbents instead, due to their ultimate characteristics such as selectivity, porosity , high stability and low cost [4]. In the next sections, the characteristics of adsorbents and the corresponding mechanisms for oil adsorption will reviewed.

2.5 Types and characteristics of adsorbents

To achieve an efficient process of separation, either a polishing step or bulk separation**,** it is necessary to consider several factors that relate to choosing the ultimate adsorbent for the separation system. One of these factors is the high internal volume, which allow the easy attraction of effluent to be removed such as oil to the surface of the adsorbent [81]. In addition, given that adsorption is a surface phenomenon, the adsorbent surface area is a key factor controlling the selection process. The higher the surface area the more elevated capacity is needed to make the separation process effective [14]. Generally, the internal surface area of adsorbents can vary from 100 m^2 / g to approximately 300 – 1200 m^2 / g [89]. Adsorbents can be divided into three basic categories: natural organic, natural inorganic and synthetic materials. The natural organic category involves readily available and low-cost materials such as walnut shell, rubber powder, straw, fungal biomass, flake, vegetable fibers and chitosan powder [4]. Nonetheless, these materials required pretreatment process to improve the oil take up capacity they can soak up only from 3-15 times their weight in oil. while, the natural inorganic such as clay, wool, glass, sand, vermiculate and volcanic ash [90], they show slightly better adsorption capacity. They are able to absorb from 4 - 20 times their weight of oil. Synthetic materials category it includes materials processed equivalent to plastics, i.e. polyurethane, polyethylene, polypropylene, and nylon fibers [27]. These materials can be used as oil adsorbents due to their oleophilic and hydrophobic nature and ability to absorb up to 70–100 times their weight in oil [91]. Recently, several nanomaterials have shown better performance than conventional adsorbents. For instance, membranes made of nanowires, and nanoparticles such as Fe_2O_3 / C. Also, there has been extensive use of carbon nanomaterials, such as graphene and carbon nanotubes [27]. Table 4 below, shows a synopsis of adsorbents used for separation processes in different emulsified oils and their of adsorption capacities.

Table 4. Adsorption capacities of adsorption with multiple adsorbents from literature.

Adsorbent	Emulsified oil	adsorption capacity (g/g)	Reference
Bentonite	Crude oil	0.5	[92]
Activated carbon fibres	Heavy oil	12	[93]
Exfoliated graphite	Crude oil	75	[94]
Peat	Heavy oil	3	[4]
Chitosan (powder form)	Palm oil	3.4	[82]
Walnut shell media	mineral oil	0.56	[4]
Polystyrene mats	Sunflower oil, motor oil, soybean oil, diesel oil	74–75	[95]
Polyurethane foams	Crude oil	20	[30]
Sepiolite	mineral oil	0.19	[96]
Raw eggshell	Crude oil	0.11	[97]

2.6 Types and characteristics of polymeric adsorbents

In industries worldwide, activated carbon (AC) due to its high adsorption efficiency, it has always been the most widely used adsorbent for traditional contaminants (such as organic acids and heavy metals) that is originated from various sources [93] . However, AC becomes a less attractive prospect due to several reasons as the high attrition rate, costly regeneration and the tendency to adsorb indiscriminately organic chemicals, which makes it impossible for some organic chemicals to be reused [98]. Meanwhile, economically attractive and low cost adsorbents such as clay soil materials, silica gel, molecular sieves and zeolites [4] have been reported also as an effective adsorbent for the for the removal of organic compounds. Nevertheless, these materials require further enhancement for their adoption capacity, porosity, mechanical strength and other characteristics [93]. Recently, Polymeric adsorbents have been emerging as a potential alternative to namely AC as filtration media in tertiary filtration system with regard to the crucial parameters that determined their adsorption ability. The parameters that determine the ideal polymeric adsorbent are: large surface area, great mechanical stability, flexible surface chemistry, good mutual solubility, porous structure, and potential regeneration under moderate conditions [98] . Polymeric adsorbents such as polyvinyl chloride, polyurethane, nylon polystyrene, or vinyl chloride-vinyl acetate copolymer in the form of powdered, shredded, chopped, disintegrated, ground or granular can absorb various ubiquitous organic contaminants effectively, including organic acids, poly-aromatic hydrocarbons, phenolic compounds and alkanes and their derivatives [89]. Table 5 summarizes the polymeric adsorbents used in oil adsorption application. Generally, the polyolefins (focus of this study) represent pure hydrocarbon polymers with high sorption efficiency (as high as 50g of oil per gram of adsorbent (50g/g)) for low-molecular weight hydrocarbons present in the water [32]. Crosslinked polyolefins were polymer prepared by a polymerization of a monomer (alkene C_nH_{2n}) having as a main moiety thereof an alkyl (meth)acrylate the alkyl group [25]. Nowadays, the most available commercial oil adsorbents from the water surface are made of polyethylene (PE) and polypropylene (PP) excelled by a fast adsorption, high sorption capacity and recyclability potential compared to other adsorbents. Consequently, they can be regenerated using different post-treatment methods for reuse. Furthermore, these materials are widely used in harsh environments typical of oil spills in sea due to their robustness, hydrophobic and oleophillic characteristics [27]. Several studies prove the potential of different forms of PE and PP as adsorbents for different pollutants. A study by Saleem et al.[99] showed the feasibility of synthesized plastic waste in film form made up of 7.5% high-density polyethylene (HDPE) and 2.5% of ultra-high molecular weight polyethylene (UHMWPE) to possess a fast and high oil uptake capacity of 100g/g in diesel oil, 45 g/g in mineral oil and 30 g/g in vegetable (corn) oil [100]. Furthermore, Ha et al. [101] established a success of adsorption process via using Methacrylic Acid (MAA) grafted onto PP fibers using Divinylbenze (DVB) as cross-linking level which shown a maximum oil sorption capacity of 21 g/g in crude oil [27]. Gheit et al. [91], found that PP powder and sheets form as will as PP powder the ability to absorb more strongly heavier crude oils than lighter ones, the maximum uptake capacity of both is 30 g/g. According to Lin et al. [102] study, non-woven PP fibrous mats have high uptake capacities of motor oil for 40 g/g, 30 g/g and 22 g/g for bean oil and sunflower oil respectively [100]. Despite all this, to our knowledge, a comprehensive study on complex adsorbing behavior of such materials in the respect of key parameters, which determine their adsorption ability, is still missing. These parameters are as follow: the total surface area, which is given by size of medium and its surface porosity, polarity of surfaces (olefin character is preferred), and, in former studies often underestimated internal morphology of these polymers (degree of crystallinity and degree of branching, an influence of long and short branches, molar mass, molar mass distribution) [32, 35]. In response to this issue, surface modification through plasma treatment with respect to the surface and chemical changes will be implemented.

Table 5. Summary of reffered polymeric adsorbents [27].

Polymer name	adsorption capacity (g/g)	References
PP and PE (powder and sheets form)	30	[103]
Waste HDPE	100	[99]
Polypropylene (PP)	21 (in crude oil)	[104]
PP/kapok blend	27 (in kerosene oil), 21 (in soybean oil)	[104]
Polyurethane (PU) foam	41 (in kerosene)	[105]
PU sponge	100 (in gasoline)	[27]
Polystyrene (PS)/ PU fibers	64 (in motor oil), 47 (in sun flower oil).	[106]
PS Porous fibrous mat	80	[102]
Nanoporous polyacrylonitrile (PAN) and PS fibers	195 (in pump oil)	[107]
Polyethylene terephthalate (PET)	1.5 -2.5	[108]
Co-polymer from (styrene based) resin	13	[109]

2.7 Improvement of polymeric surface by plasma treatment

Plasma treatment represents powerful tool for modification of polymeric surfaces and it is frequently used in many polymer-oriented industry applications [36]. Generally, it is a clean, dry, eco-friendly technique for the surface modification of various materials (polymer, metal, wood, glass, etc.) [110]. The key advantages of surface treatment with plasma relative to the other techniques are summarized in Figure 3. The interactions of plasma created species with the polymer surface can lead to the different processes depending on the used conditions such as used gas/gas mixture (Ar, N_2, O_2, CO_2, NH_3) and processing parameters (pressure, nominal power, treatment time, gas flow rate) [111]. As mentioned earlier, treatment by plasma in air/oxygen atmosphere leads to the attachment of polar functional groups such are various carboxyl and hydroxyl groups, which not only increases polarity of those surface, but also enables further chemical reactions with other low and high molecular species. The introduction of chemical functionalities can be occurred as result of plasma oxidation, amination or nitration, while using gasses without susceptibility for a formation of the polymerisable intermediates after an excitation. Moreover, the formation of free radical’s on polymer surfaces can lead to the surface activation, etching; or crosslinking processes [37]. Plasma treatment is thus responsible for chemical composition changes attended by topography/roughness changes. Besides, it allows further interactions with other low and high molecular species and consequently it enables a modification of surfaces by various compounds (grafting) with desirable functionalities. Since all these changes are realized only in the top surface layer, the original physical bulk properties are unchanged.

All these modifications can be realized on the final product, which is very appropriate technological route [112, 113].

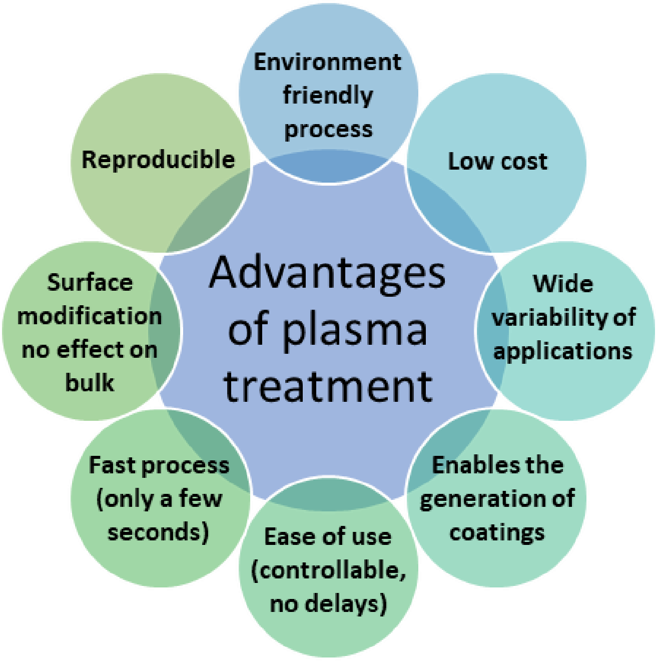

Figure 3. The key advantages of surface treatment by plasma relative to the other techniques [114].

Large attention in literature was paid to applying the plasma processing on flat polymer substrates (i.e. films, foils). Whereas, relatively slight focus has been devoted to polymer treat the powders form of polymer. This can be due to several factors such as the tendency of powders to form agglomerates that result in poor flowability or dust formation imposing distinct safety precautions. In addition to the lack of realistic and economical approaches for building new solid mixing reactors or modifying existing plasma reactors with the ability to handle polymer powders. After all, the basic principle of plasma-polymer interaction can be applied to powders. Furthermore, modified powder polymers are of great interest as over 70% of polymers used in various applications must be painted, coated, emulsified, printed, glued, or dispersed [114]. In addition to that, they are commonly used as a raw material in industry, primarily in processes i.e. powder sintering, rotational molding, powder coating, ram extrusion and compression molding [114]. As shown in Figure 4, plasma modification on powders polymer can be achieved using several surface modifications classified as etching /cleaning, activation of surface (functionalization), deposition/coating of film via plasma polymerization, and deposition of spacer.

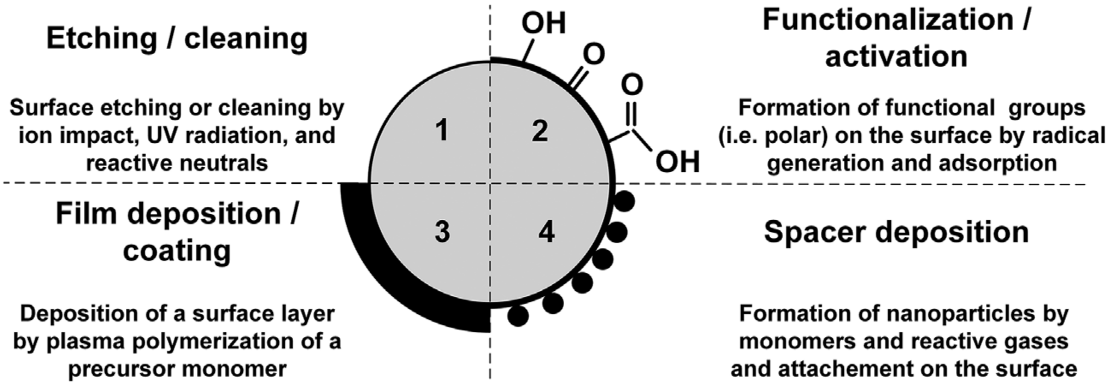

Figure 4. Functionalities on polymer powder using different surface modifications [114].

The optimal plasma treatment requires experimental determination of the best relation among powder filling amount, plasma reactor duration, treatment time and selection of powder gas mixing [38]. In addition to that, the storage time and conditions of treated powder after plasma exposure (i.e., temperature, light, storage scattered in water or ambient air), which influence the quality status of the plasma-treated surfaces. As such, when the surface polymer got exposed to atmospheric oxygen or water vapor, it will undergoes post-plasma oxidation via stable long-term radicals in the material undergoes [114]. Investigation of effect of plasma modification can be achieved by using several characterization techniques. The most popular analytical techniques for characterizing plasma treated polymers are: X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), Time of flight secondary ion mass spectroscopy (TOF-SIMS), Scanning electron microscopy (SEM), Atomic force microscopy (AFM) and contact angles measurements (wettability). Generally, plasma-treated polymer powders are used in numerous industries for wide variety of applications. Figure 5, summarize application fields of plasma-treated polymer powders. Several polymer powder types are listed in the literature to serve these applications. The list includes in particular PE (LDPE, HDPE), PP, PS, PET, PA, PMMA, PTFE, and silicone or tire rubber. Among these, polyolefins such as PE and PP have received most attention due to their simple structure, recyclability potential and their wide uses [114]. Numerous studies conducted by researchers investigated the use of treated of PE powders. As an illustration, Špatenka et al. [115] and Horakova et al. [116] have used PE plasma treated using O_2 and N_2 gas as raw material in rotational molding (adhesion) as well as hot melt adhesives (e.g., in powder dot coating processes for textiles). Whereas, Nessim et al. [117] and Put et al. [118], they apply it as an aqueous dispersions and pastes (e.g., dispersion without surfactants). Furthermore, many authors also pointed on the use of sintered plasma-modified PE powder adhered on PU foam products in the production of seats for automotive industry or better-isolated thermoboxes for food industry [114]. Interestingly, Gheit et. al. [103], have used powder PE waste polymers treated by γ-radiation with 3 Mrad in enhancing the efficiency for oil sorption.

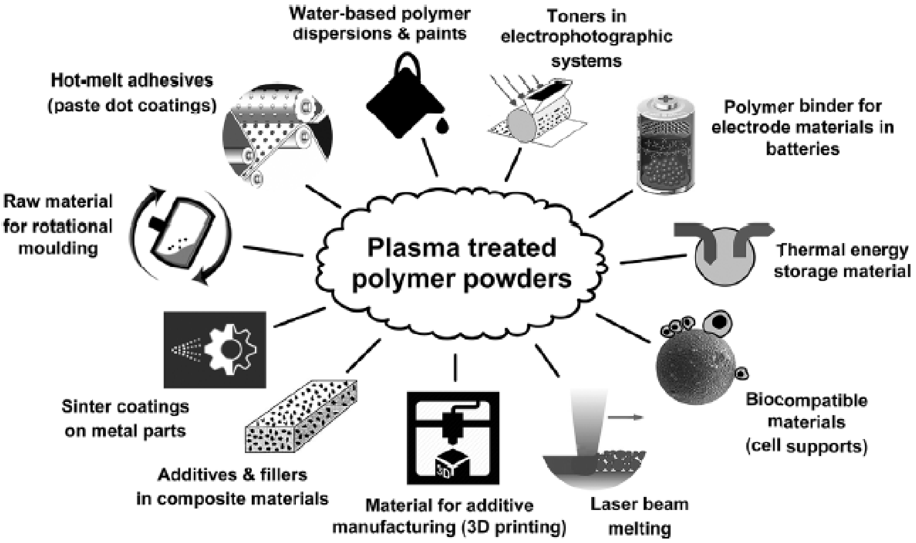

Figure 5. Summary of application fields of plasma-treated polymer powders [114].

2.8 Principles of the adsorption process

Generally, the oil uptake occurs via partitioning between the sorbate and the sorbent that is achieved through the mechanisms of absorption, adsorption, or both. Absorption is promoted by allowing the penetration of absorbate into absorbents with hair-like features via capillary forces[4]. By contrast, the adsorption is a phenomenon wherein a measure of the physical adherence due to binding forces originated from electrostatic interactions between the individual atoms, ions, or molecules of an adsorbate and the surface. Generally, there are two major type of the adsorption mechanism: chemical and physical adsorption. Physical adsorption, also known as physisorption, occurs due to weak intermolecular forces (i.e. Van der Waals forces) between adsorbate and adsorbent. Physisorption is a nonselective mechanism that generally runs at low temperatures, with rapid, often multilayered adsorption, and low adsorption heat. Due to the weak intermolecular attraction structure of the adsorbed molecules dose not change, the energy of adsorption is low, and the adsorbed material is easily removed [119]. On the opposite, in chemical adsorption or chemisorption, happens due to strong chemical forces of bonding between adsorbate and adsorbent. These bonding type forces are Lewis acid-base, hydrogen, ionic, or covalent bonds [120]. Chemisorption is a selective adsorption mechanism where chemisorptive bonds are typically stronger than those based on Van der Waals electrostatic forces. Chemisorption and physisorption are not isolated and often may coexist. However, in the wastewater treatment system, only physisorption occurs dependently on the character of adsorbents, adsorbates, and the treating conditions (pH, for instance). Generally, adsorption from emulsion onto a solid substrates is driven by solvophobic character of adsorbate-adsorbent system. Hence, that indicates the great impact of adsorbate-adsorbent properties on the adsorption process. According to Braga et al. [25], the adsorption phenomenon is closely connected to the surface tension of solutions and its intensity depends on the temperature, a nature and concentration of the adsorbed substance, a nature and the physical state of the adsorbent and the fluid, which is in contact with the adsorbent [10]. As such, the adsorption from aqueous emulsion increases with increasing molecular size or molecular weight of emulsified compound. As a result of that, the water solubility of organic compounds within a specific chemical class diminishes with an increase in molecular weight [119]. Furthermore, polarity affects the mechanism of adsorption too. A polar solute is easily absorbed by a polar adsorbent from a non-polar solvent [62]. In addition to that, charge neutralization of oil droplets via decreasing the pH of solution or by bringing the zeta potential of sorbent closer to zero can result in an enhancement of adsorption [4]. As for the surface topology, adsorption is a surface phenomenon, thus the surface area and the pore size distribution strongly influences typically the adsorption capacity [121].

2.9 Adsorption equilibrium isotherms

The adsorption equilibrium isotherms enable understaning and the interpretation of the parameters of adsorption and compares the adsorbent behavior in various adsorption systems under various experimental conditions [119, 121]. Adsorption isotherms, describe the dependence between the quantity of adsorbed species per unit weight of adsorbent, q_e , and the remaining quantity of those species in the solution (the residual equilibrium concentration, C_e) at constant ambient conditions [7]. Generally, the adsorption isotherms are based on various physical preconditions and models; and serves for a fitting of experimental data. [4]. Here we will discuss just two of the most common adsorption models, namely Langmuir and Freundlich isotherm.

2.10 Adsorption Models

2.10.1 Langmuir Isotherm Model

The Langmuir isotherm adsorption model is of the most common model that correlates relationships between an equilibrium concentration of dissolved/dispersed species in the bulk liquid phase and a concentration of those species adsorbed on the solid sorbent surface [121]. It gives prediction for a monolayer adsorption mechanism where only one active site can be occupied by one adsorbed molecule (there is no additional adsorption) without interference or steric damage from adjacent occupied sites [7]. This model describe a homogeneous adsorption mechanism in which all sites have equal affinity to adsorbate molecules, so that all adsorbed molecules have equivalent enthalpies and energy activation. The Langmuir equation can be expressed by Eq, (1):

$$q_{e=} \frac{q_m \, C_e k_l}{1+ \, C_e \, k_l} \tag{1}$$

Where,

q_e is the amount of substance adsorbed at equilibrium per amount of adsorbent (mg/g), C_e the equilibrium concentration (mg/L), q_m is the saturation monolayer adsorption capacity (mg/g), k_l is the equilibrium adsorption constant (L/mg).

2.10.2 Freundlich Isotherm Model

The Freundlich model is an empirical expression for the description of the multilayer adsorption over the heterogeneous surface with non-uniform affinities [7]. The Freundlich model is given by Eq. (2):

$$q_{e=} \; K_f \, C_e^{\frac{1}{n}} \tag{2}$$

Where,

q_e is the amount adsorbed at equilibrium per amount of the adsorbent (mg/g), C_e the equilibrium concentration (mg/L), 1/n is the heterogeneity factor, n characterizes the intensity of the adsorption process and characterizes the relative distribution of the energy and the heterogeneity of the adsorbent reactive sites, and K_f [L/mg] is the Freundlich adsorption constant.

2.11 Kinetic Studies of Adsorption

Kinetic models serve to estimate the duration of adsorption processes and thus to estimation the time needed for the effective treatment of liquids. In batch systems, the solute concentration in the treated liquid gradually decreases with time until it reaches equilibrium with the adsorbed species. In this study, the most common pseudo-first- and second-order kinetic models were applied to examine the sorption kinetics. Equations 3 - 6 describe, respectively, the pseudo-first- and pseudo-second-order models used to fit experimental data [19, 122].

2.11.1 Pseudo-first order model

The pseudo first order model derived by Lagergren [86] , is based on the simplified precondition that the rate of adsorption is controlled by an adsorbed amount (concentration of occupied sites on the sorbent) rather than a concentration of adsorbing substances in solution. The first-order kinetics imply that one element interacts with one unoccupied reaction site on the sorbent, and this process is described by Eq. (3):

$$\frac{dq}{dt} = k_1(q_e - q) \tag{3}$$

Where,

q is the amount of adsorbed species per mass of adsorbent (mg/g), k_1 (min^{-1}) is the pseudo-first-order rate constant, q_e is the amount of adsorbed species per mass of adsorbent in equilibrium (mg/g), and t is time (min). An integrated form of Eq.(4) gives Eq.(4a):

$$q = q_e(1 - e^{-k_1 t}) \tag{4a}$$

which enables the determination of parameters q_e and k_1 from nonlinear fitting. Eq.(4a) can be expressed in the linear for form given by Eq. (4b); which is mostly applied and cited in the literature.

$$\ln(q_e - q) = lnq_e - k_1 t \tag{4b}$$

The value of rate constant k_1 is obtained from the slope of a linear dependence.

2.11.2 Pseudo-second order model

The Pseudo-second order model represents the most common model for a quantitative description of the sorption rate of substances onto sorbent media. Eq. (5) expressed this model as follow:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{5}$$

Where,

k_2 is the pseudo-second-order rate constant. Unlike k_1, which has always the dimension reciprocal to time, the constant k_2 may have various dimensions (mg/g.min, g/g.min, mmol/g.min, *etc*.) [82, 119].

Analytical solutions of Eq.(5) can be expressed in various forms; however, the most common solutions are given by Eq.(6a) and Eq.(6b), which serve for a non-linear (6a) and linear (6b) fitting of experimental data and a calculation of q_e and k_2.

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{6a}$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6b}$$

2.12 Desorption/recovery

The majority of studies in the literature focus on adsorption, whilst relatively little attention was paid to desorption or recovery. Desorption is the inverse phenomenon of sorption (that is, either adsorption or absorption), by which the compound is released from or through surface of another compound [123]. In the wastewater treatment systems, the possibility of adsorbent regeneration and oil recovery considered to be a great advantage for the adsorption technology. As it allows expanding the technology's life cycle and generating possibilities for product recovery [4]. Furthermore, successful adsorption should recover the original take up capacity of the adsorbent without altering its porous structure and without any significant losing of mass [7]. A fraction of the removed contaminant can be adsorbed irreversibly during the adsorption process, which prevents the adsorbent from reusing it. Thus, it is crucial to preform desorption and evaluate the reusability of the adsorbents for the maximum number of cycles. Desorption/ recovery in the wastewater treatment systems can be performed using the following two methods [4]:

Chemical desorption: it a vital solvent extraction mechanism used to preform elution of oil effluents via aqueous solution such as n-hexane and NaOH solution and other chemical agents.

Physical desorption: it involves desorption of oily contaminants from adsorbent via using physical forces such as squeezing, centrifugation, compression and vacuum filtration.

CHAPTER 3: METHODOLOGY

This chapter demonstrates the experimental plan that was proposed to meet the objectives of this research. It describes the type of modifications, and the operation parameters that were used to control and optimize the PE-based media efficiency for oil removal from diluted emulsions. Besides, it discloses the high quality and accredited equipment utilized to characterize the samples.

3.1 Materials:

The raw material utilized throughout this research work was commercial grade low-density polyethylene Lotrene FB3003 (LDPE) in pellet form supplied by Qatar petrochemical company (QAPCO, Doha, Qatar). Main characteristics of LDPE are listed in Table 6 below.

LDPE powder was prepared by additional grinding of PE pellets. Ethanol (Sigma Aldrich), ultra-pure water (Purification System Direct Q3, France), and liquid Diesel (nonpolar) oil (DO) was obtained from a local petrol distribution company Woqod in Doha, Qatar.

Table 6. Characteristics of Lotrene FB3003 LDPE homopolymer [124]

Polymer Characteristics	Value
Melt Flow Index MFI (g/10min, 190^{o}C, 2.16 kg)	0.3
Specific density at 23 °C (g/cm^3)	0.92
Melting Point (°C)	109

3.2 Preparation of adsorbents:

3.2.1 Particle size analysis

Grinded PE powder with broad size distribution of particles were separated according to the size via the dry sieving method (ASTM D 422 - Standard Test Method for Particle-Size Analysis) in sieve shaker machine, as illustrated in Figure 6 below. The mean particle sizes of the five sets of LDPE particles were 500 µm, 150 µm, 100 µm, 75 µm and 63 µm. The 500 µm fraction was selected for the whole experiments.

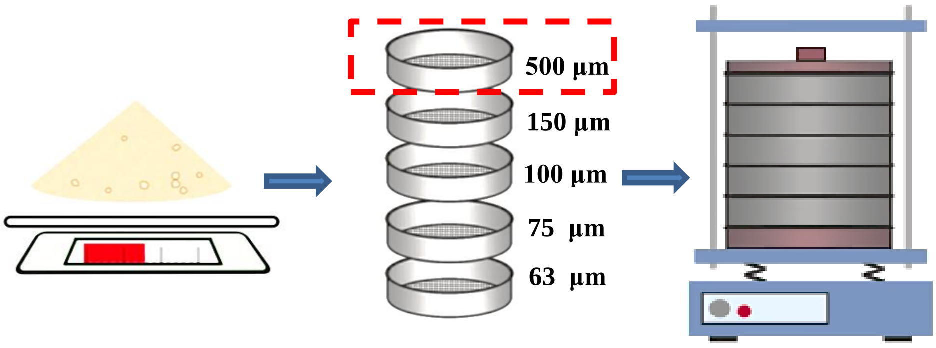

Figure 6. Schematic diagram of size analysis experimental procedure.

3.3 Surface modification: activation of polymer surface using plasma treatment.

3.3.1 Plasma Treatment of LDPE powder samples:

The low temperature plasma treatment of LDPE powder was carried out at vacuum pressure using radio frequency (RF) plasma system Venus75-HF (Plasma Etch Inc, Carson, USA). The schematic representation with description of this system is given in Figure 7. During the plasma treatment, plasma created reactive species in this system were generated by the means of RF power supply operating at a typical frequency 13.56 MHz. The chamber of the plasma system was evacuated to a pressure of approximately 0.2 Torr using a rotary vacuum pump before plasma ignition. Optimization of the treatment process was carried out by varying treatment time to obtain the maximum level of hydrophilicity in the LDPE surface [38]. The treatment time ranged from 30 s to 120 s at a constant optimal nominal power of 80 W. The gas flow rate was 10 cm^3/min. The LDPE powder samples were placed in closed Petri dishes wrapped by paraffin film during the plasma treatment in air and were turned over several times to ensure homogenous treatment from each side (Figure 7).

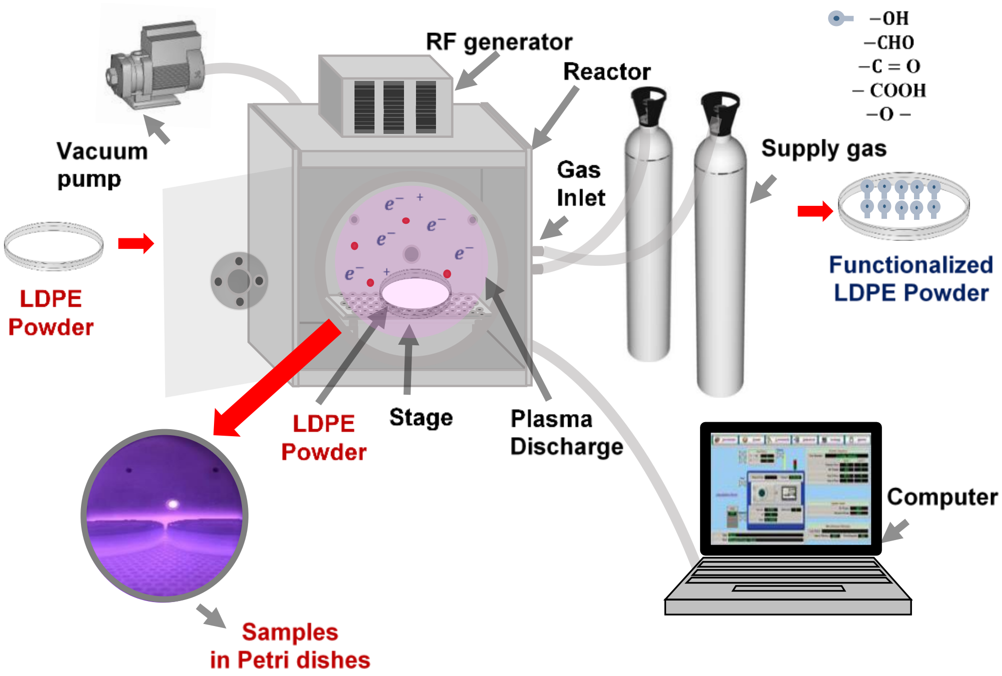

Figure 7. Schematic diagram of the surface modification process using radio frequency (RF) plasma setup.

3.3.2 Surface wettability analysis

An OCA35 optical system (DataPhysics, Germany) equipped with CCD camera were employed to measure the wettability of the flat LDPE surfaces (films) after plasma treatment thru static contact angle measurements via the sessile drop technique. Liquids with different surface tensions were tested to characterize the wettability of PE by an assessment of surface free energy (γ) and its dispersive (γ_d) and polar (γ_p) components by the Owens-Wendt-Rabel-Kaelble regression model [38]. From preliminary experiments, a main attention was devoted to the surface modifications of PE films, it was found that the optimum plasma treatment for LDPE film arises at an exposure time of 60 s and 80 W of nominal power in the presence of air plasma. As the highest wettability was achieved as result of formation of more polar (hydrophilic) surface. Thus, this treatment time was selected to preform modification on the powder form of the LDPE. Furthermore, the untreated and plasma treated PE films were analyzed in terms of their surface wettability using water , diesel oil and 100 ppm emulsion. The untreated LDPE surface has hyrophobic and oleophilic character, while water contact angle (WCA), oil contact angle (OCA) and emulsion contact angle (ECA) achieved value about 95.3, 91.2° and 12.6, respectively (Figure 8). The functionalization and roughness changes in the PE surface after RF plasma treatment in air led to the significant changes in wettability. The WCA and ECA of PE treated by RF plasma decreased to 57.8° and 52.8° °, respectively after 60s of treatment time, while OCA achieved 5.2° indicating maximal possible oleophilicity. Oil droplets were attached on untreated PE with well defined shape. However, oil droplets were totally spread on RF plasma treated PE indicating high oil affinity. These preliminary findings predicts a potential use of these plasma techniques for the improvement in oil/water separation.

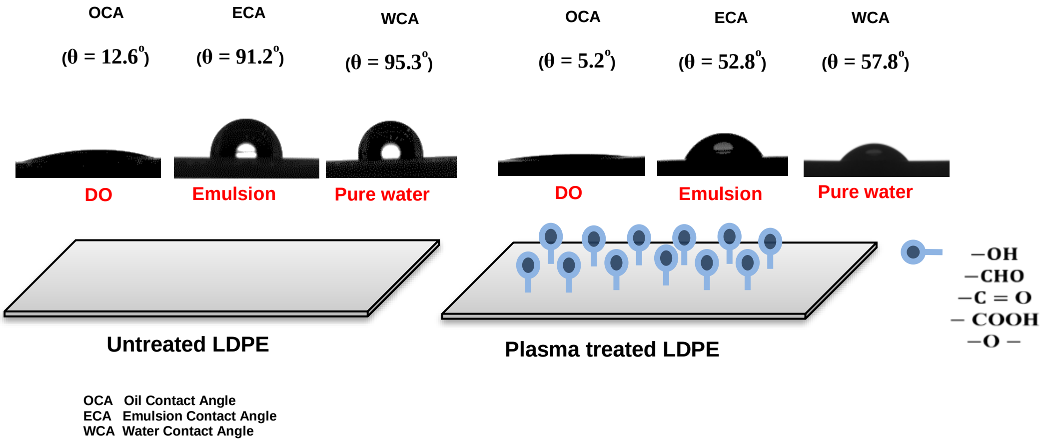

Figure 8. Illustration of surface wettability of LDPE films.

3.4 Characterization of sorbents

3.4.1 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC 8500 Perkin Elmer) was used to check the influence on thermal characteristics of LDPE samples resulting from the grinding process, particularly the degree of crystallinity which influences sorption ability of PE. It is known that mechanical grinding may lead to the scission of polymeric chains, resulting in the decrease in molar mass and finally in the decrease in the degree of crystallinity. The measurement was carried out over a temperature range from 80°C to 140°C at a heating rate of 10°C/min under nitrogen atmosphere. Nitrogen gas was passed through the instrument at a flow rate of 40 ml/min. Specific enthalpy of melting (ΔH_m) was calculated from the second heating and cooling curves in order to eliminate the thermal history of the samples. Results obtained from DSC were calculated from three measurements. The weight of the tested samples varied from 5 to 9 mg.

3.4.2 Surface morphology analysis

The surface morphology of the untreated and treated LDPE (powder) samples was examined with a field emission scanning electron microscope (FEI-SEM, Nova Nano SEM 450) equipped with energy-dispersive X-ray spectroscopy (EDS) with secondary electron images at 3 kV and different magnifications. All specimens were sputter-coated with 2 nm of gold before SEM images were taken to avoid the accumulation of electrons in the measured layer and to get SEM images with high resolution.

The surface topography of LDPE powder sample was characterized by profilometry (The Optical Surface Metrology System Leica DCM8, 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, 100x) allowing analyzing samples from different size of areas and a highly sensitive detector (1.4 million pixels resolution) can be used for obtaining confocal images. A EPI 100X-L objective (1360 x 1024 data points) was used for obtaining the maximal detailed images from a 175.31 x 131.97 μm^2 area.

3.4.3 Surface area measurements

BET surface area analyzer (Micromeritics – TriStar) was used to measure the overall surface area and pore size of the chosen grinded fraction of LDPE . The BET (Brunauer-Emmet-Teller) multipoint approach has been employed to assess the surface area, and pores distribution through nitrogen gas. Samples specific surface area was extrapolated at low temperatures 70 °C from the amount of nitrogen (extremely small molecule) adsorbed to the LDPE sample layer.

3.4.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to qualitatively evaluate changes in the chemical composition of LDPE untreated and plasma treated surfaces. For this analysis, FTIR spectrometer frontier (PerkinElmer, Waltham, MA, USA) fitted with a ZnSe crystal was utilized to capture information from a penetration depth of 1.66 μm. Besides, the spectral resolution and number of scan were set up to 4 and 8, respectively. Qualitative information was obtained for the absorption of chemical groups in the middle infrared region (4000–500 cm^{-1}).

3.4.6 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was employed to further investigate the chemical composition changes caused by plasma treatment on LDPE powder samples. XPS spectra was captured using an Axis ultra DLD system (Kratos Analytical, UK) containing Al Ka X-ray source. The sampling depth was in the range (1-10 nm) allowing to analyze only the top layer affected by plasma treatment (few tens nm). This XPS system contains a spherical shape mirror analyzer with the delay-line detector ensuring fast and highly sensitive analysis of the chemical composition quantification.

3.5 Preparation of emulsions

Generally, the specific density of oil (~0.85 g/cm^3 for DO) is lower than the one of water. When oil and water are placed together in a container, a layer of oil is formed over a top surface of water; this reflects their most stable thermodynamic condition. Such a 'layer location' minimizes the region of interaction between the two phases, thereby reducing their free energy. To form an emulsion, this location of the layer must be modified by either addition of surfactants delivering energy into the system. In order to minimize the number of components in the investigated systems, the ultrasonication was used for the emulsions preparation.

The goal of this preparation is to develop a recipe for oil in water emulsion with concentration within the range of 75-200 mg / L, which is an effective feed for a tertiary filtration step. The amount of carbons in a hydrocarbon chain has an effect on its liquid solubility. Therefore, the emphasis will be on hydrocarbon chains with low molecular weight. In this study, DO was chosen to act as the origin of hydrocarbons since they include hydrocarbon chains of 5-12 carbon atoms, which is a good representation of the target oil for water emulsion. To ensure good dispersion, a mixture of 500 mL of 200 ppm DO in water emulsion was sonicated for 15 min at 40% amplitude using the ultrasonic sonicator (HIELSCHER UP400S) device with 22mm titanium probe as homogenizer (Figure 9). Then, stock solution was diluted with deionized water to prepare several concentrations. Note that, several trial and error experiments were performed to optimize the conditions.

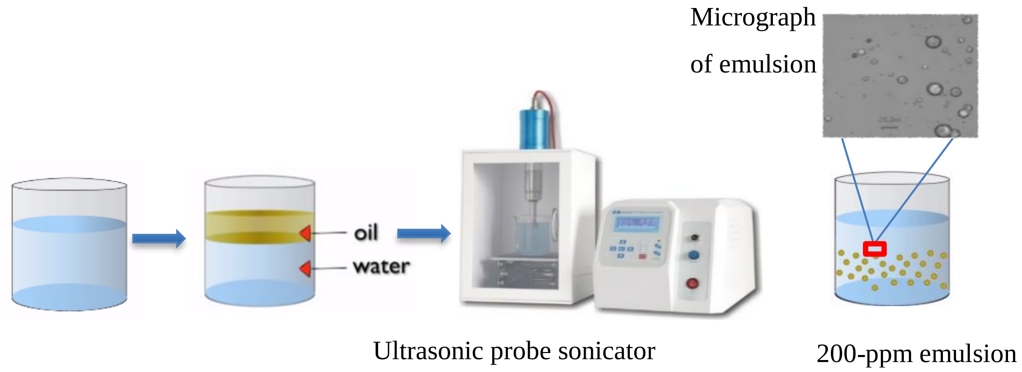

Figure 9. Schematic diagram of preparation of emulsions.

3.6 Characterizations of emulsions

3.6.1 Emulsions stability:

An emulsion usually consists of two or more immiscible liquids where one liquid is dispersed into another liquid (the continuous phase) in the form of droplets, (the dispersed phase) [92]. A key step in optimizing emulsion stability and performance is the analysis of droplet size. Many external factors, including storage methods (glass vs. plastic), temperature, sonication time and frequency can affect the stability of an emulsion. Also, there are many phenomena that can alter emulsion properties: coalescence, flocculation, creaming, Ostwald ripening, *etc.* [125]. Techniques of light scattering are the standard for evaluating emulsion particle size distributions. In this study, a 500ml solution of a 100ppm diesel in H_2O emulsion was prepared using probe sonication. The sonication was carried out for 60 mins at 40% Amplitude. At every 10 minute intervals, 5 ml was removed from the emulsion and analyzed using UV-VIS. Samples were labelled A1-A6 as illustrated in Figure 10. To study the stability of the emulsion, each sample (A1-A6) was tested every 24 hrs. for four days.

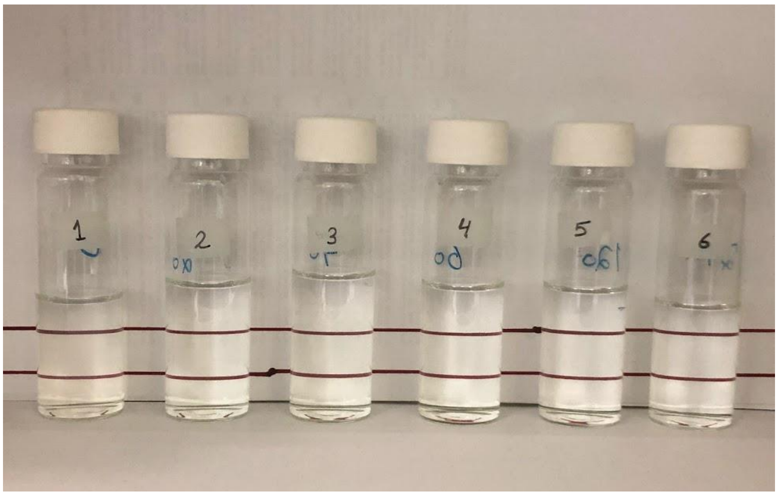

Figure 10. 100ppm DO in water emulsions labelled as A1-A6.

The droplet sizes of the prepared emulsions were assessed by dynamic light scattering (DLS). DLS is a powerful nondestructive technique to quantify the hydrodynamic size of particle in suspension form (typically in the submicron level) [125]. DLS generates key data as Z-average size (mean size), which originate from Brownian motion. Brownian motion is spontaneous particle movement caused by the interactions with the solvent molecules surrounding them induce laser light to be scattered at different intensities. Furthermore, a property known as the coefficient of translational diffusion (usually assigned symbol D) defines the velocity of the Brownian motion which yield from the analysis of intensity fluctuations. In addition to that, it determines the particle size via using by using the Stokes-Einstein Equation [125]:

$$d_{H=} \frac{KT}{3\pi\ \eta D} \tag{7}$$

Where,

d_H is the hydrodynamic diameter (that measures how a particle diffuses inside a liquid) , k is the Boltzmann constant, T the absolute Temperature, the η viscosity and

D is the diffusivity of particles in the solution.

Schematic illustration of typical experimental setup for DLS measurement is presented in Figure 11.

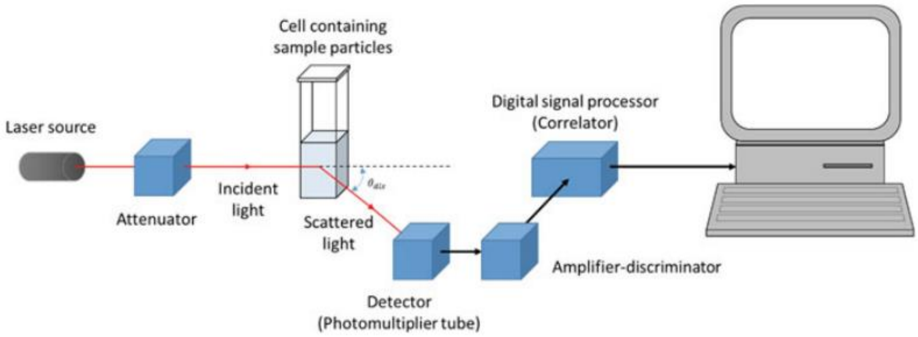

Figure 11. Schematic illustration of typical experimental setup for DLS [125].

3.6.2 Density of emulsions

Emulsion of oil in water (o/w) is not a homogeneous solution, but a colloidal dispersion of one liquid phase into another liquid phase [126]. The density is a crucial factor regulating the adsorption of oils on polymeric material [126, 127]. In this regard, standard analytical methods were used to characterize the prepared emulsion. The density of the DO based emulsions was measured using 25 mL pycnometer (ASTM D70, NFT 66007) (Figure 12). First, the volume pycnometer was determined by filling it with distilled water as the temperature dependent value of density of the water (ρ_{H2O}) is already known. The volume of water that fills the pycnometer and the stopper was determined according to Eq. (8) [128]:

$$V = \frac{m_{H2O}}{\rho_{H2O}} \tag{8}$$

Where,

m_{H2O} is experimentally determined weight of water (empty pycnometer weight subtracted) and $\rho_{H2O}$is the temperature dependent theoretical value of density of the water ($\rho_{H2O} =$ 0.99820 g cm^{-3} at 20°C) [128]. Then, the same procedure was repeat for the liquid (emulsions) with unknown density (ρ_L), and their weights were determined m_L (measured weight minus weight of empty pycnometer). The density of the liquid (emulsions) was obtained by using Eq. (9):

$$\rho_{L} = \frac{m_l}{m_{H2O}}\rho_{H2O} \tag{9}$$

Where, $\rho_L$is the density of measured liquid (emulsions), m_l is the weight of liquid (emulsions), m_{H2O} is experimentally determined weight of water and ρ_{H2O} is the temperature dependent theoretical value of density of the water. The preliminary properties of the tested emulsions are presented in Table 7 below. The values were recorded as an average of four measurements.

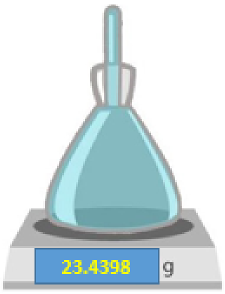

Figure 12. Pycnometer (ASTM D70, NFT 66007).

Table 7. The reported values of density of DO emulsion.

Emulsion Oil type	DO emulsion	
ppm	density (g/ml)	Std. dev. ±
75	0.9971	0.0014
100	0.9971	0.0029
150	0.9970	0.0010
175	0.9970	0.0006
200	0.9970	0.0004

3.7 Adsorption experiments (Testing of adsorption capability of materials)

2.7.1 Neat oil sorption

Neat oil sorption tests were performed according to the standard (ASTM) F726-06 [81] method. Briefly, in a 100 ml glass bottle (Figure 13), 1 g of untreated and plasma treated LDPE powder were immersed into 50ml DO under slight stirring at ambient temperature for 0.5 and 24 hr. Afterwards, the powders were poured out of, filtered through steel mesh and weighted. The capacity of sorption was quantified by weight ratio as oil absorbency (g/g) according to Eq.(10):

$$Q_{oil} = \frac{m_s - m_i}{m_i} \tag{10}$$

Where,

Q_{oil} is the oil sorption capacity (g/g) of the LDPE powder samples, m_s is the weight of the wet sorbent after sorption (g), and m_i is the initial weight of the dried sorbent before sorption (g).

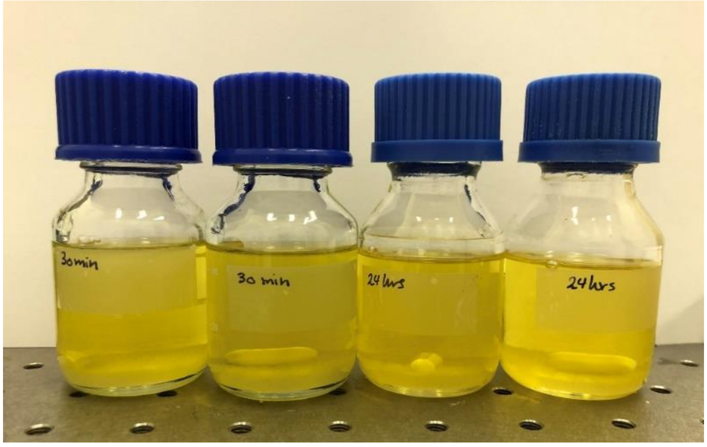

Figure 13. Untreated and plasma treated 500µm LDPE powder (1g) immersed in 50 ml neat DO for testing sorption capacity.

3.7.2 Testing of sorption efficiency of powders in batch

The powders were investigated by varying the adsorbent dosage, contact time, and initial oil concentration for the LDPE powder. The experiments were conducted in triplicates at room temperature and at a fixed volume of emulsions along with a control sample to see if oil content can be lost due to handling and shaking. Powders were placed in glass bottles with a volume of 40 ml of model PW. The bottles were then placed in a magnetic stirrer and agitated for 24 h at a fixed stirring speed around 350 rpm. Figure 14 gives a brief illustration of the experimental procedure performed in the lab.

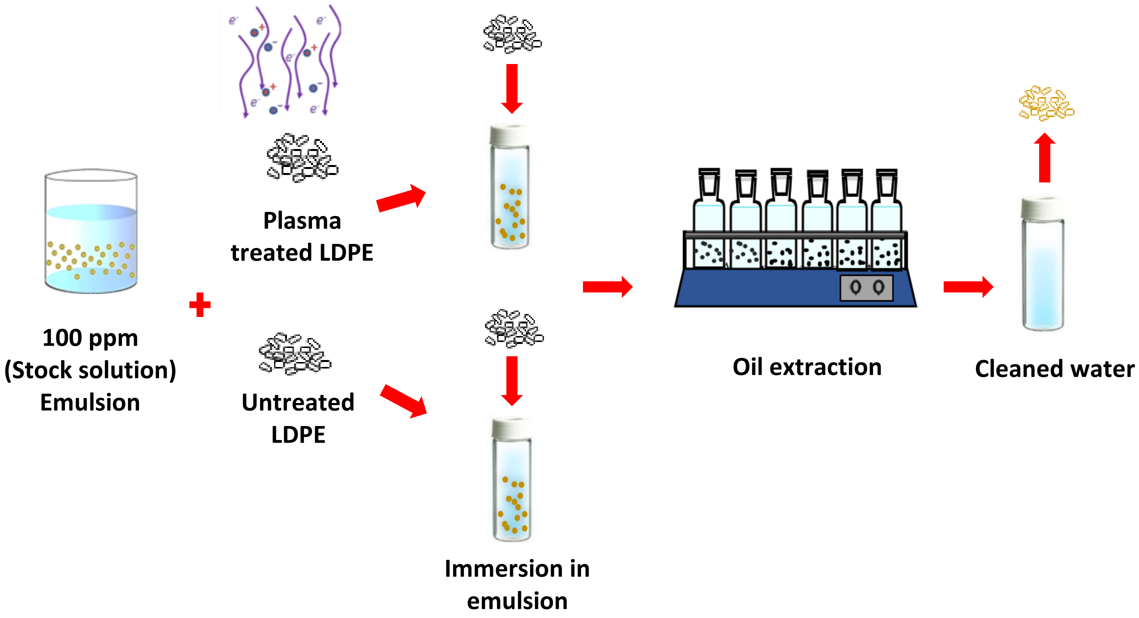

Figure 14. Sketch of experimental procedure.

3.7.2.1 The influence of dosage.

The effect of dosage was investigated in the manner explained above by varying the powder dosage from 0.5 to 3 g for LDPE powder while other parameters were kept constant. After the run was completed, the bottles were kept aside for 5 to 7 minutes to allow the powders to settle to the bottom of the containers. Thereafter, the permeate samples were separated from the powders and placed in another glass vials for total organic carbon (TOC) analysis. From this experiment, the best performing mass dosage was selected as the constant mass dosage to perform further experiments.

3.7.2.2 The influence of initial oil concentration.

The initial oil concentration was varied while the rest of the parameters were kept constant. A stock solution of concentration of 200 mg/L was prepared and diluted with water to obtain solutions with the concentrations of 75, 100, 150 and 175 mg/L. A similar procedure as mentioned above was followed.

3.8 UV- analysis

Libra Biochrom Spectrophotometer (SEC2000-UV/VIS, ALS, Japan) was used for transmittance measurements of emulsions. The machine for wavelength range between 200 nm and 600 nm created the transmittances spectra for both various oil concentration and filtrates after sorption, then the values corresponding to 450 nm were obtained.

3.8.1 Preparation of Standard Solutions of Oil for Plotting Calibration Curve.

In order to correlate transmittance to emulsion concentration, we need to plot a calibration curve; this was done by measuring the transmittance for different concentrations of the stock solution. As shown in Figure 15a, 100 ppm of DO in water stock solutions was diluted to prepare several concentrations. Then, the transmission spectra were obtained using Libra Biochrom Spectrophotometer. The value of transmission for each concentration corresponding to 450 nm were collected, plotted and subsequently values were linearly fitted. As an illustration, the graph below (Figure 15b) summarize the transmittance values for 100ppm diesel in water stock solution diluted to several concentrations.

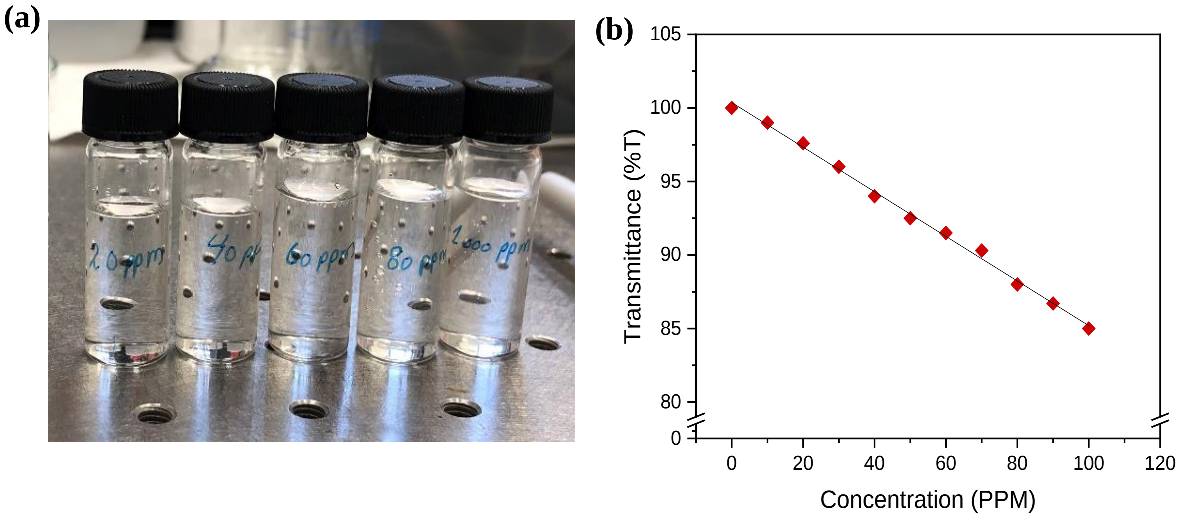

Figure 15. Illustration of a) diesel in water stock solution diluted to several concentrations, b) Calibration curve (T %) versus concentration (ppm).

3.9 TOC analysis

Total organic carbon (TOC) is an analytical tool used to assess the adsorption process of oils onto PE powders. TOC analysis was performed using Formacs TOC/TN analyzer by Skalar Analyzer (Breda, The Netherlands). The samples were injected into the high temperature combustion furnace where total carbons (TC) are converted to carbon dioxide at temperature of 850 °C by catalytic oxidation (Pt catalyst). The formed carbon dioxide is then dispersed into the carrier gas and, the concentration is measured by a non-dispersive infrared detector (NDIR). Then, the total inorganic carbons (TIC) are measured by injecting the sample into a reactor containing acid (H_3PO_4) converting TIC into carbon dioxide. The concentration of the resulting CO_2 is then determined by the NDIR. Finally, TOC is calculated by subtracting TIC from TC. The amount of oil adsorbed on the LDPE powder was calculated according to Eq. (11).

$$q_e = \frac{(Co - Cf) * V}{m} \tag{11}$$

Where,

q_e (mg/g) is the adsorption capacity, C_0 and C_f (mg/L) are the TOC concentrations of oil feed and permeate, respectively, and V (L) is the volume of the solution and m(g) is the mass of the dry powder sample.

Percentage removals were calculated using Eq. (12):

$$\%\ \text{Percentage removal} = \frac{(Co - Cf)}{Co}\ x\ 100 \tag{12}$$

CHAPTER 4: RESULTS AND DISCUSSION

In this chapter, all the results attained by using various characterization tools before and after conducting adsorption process are summarized. The trends and relationships among the operating parameters that indicate the efficiency for the sorption process performance of PE-based media are discussed. The results are compared with those ones reported in the literature. The key focus is on the investigation of the plasma treatment on the surface morphology, chemical composition, wettability and sorption capability of the adsorbents.

4.1. Characterizations of adsorbents:

4.1.1 Differential Scanning Calorimetry (DSC):

The DSC measurements were preformed to check if there exist any influence resulting from the grinding process on thermal characteristics of LDPE samples. Figure 16 shows the DSC scans (normalized thermograms) of LDPE pellet in addition to two selected fractions (500μm and 150μm) of LDPE powders prepared by grinding. The melting (T_m) and crystallization (T_c) temperatures as well as the specific enthalpies of melting (ΔH_m) and crystallization (ΔH_c) are summarized in Table 8. The heating cycle in Figure 16 shows that the LDPE does not contain a moisture as no related peak was appearing at around 100 °C. Theoretically [118], the endothermic peak that corresponds to the melting point of LDPE is characterized by broad and concave shape in nature, which proves that LDPE is semi-crystalline material with relatively broad molar mass distribution that depends mainly on size and orientation of the molecular chains. This is clearly seen in Figure 16. No considerable difference in the melting peaks for all three samples was observed. Besides, the melting points of LDPE pellets, grinded 500μm and 150μm were observed at 111.3 ±0.4 °C, 110.5±0.8 °C and 109.9±0.1°C respectively along with an almost constant value of heat of melting ΔH_m about 65.1±0.4 J/g. In Figure 16, it seen that the cooling curves of the different forms of LDPE show similar crystallization exothermic peaks upon cooling cycle. The exothermal transitions of all of them occurs at 95.8 ±0.4 ^{o}C with an enthalpy of crystallization (ΔH_c) about 63.5 J/g± 0.1. The obtained results proof the claim that the grinding process does not cause any significant alteration to thermal properties of the crystalline structure of the LDPE chains.

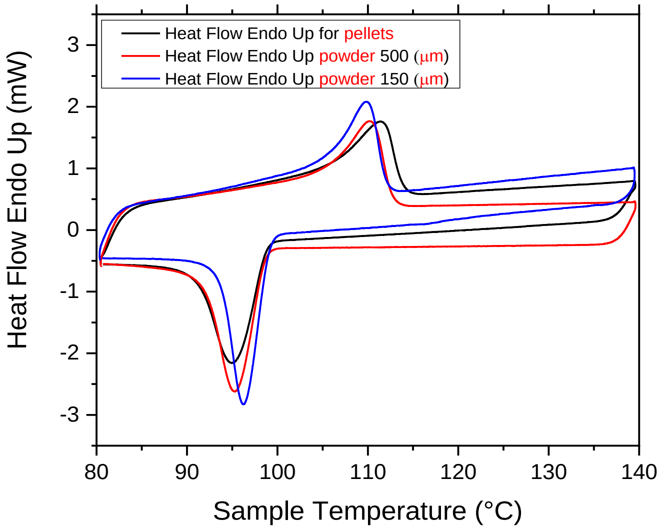

Figure 16. DSC scans (normalized thermograms) of LDPE pellets, grinded 500µm and 150µm.

Table 8. DSC results of LDPE samples: pellets, grinded 500µm and 150µm

Sample Type	Melting		Crystallization	
	T_m (° C)	ΔH_m (J/g)	T_c (° C)	ΔH_c (J/g)
LDPE pellets	111.3±0.4	64.9±0.8	95.2±0.6	63.3±0.2
LDPE powder (500 µm)	110.5±0.8	65.7±0.7	95.6±0.4	64.5±0.4
LDPE powder (150 µm)	109.9±0.1	65.1±0.4	95.8±0.4	63.5±0.1

4.1.2 Surface morphology analysis

Surface roughness is parameter significantly influences the wettability, so a study of the surface morphology is has a high significance. In this study, an analysis of surface morphology changes on the surface of powder form LDPE samples before and after plasma treatment was conducted using SEM. SEM micro-size images at 5000x magnification of untreated and plasma treated LDPE powders at 60s and 80W, representing optimal conditions are illustrated in Figure 17. The surface of untreated LDPE powder sample in Figure 17a is characterized by specific nano-sized irregularities appearing in its texture, which originally came from the grinding process. The 60s RF treatment in the presences of air led for minor changes in surface morphology, creating some textured grooves, cavities and valley-like areas. These changes in the surface morphology of treated LDPE are attributed in particular to the etching effect via plasma-gaseous species (electrons, ions or free radicals). As per literature [38], this phenomena is boosted by physical surface bombardment with highly energetic particles that are generated during plasma treatment.

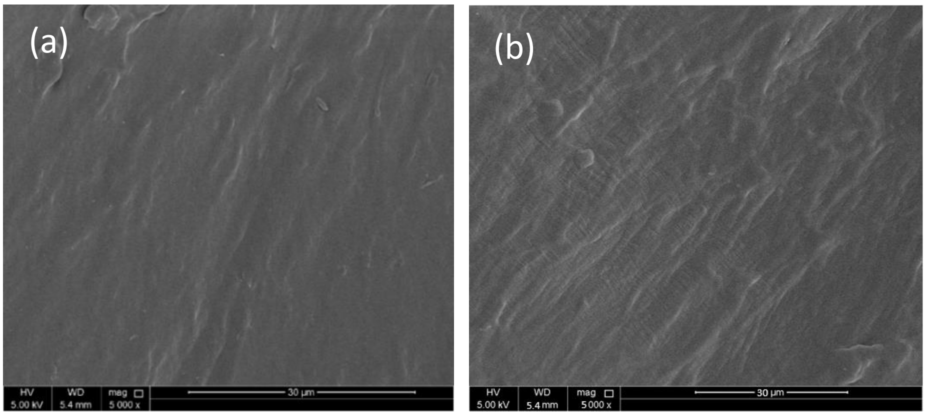

Figure 17. SEM micro-size images of LDPE powders: (a) untreated, (b) plasma treated.

Unlike PE pellets, which have always smooth surface as a consequence of the route of preparation**,** it is not always like for PE powders, as shown in Figure 18. These powders, prepared by additional grinding of PE pellets have a very porous surface structure.

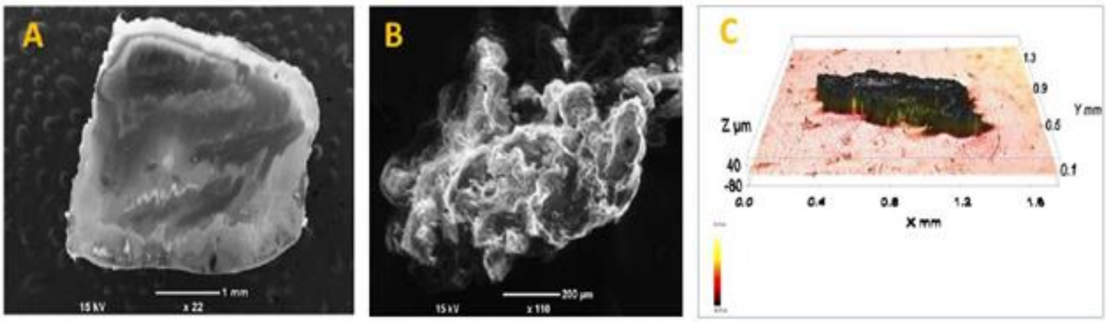

Figure 18. SEM micrograph of common LDPE pellet as produced (A), SEM micrograph (B) and profilometry image (C) of LDPE powder prepared by grinding.

4.1.3 Surface area measurements

A comparison of a simple estimation of the specific surface area of smooth pellets and porous grinded powders demonstrates and enhancement of the specific surface of grinded powders. Let us consider that pellet is approximated by perfectly smooth sphere with diameter D=500 μm what corresponds to the size of the powder used in this study. The specific surface area of perfectly smooth spheres (s_a) can be calculated from Eq. (13):

$$s_a = \frac{6}{\rho D} \tag{13}$$

Where,

D is diameter of the uniform spheres and ρ is a bulk density of material. In our case, for D=500 μm and $\rho = 0.92$ g.cm^{-3} we get $s_a = 0.013$ m^2/g, whereas the experimentally determined value of the specific surface area of powder is 4.7 m^2/g. This value is 362 times higher than the surface area of smooth spheres of the same size. It supports the statement that grinding of neat pellets significantly enhances surface porosity of materials and thus enhances the surface area of powders.

4.1.4 FTIR Spectroscopy

As per literature, the physical characteristics of any polymeric systems depends primarily on the chemical components and macromolecule configuration, which can be investigated via using several spectroscopic techniques such as FTIR [129]. Thus in this research work, the main goal of FTIR spectroscopy analysis was to qualitatively investigate the changes in the chemical composition of LDPE powder surface prior to and post the plasma treatment. Figure 19 below, shows the normalized FTIR spectra of the LDPE powder; for the untreated/virgin (in black), for the plasma treated (in red). Generally, different functional groups absorb characteristic frequencies of IR radiation. As noted from the plots in Figure 19, the IR spectrum of untreated LDPE (in black) contains mainly CH stretching, bending and rocking vibrations in the areas of 2900–2850, 1500-1400 and 750-650 cm^{-1}, respectively, as virgin LDPE comprises only hydrocarbon chains. A similar observation was achieved by Abusrafa et al. [38]. Interestingly, both the untreated and treated LDPE samples tested in this part have the same signature peaks of absorbance bands for non-polar groups. The evidence for that statement is the appearance of several identical intense bands as visualized in Figure 19. The first two strong bands were observed at the regions 2918 and 2849 cm^{-1}, assigned to asymmetric and symmetric stretching vibration of C-H and $-CH_2-$ respectively. Additionally, another two strong bands were observed at 1470 and 1463 cm^{-1}, assigned to C-H asymmetric bending deformation. At the regions 731 -719 cm^{-1} and 1367 cm^{-1}, medium bands appeared as an evidence of both rocking and wagging deformation in the spectrum. Whereas, the $-CH_3$ symmetric deformation was assigned to weak band observed at the 1376 cm^{-1}. Besides, at the region 1306 cm^{-1} another weak band belonged to the C-H as twisting deformation. The remarkable difference in the measured spectrum after plasma treatment can be seen clearly in Figure 19 as some polar groups were formed on the LDPE powder surface. These polar groups mainly comprise of hydroxyl, carboxyl and carbonyl [114], which is owed to the interaction of LDPE surface with the plasma. At regions 3000–3500 cm^{-1} and 1200 cm^{-1} vibrational absorbance bands assigned to–OH (wide absorbance band) and C-O were observed as proof of incorporated oxygen-containing functional groups after plasma treatment. Moreover, absorbance bands associated with vibrations of C=O and –COOH in carboxyl group also appeared after plasma treatment in the region 1800–1500 cm^{-1}.

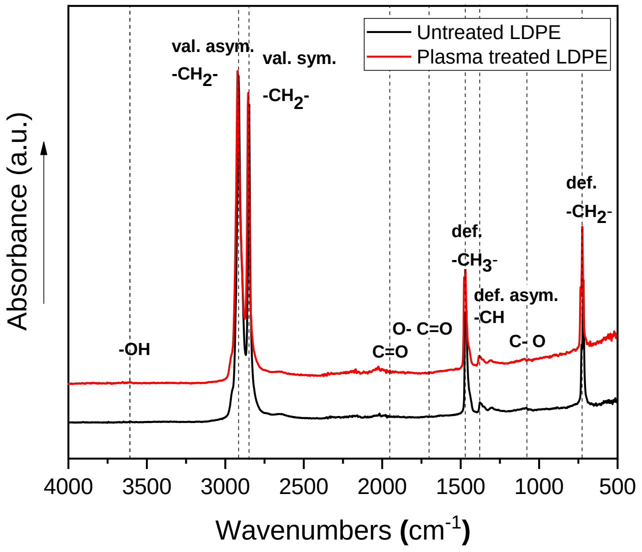

Figure 19. Normalized FTIR spectra of untreated and plasma treated LDPE powder.

4.1.5 X-ray photoelectron spectroscopy (XPS)

The XPS technique has been employed to quantify the changes in surface chemical composition of LDPE samples before and after the plasma treatment. The XPS spectra of LDPE powder prior to and after treatment are shown in Figure 20. Quantification report of the atomic compositions of all samples is listed in Table 9. All samples were investigated for the spectra of C1, O1s, and N1s. The highest proportion in the XPS spectrum of untreated LDPE samples was reflected by C1s peak at ~280 eV. As seen in Table 9, the spectrum of untreated powder LDPE revealed high carbon atomic concentrations (at.%) equal to 99.03 at.%. Besides, negligible traces of oxygen and nitrogen-containing functional groups present in the spectra of untreated LDPE samples likely attributed to processing additives or residual air within plasma chamber as established by Abusrafa et al. [38]. The atomic concentrations of O1s and N1s peaks for untreated LDPE are equal to 0.45 at.% and 0.51 at.%, respectively. By contrast, post plasma treatment significant changes in the XPS spectra of LDPE samples were observed. Theoretically, plasma treatment of the LDPE surface is responsible for the incorporation of new functional groups. Evidence of this declaration was the appearance of significant increase in the intensity of the O1s and N1s peaks at ~528 eV and ~400 eV of binding energy, as illustrated in Figure 20. The outcomes after applying plasma reveal newly formed functional groups of oxygen by functionalization processes, which were responsible for higher enhanced wettability. The atomic percentage of O1s and N1s increase was 9.75 % and 0.80 % in powder LDPE post-treatment, respectively. Nonetheless, this increase led to a reduction in the intensity of the C1s peak to 90.18 %. Theoretically, this redaction is due to the loss of certain carbons throughout etching, radicalization, and substitution with groups containing oxygen [38]. Furthermore, as confirmed by Arpagaus et al. [114], the increase of peaks intensity for the powder LDPE (core of this study) is proof of an effective and homogeneous treatment, which is due to an intimate contact between the powder surface and the plasma created species [118].

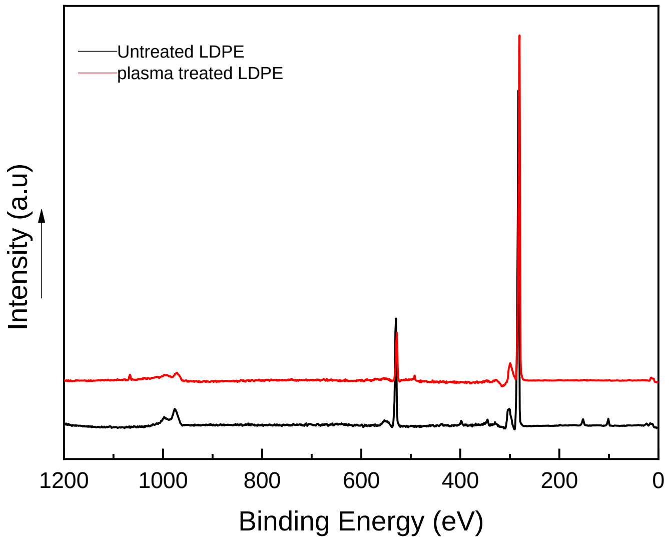

Figure 20. XPS spectra of treated and untreated LDPE samples.

Table 9. XPS of atomic composition summary of LDPE samples.

Elements / Samples	Atomic Conc. (at %)		
	C1s	O1s	N1s
Untreated powder	99.03	0.45	0.51
treated powder	90.18	9.75	0.80

4.2 Characterizations of emulsions

4.2.1 Emulsion stability

From a thermodynamic point of view, an emulsion is an unstable system due to its natural liquid / liquid mixture tendency to minimize its interfacial interactions [126]. Hence, it is vital to know if the prepared emulsions are stable over time. The evolution of droplet size over time is the principal parameter for the stability of emulsions since the instability affected *via* the droplet size changes. As per literature [125], droplet size measurement is of great importance as it provides a lot of information about the emulsion stability. In this study, the stability of oil-in-water emulsions was investigated using DLS. Besides, the DLS results were compared with the transmittance values obtained from UV-VIS spectrophotometry to ensure UV-VIS is a suitable method to record changes in oil concentration. Emulsion stability determined using change in transmittance over time is illustrated in Figure 21. whereas, the transmittance values obtained from UV-VIS are summarized in Table 10. As noted from the plots in Figure 21, turbidity is directly proportion to sonication time. Higher the sonication time result in lower the turbidity. In the case of low sonication time (10 mins), turbidity seems to increase over time, indicating that the oil droplets might be agglomerating over time to form larger droplets resulting in higher turbidity. Thus, it can be concluded that the size of emulsion droplets is function of the rotating speed and/or the emulsification time. A similar relation has been observed Leong et al. [125]. However, this conclusion is not supported by the particle size measurement. Consequently, DLS was performed, and the results are summarized in Figure 22 and Table 11. As visualized in Figure 22, droplet size remains fairly consistent over four days and is directly proportional to sonication time. Higher the sonication time, smaller the droplet size. Twenty minutes seems like enough time for sonication to prepare a stable emulsion. In addition, from the obtained results it was noted that with the exception of the sample that was sonicated for 10 mins, all other samples show an increase in droplet size over time (albeit negligible).

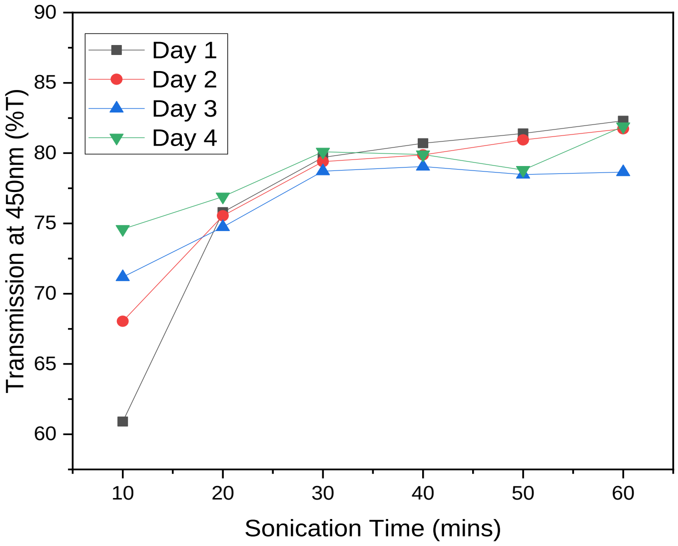

Figure 21. Emulsion stability determined using the change in transmittance over time.

Table 10. Summary of the transmittance values obtained from UV-VIS analysis

Sonication Time	Transmission at 450 nm				
(mins)	(%T)				
	Day 1	Day 2	Day 3	Day 4	Average
10	60.9	68.0	71.1	74.6	68.7 ± 5.8
20	75.8	75.5	74.7	76.9	75.7 ± 0.9
30	79.7	79.3	78.7	80.1	79.5 ± 0.6
40	80.7	79.8	79.0	79.9	79.9 ± 0.7
50	81.4	80.9	78.4	78.8	79.9 ± 1.5
60	82.3	81.7	78.6	81.9	81.1 ± 1.7

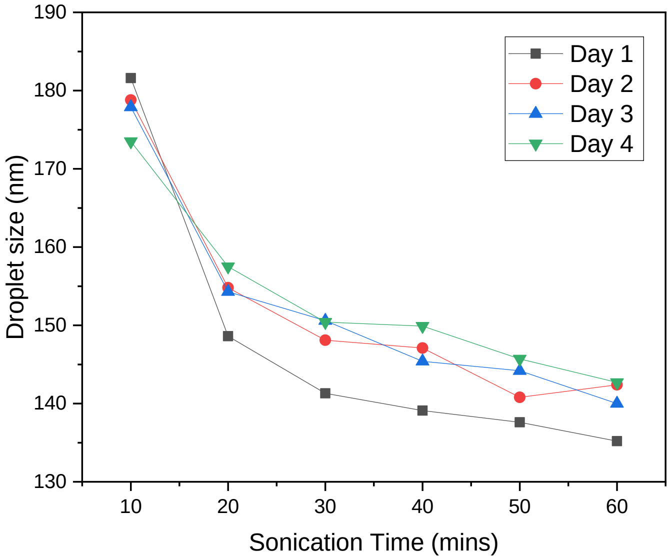

Figure 22. Change in oil droplet size over time.

Table 11. Summary of results obtained from DLS analysis.

Sonication Time (mins)	Droplet size (nm)				
	Day 1	Day 2	Day 3	Day 4	Average
10	181.6	178.8	177.9	173.5	178.0 ± 3.4
20	148.6	154.8	154.3	157.5	153.8 ± 3.7
30	141.3	148.1	150.6	150.4	147.6 ± 4.4
40	139.1	147.1	145.4	149.9	145.4 ± 4.6
50	137.6	140.8	144.2	145.7	142.1 ± 3.6
60	135.2	142.4	140.0	142.7	140.1 ± 3.5

4.3 Adsorption experiments (Testing of adsorption capability of materials)

4.3.1 Neat oil sorption

High oil adsorption capacity is the high porosity of sorbents and an appropriate wettability of a sorbent's surface [123]. The adsorption capacity of the LDPE samples was determined from the mass changes of controlled amount of adsorbent after oil sorption. Figure 23, shows the oil sorption capacities of untreated and plasma treated LDPE powder immersed into DO for 0.5 and 24 h. The results showed that 1 g untreated LDPE powder absorbed 0.93g ± 0.036 of DO within the first 0.5 h. whereas, after 24 h of immersion, the sorption capacities increased to 1.24 ± 0.028 g. On the other hand, post plasma treatment, the powders surface was altered toward a hydrophilic character, showing a remarkable increase in the oil uptake capacity. During the first 0.5 h, the treated LDPE powder absorbed 1.23 ± 0.056 g. This demonstrates that plasma enhances the surface wettability of LDPE powders even at short exposure times, mainly due to the formation of new polar functional groups on the surface by plasma treatment what leads to the enhancement of the surface free energy. High energetic surfaces are better wettable by both polar and unpolar liquids. After 24h of immersion, the surface hydrophilicity has improved further. That was evident by the further increase in the adsorption efficiency (as illustrated in Figure 23). The oil removal efficiency reached 1.36 g ± 0.08. These findings anticipates the positive influence of the plasma treatment on the improvement in oil/water separation.

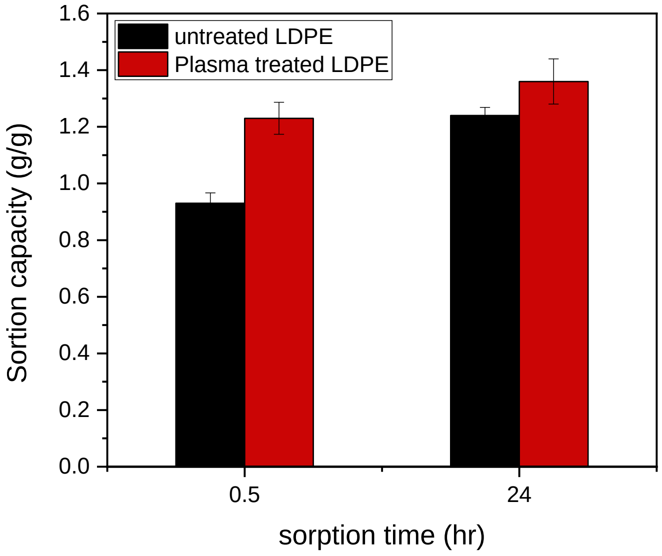

Figure 23. Oil sorption capacity measurements of untreated and plasma treated LDPE powders in neat DO.

4.3.2 Testing of sorption efficiency of powders in batch

4.3.2.1 The influence of dosage.

The influence of LDPE dosage (adsorbent) on the adsorption capacity is shown in Figure 24 and Table 12. The adsorption capacity of the adsorbent is expressed as an amount of adsorbed compound (DO) per mass of the sorbent. To establish the optimal dosage of LDPE for the adsorption, the mass of powder was varied from 0.5 to 3 g, whilst preserving other parameters such as mixing speed, contact time, and initial oil concentration constant. The mass of the powder was selected in order to respect the volume restrictions of the used vial. Just for an example, 3g of powder occupied at about 2/3 of the total volume of the vial. The data in Table 12 show following founding. Firstly, the percentage of removal as well as the residual oil content within the emulsion is positively influenced by an increase in the dosage content- the percentage of removal increases whereas the residual oil content decreases. This is in line with what we would expect because the surface area of sorbent gradually increases with an increase in the mass content and therefore the number of available binding sites also increases [82]. On the other hand, it is seen that the adsorption capacity (q_e) decreases with an increase in the dosage. It indicates that an increase in the surface area does not proportionally influence a sorption ability of sorbents. It seems that the coverage of the surface in the case of lower dosage is higher than the coverage of the surface for higher dosage. As it is shown in Figure 24, increasing the dosage of LDPE from 0.5g to 3.0 g rise the oil removal percentage from 8.7 % to 34.4 % on treating samples of 100 ppm (initial concentration) and after 24 hr of stirring time. Furthermore, it was noted that, with the increase of adsorbent dosage from 2.0 g to 3.0 g, the increase in the removal rate tended to be slow. From this reason, in this study the dosage for the all batch experiments was kept constant at 3.0 g of adsorbent in 40 mL of investigated emulsions.

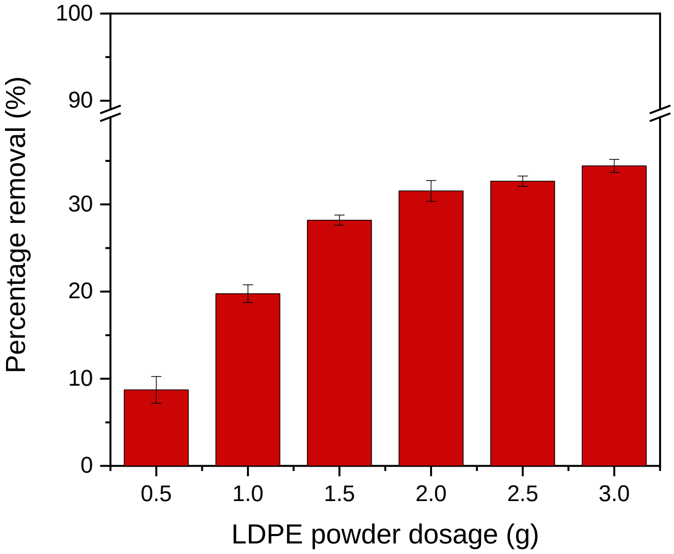

Figure 24. Influence of LDPE powder dosage on the adsorption of diluted emulsions.

Table 12. Influence of LDPE powder dosage on the adsorption of emulsified DO at initial oil concentration 100ppm.

Emulsified oil	Weight of adsorbent (g)	Residual oil C_e (mg/L)	*q_e (mg/g)	%Percentage removal
DO	0.5	19.7	6.43	8.7
	1	14.8	3.41	19.8
	1.5	13.4	2.31	28.2
	2	12.3	1.75	31.5
	2.5	12.0	1.41	32.7
	3	11.3	1.18	34.4

*q_e oil adsorbed per unit weight of adsorbent.

4.3.2.2 The influence of initial oil concentration.

As per literature [82], the initial oil concentration in solute can influence the kinetics of the adsorption, and therefore this parameter has to be taken into account. In this regard, the effect of the initial concentration of DO on the adsorption process under optimized conditions (3.0 g treated adsorbent and 24 h of stirring time) was investigated by varying the initial concentration from 75 to 200 ppm. The results are shown in Figure 25 and Table 13. As can be seen, the quantity of oil adsorbed per unit weight of adsorbents q_e increases by increasing the initial oil concentration. On the other hand, the efficiency of oil removal decreases with an increase in the initial concentration of oil. Specifically, the oil removal efficiency decreased from 96.7 % to 79.5% as the initial oil concentration of the DO emulsion increased from 75 to 200 ppm. These decreases could be attributed to saturation of the available adsorption sites. Similar results were achieved by the Okie et al. 2011; Dirak et al. 2018 [130] [92], but with different adsorbent. These findings show that for fixed adsorbent dosage, the removal efficiency of emulsified oil decreases with increasing initial oil concentrations due to an increase in the extent of surface coverage, which leads to reduction of available adsorption sites and consequently lower adsorption capacity was observed. In other words, the equilibrium between adsorbed oil and oil in the emulsion is reached at higher concentration of oil in emulsion.

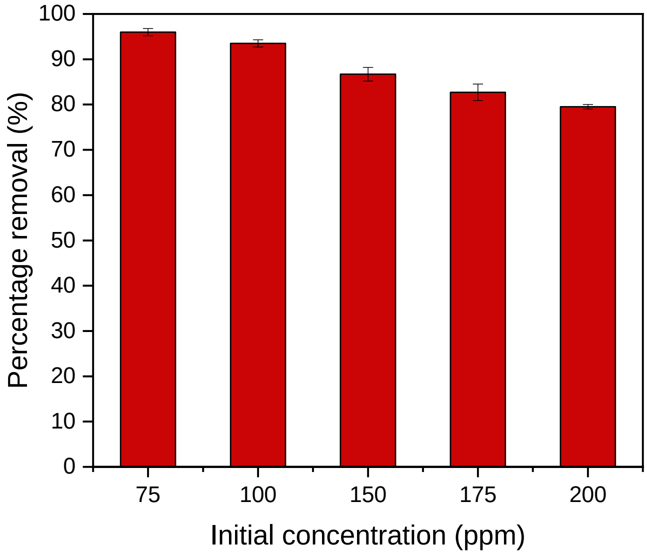

Figure 25. Influence of initial concentration (ppm) in the adsorption of DO emulsions.

Table 13. Influence of initial oil concentration on the adsorption of emulsified DO onto 3.0 g treated dosage, at contact time 24h.

Emulsified oil	Initial oil concentration C_0 (mg/L)	Final oil concentration C_e (mg/L)	Oil removed, C_0-C_e (mg/L)	*q_e (mg* g^{-1})	%Percentage removal
DO	75	5.5	70	0.93	96.7
	100	11.0	89	1.19	93.5
	150	22.3	128	1.07	86.7
	175	29.1	146	1.95	82.7
	200	34.5	166	2.21	79.5

*q_e oil adsorbed per unit weight of adsorbent.

4.4 Adsorption isotherms

Adsorption isotherms help to design the adsorption systems as they assess theoretically the maximum adsorption capacity that can be attained throughout the treatment process. As per literature [34], valuable information regarding the adsorption mechanism, surface properties and affinity of the adsorbents can be obtained from the equilibrium parameters. In this study, experimental results were modeled by the two of the most common isotherms , namely Langmuir and Freundlich adsorption isotherms (Table 15). The maximum adsorption capacity q_m [mg/g],, and adsorption (equilibrium) constants were determined. The fitting data are summarized in Table 14 and Figures 26 - 27. Results showed that the batch experimental data obtained from the adsorption of emulsified oils onto adsorbent are perfectly fitted by both Langmuir and the Freundlich isotherms with high correlation coefficients (R^2).

A useful parameter associated with the Langmuir isotherms is called the separation factor R_L (Eq.14).

$$R_L = \frac{1}{1 + K_L c_0} \tag{14}$$

R_L corresponds to the adsorption processes according to the following criteria [131]:

Case I. RL > 1: The adsorption is unfavorable (an increase in Gibbs free energy of adsorption)

Case II. 1 > RL > 0: The adsorption is favorable (a decrease in Gibbs free energy)

Case III. RL =1: It characterizes a linear adsorption (unoccupied sites at the adsorbent are randomly occupied by adsorbate proportionally to their concentration, and only one reaction site is occupied by one species).

Case IV. RL = 0: The desorption process is irreversible.

The R_L values are significantly lower than 1 for all tested initial concentrations (c_0) indicates highly favorable adsorption of oil droplets on the adsorbent.

The graphical depiction (linear and non-linear) of the Freundlich isotherm are shown in Figure 27 and parameters (K_f, 1/n) were determined from both linear and non-linear fitting of experimental data. The exponent 1/n gives an indication of the favorability of adsorption. It was demonstrated that if values $n>1$, it indicates a favorable adsorption [52]. Table 14 reveals that, value of exponent n is larger than one, indicating the adsorption is favorable. A similar finding has been reported by Ahmed et al. [86] and Diraki et al. [130] for adsorption using powder-based adsorbents.

Table 14. Equilibrium adsorption parameters of isotherms

Fitting Type	Langmuir model						Freundlich model		
	q_m (mg /g)	K_L *(L /mg)*	$\frac{1}{q_m}$ (g /mg)	$\frac{1}{k_l q_m}$	R_L	R^2	K_F (L /mg)	n	R^2
Non-linear	3.04	0.06	-	-	0.1	0.9887	0.377	2.03	0.9964
Linear	3.27	0.06	0.33	5.0	0.1	0.9999	0.377	2.04	0.9999

Table 15. Non-linear and linear forms of the adsorption isotherm models.

Equation Form	Langmuir model	Freundlich model
Non-linear	$q_{e=}\, q_{mK_L}\dfrac{C_e}{1+K_LC_e}$	$q_{e=}\ K_fC_e^{\frac{1}{n}}$
Linear	$\dfrac{C_e}{q_e}=\dfrac{1}{k_Lq_m}+\dfrac{C_e}{q_m}$	$\ln q_{e=}\ \ln k_f\ +\ \frac{1}{n}\ \ln C_e$

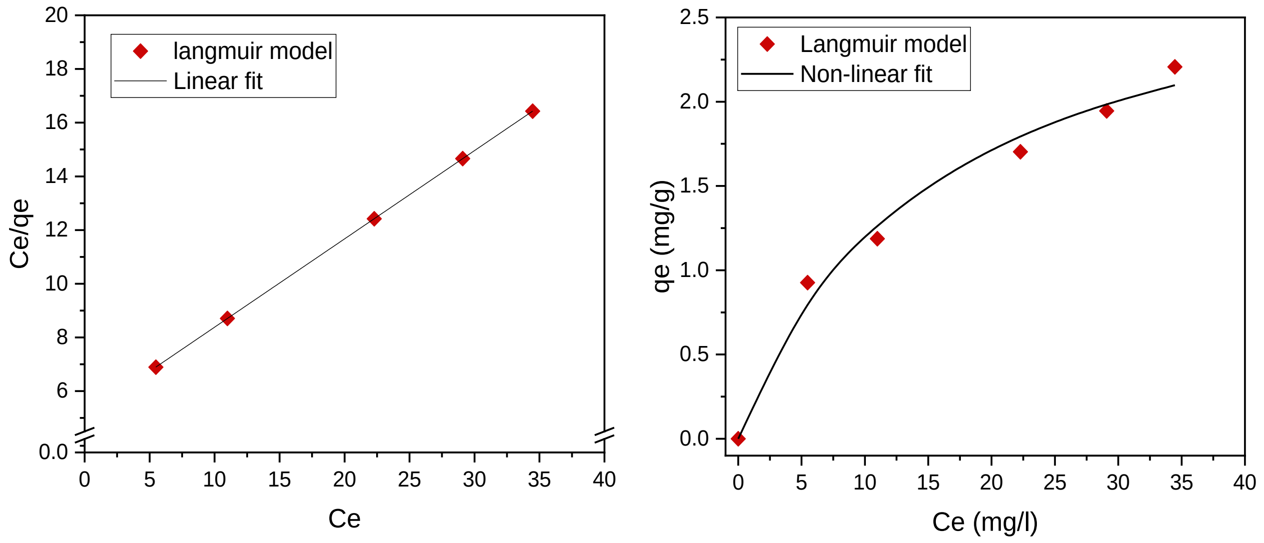

Figure 26. Langmuir adsorption isotherm non-linear fit (right) and linear fit (left) for adsorption of DO on powdered LDPE.

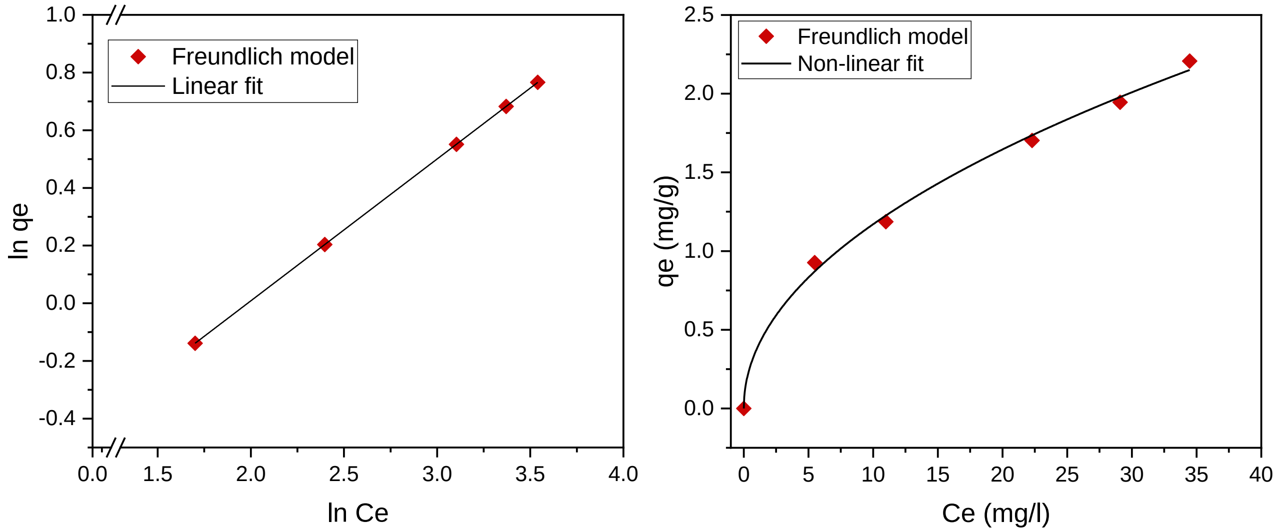

Figure 27. Freundlich adsorption isotherm non-linear fit (right) and linear fit (left) for adsorption of DO on powdered LDPE.

4.5 Kinetic Studies of Adsorption

Kinetic models serve to estimate the duration of adsorption processes and thus to estimation the time needed for the effective treatment of liquids. In batch systems, the solute concentration in the treated liquid gradually decreases with time until it reaches equilibrium with the adsorbed species. Hence, to establish the equilibrium time related to the maximum oil removal from emulsified oils, the amounts of adsorbed oil onto the powdered LDPE (adsorbent) were studied as a function of contact time, which varied from 30 to 1440 min, using initial oil concentration of 100 ppm and 3.0 g of treated adsorbent dose. While keeping other parameters such as mixing speed and vial size the same as in the previous study. Theoretically [92], the equilibrium contact time refers to the time necessary to attain equilibrium in the adsorption process. This equilibrium is achieved when the rate of adsorption from the solution onto the surface of the adsorbent corresponds to the rate of desorption from the adsorbent to the solution [7]. Figure 28 and Table 16; show the results for the influence of the adsorption times on oil percentage removal. As expected, the adsorption capacity increased as the sorption time increased from 5 to 1440 min. However, within the first minutes, the oil sorption rate was rapid. Thereafter, the oil removal efficiency reaches equilibrium when the rate of adsorption and the desorption are equilibrated. This does not necessary mean that the whole surface area is occupied and the surface of adsorbent need not be saturated with the oil. The highest removal efficiency of 91.0 % was achieved. The effect of contact time on the residual oil content C_e was also studied. The results are shown in Figure 29 and Table 16. It can be clearly seen in Figure 29 that the residual concentration decreases with increasing the contact time until 720 min after which no further effect was observed in the emulsified DO system.

Table 16. Influence of contact time on the adsorption of emulsified DO onto 3.0 g treated dosage, at initial oil concentration 100 ppm.

Emulsified oil	contact time (min)	Residual oil concentration Ce(mg/L)	q_t (mg/g)	%Percentage removal
DO	5	62.0	0.64	38.1
	10	64.7	0.61	35.3
	15	65.9	0.60	34.2
	30	14.0	1.19	87.2
	60	13.2	1.20	87.7
	90	11.4	1.21	88.7
	120	11.1	1.21	88.9
	240	10.0	1.22	89.4
	360	9.8	1.22	89.7
	480	9.2	1.22	90.3
	720	8.5	1.23	90.9
	1440	7.9	1.24	91.0

*q_t oil adsorbed per unit weight of adsorbent

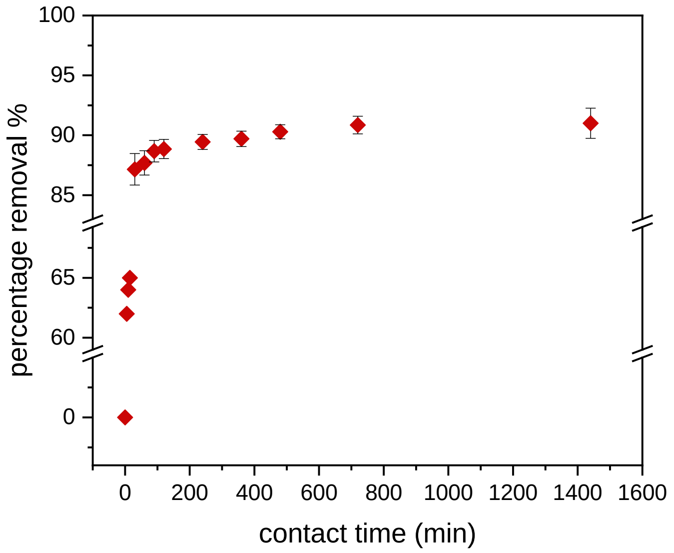

Figure 28. Influence of contact time on the adsorption efficiency of diluted DO emulsion.

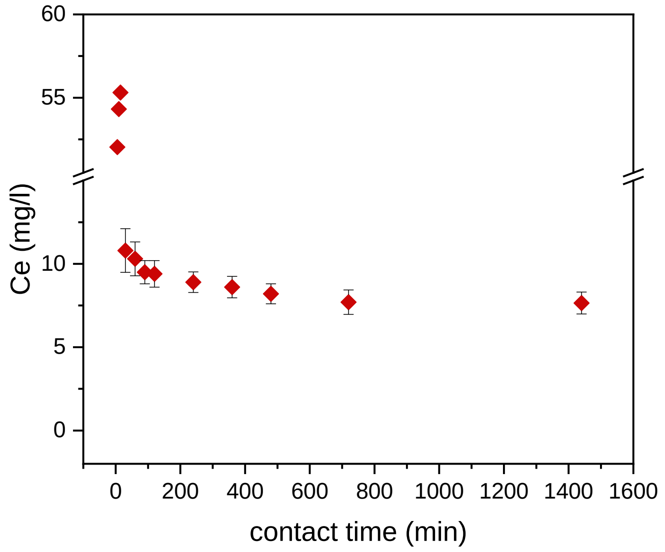

Figure 29. Influence of contact time on the residual oil content C_e.

In order to describe the adsorption kinetics, two widely used models, namely, the pseudo first (Lagergren) and second order kinetic models have been tested to fit experimental data obtained via the adsorption of emulsified oils onto powdered LDPE in the dependence on the time. For pseudo-first-order model, the values of k_1 and q_e were obtained from non-linear fitting of data by Eq.(4a) (Figure 30). Parameters of pseudo-second order, q_e and k_2 were determined from both non linear (Eq.6a) and linear fitting (6b). (Figure 31). All the parameters and constants determined from pseudo-first and second-order models are summarized in Table 17. Table 17 summarizes both experimentally determined value of q_e (q_e, exp) and the calculated one (q_e, cal). By observing the obtained results it was found that, the pseudo-first-order (Lagergren model) provided a poor fit to the experimental data from emulsified DO system; as the correlation coefficient R^2 value for the first-order reaction were lower than 1.0. On the contrary, as shown in Figure 30, the straight linear line in plot t/q_t vs. t proves a good agreement of experimental data with the second order kinetic model. As, the correlation coefficient R^2 for the second-order kinetic model are almost equal to 1.0 emulsified DO. Beside the calculated qe values in Table 17 obtained from the second-order kinetic model agree very well with the qe of the experimental data values. Oppositely, the first-order kinetic model does not give reasonable values and the values were low compared to the actual experimental values. Therefore, these results confirmed that the adsorption kinetics of emulsified oils onto powder LDPE follows pseudo-second-order kinetic model. Similar observations were achieved by Ahmed et al. [86] for the adsorption of residue POME effluent using powder and flake chitosan.

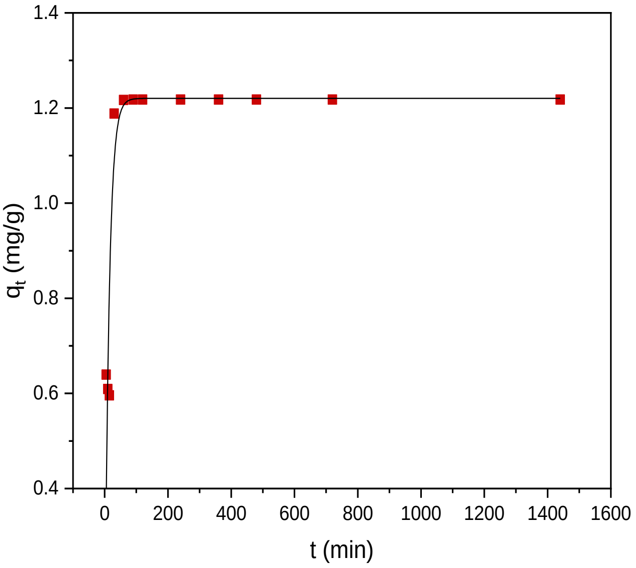

Figure 30. Pseudo-first-order kinetic model.

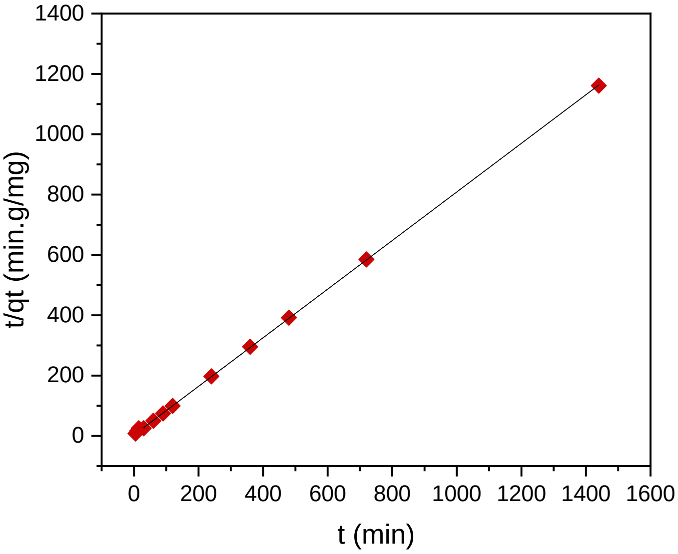

Figure 31. Pseudo-second-order kinetic model.

Table 17. Kinetic model parameters.

Fitting Type	Pseudo-first-order				Pseudo-second-order		
	qe exp. (mg/g)	qe calc. (mg/g)	k_1 (min^{-1})	R^2	q_e calc. (mg/g)	k_2	R^2
Non-linear	1.23	1.22	0.0741	0.8405	1.23	0.7092	0.9995

Table 18. Non-linear and linear forms of the kinetic models.

Equation Form	Pseudo-first-order	Pseudo-second-order
Non-linear	$q_t = q_e(1 - e^{-k_1 t})$	$q_t = \frac{t q_e^2 k_2}{1 + t q_e k_2}$
Linear		$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e}$

CHAPTER 5: CONCLUSIONS AND FUTURE WORK

In this research study, low-density polyethylene in powder form prepared by grinding of pellets and modified by radio-frequency plasma discharge have been used as polymer-based filtration media of emulsified oil/water mixtures with respect to key parameters determining their adsorption ability and the following conclusions were drawn from this study:

1. Batch adsorption experiments for the adsorption of oil from emulsions formed from distilled water and commercial DO with concentrations below 200 ppm was used as a model of oily polluted water (a simplified, artificial produced water). The emulsions were prepared without emulsifier, and emulsification was insured by ultrasonication. Long term stability of emulsions was demonstrated determining the oil droplets size evolution in time.
2. LDPE powder has been thoroughly characterized in the respect of the surface morphology, elemental composition, functional groups and surface area determination using analytical equipment like DSC, SEM, EDS, FTIR, and BET isotherm respectively.
3. The stability of oil-in-water emulsions was investigated by measuring using DLS, It was found that the droplet size directly proportional to sonication time. Higher the sonication time results in the smaller the droplet size. Sonication time of 20 min is sufficient enough to prepare a stable emulsion.
4. Pre-check test proved that the sorption of oil onto LDPE powder was significantly fast due to the fact that PE has a high affinity to the oil due to their similar chemical nature.
5. The surface properties of plasma treated LDPE powder have been qualitatively and quantitatively characterized using various analytical and microscopic

techniques. It was found that, the LDPE powders exhibit a highly hydrophilic character after plasma treatment due to the incorporation of new polar functional species on its surface. Besides, the optimum plasma treatment of LDPE samples took 60 s of the exposure at 80 W of nominal power in the presence of air plasma leading to the highest wettability by water. This is as the consequence of the formation of polar functional groups on the surface.

6. Batch adsorption experiments for the adsorption of oil from diluted emulsion have been carried out by using treated LDPE powder. Effect of adsorbent dose, contact time, and oil initial concentrationc have been studied at standard atmospheric conditions and stirring speed of 340 rpm with adsorbent particle size of 500 micron.
7. The adsorbed amount of oil increases with increasing the dosage of the adsorbent, the suitable dosage for the all batch experiments was kept at 3.0 g of powdered adsorbent in 40 mL of diluted emulsion.
8. The efficiency of oil removal is dependent on the initial oil concentration. It decreases 96.7 % to 79.5 % as the initial oil concentration increases from 75 ppm to 200 ppm.
9. The experimental data were well fitted by the both Langmuir and Freundlich isotherms.
10. The adsorbed amount of oil increases with the increase of contact time and reaches the equilibrium after 720 min. Results confirmed that the adsorption kinetics of emulsified oils onto powder LDPE follows pseudo-second-order kinetic model.

Future work:

1. Investigation of sorption kinetics at shorter adsorption times
2. Investigation of sorption processes at various temperatures.
3. Investigation of sorption processes at various pH.
4. Investigation of sorption processes in flow-through systems.
5. Investigation of desorption processes (adsorbent recovery) at various conditions.

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APPENDIX

Tabulated data of optimization of plasma treatment process that was carried out on LDPE Film form by varying the treatment time from 10s to 180s.

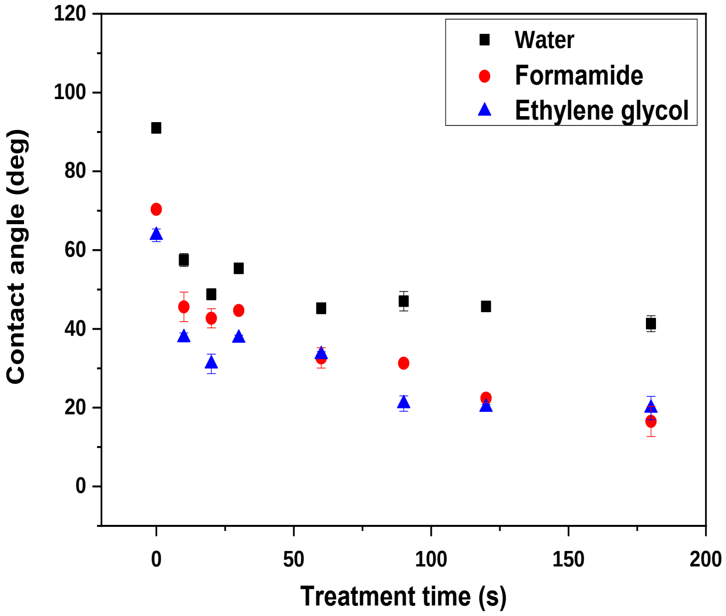

Figure 32. Plasma treatment time optimization on LDPE film.

Table 19. Plasma treatemnt time optimization.

Treatment time	Testing liquids		
	water (W)	Formamide (FM)	Ethylene glycole (EG)
0	91.0 ± 0.74	70.3 ± 0.77	63.8 ± 1.58
10	57.5 ± 1.63	45.6 ± 3.75	37.8 ± 1.13
20	48.8 ± 1.40	42.7 ± 2.43	31.1 ± 2.46
30	55.4 ± 0.80	44.7 ± 0.19	37.7 ± 0.74
60	45.2 ± 1.36	32.6 ± 2.57	33.5 ± 0.66
90	47.0 ± 2.47	31.3 ± 0.68	21.0 ± 1.94
120	45.7 ± 0.16	22.4 ± 1.09	20.1 ± 0.72
180	41.3 ± 2.02	16.5 ± 3.82	19.9 ± 2.97