Review article

Dispersants as an oil spill clean-up technique in the marine environment: A review

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HIGHLIGHTS

- Smart dispersants have the potential to minimize dispersant wastage.
- Biodegradable dispersants may bring a closure to discussions on toxicity.
- Bio-based formulations have the potential to replace chemical based dispersants.

GRAPHICAL ABSTRACT
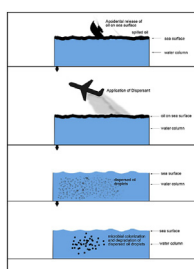
ABSTRACT

Oil is a major source of energy in the industrial world. Exploitation of oil and rigging activities, transportation via sea, and many other mechanical failures lead to oil spills into the marine environment. In view of these, the suitability and effectiveness of oil spill response methods have always been a topical discussion worldwide. It has become necessary, now than ever, for existing spill response methods used to remove oil from the environment to be improved upon and more importantly, develop new response materials that are sustainable and environmentally friendly. There exist surfactants in nature that are non-toxic and biodegradable, which can be explored to produce potential dispersants to help remove oil safely from the surface of marine water. This review comprises of the works and resourceful materials produced by various researchers and agencies in the field of oil spill response, placing emphasis on the use of dispersants in the marine environment.

Environmental significant statement

The marine environment is the home of many aquatic species, either as mammals, plants, or microorganisms. However, the release of crude oil into it sometimes destroys these organisms and their habitats. Hence, oil that spills into the water must be cleaned immediately to reduce its many adverse impacts on the environment. Dispersant application is however considered as a good response method in the quest to restore the environment after a spill incident. Microorganisms are ubiquitous in the marine ecosystem; hence this review discusses the application of dispersants onto oil spills as enhancement of microbial degradation within the water column since these organisms feed on the hydrocarbons as a source of energy.

1. Introduction

Oil spills are mostly recounted as the unintentional release of liquid hydrocarbons into land and water as a result of human operations [1]. Spills largely occur through natural seeps, oil platforms, well operation activities, sabotage, transportation, and usage as fuel by large vessels and have become an undeniable menace in global oil exploration, production, and transportation [2].

According to the International Tanker Owners Federation (ITOPF) oil tanker spill statistics in 2019, oil transportation by tanker alone has caused about 5.86 million tonnes in losses of oil into the marine environments from the periods of 1970–2019, recording about 16,000 tonnes per year in loss of oil into the oceans in 2010 [3]. Tanker incidents contribute approximately 45% of marine oil spills and is considered as the largest form of contribution of oil pollution in the oceans [4].

As cited by Zhang et al. [2], it is recounted that oil of about 6 million tonnes per year entered the oceans worldwide and over 1 billion gallons of oil were spilled globally in the last ten years [5].

A couple of major oil spills have drawn the world into an attentive mode with respect to making conscious preparations and guidelines in terms of emergency spill response. The British Petroleum (BP) Deepwater Horizon, recounted as the largest oil spill in history, occurred because of mechanical failure, leading to an explosion and wellhead blowout on April 20, 2010. It took about 5 months to finally control the spillage, resulting in about 430,000–500,000 tonnes of crude oil release into the Gulf of Mexico [2].

Oil spills adversely affect the marine ecosystem and its nearby shorelines by destabilizing and polluting aquatic habitats and the atmosphere as a result of the evaporation of volatile hydrocarbon compounds in the oil [6]. The extent of damage caused by oil spills usually depend on the chemical composition of the oil, the magnitude of the spill, area of spill, the climatic conditions, the method of remediation and the response time [7]. Oil spills upon reaching shorelines cause damage to coral reefs, mangroves, and many other flora and fauna species in and around the marine ecosystem [8].

Marine oil spills also pose gross social, commercial, and economic impacts on the fisheries and coastal tourism industries. The cost of cleaning up the spill and payment of other compensational funds also contribute to the economic losses oil spills present [2]. These impacts of oil spills on the environment and economy can be short-term or long-term depending on the response method. Several response methods are in existence and can be deployed as emergency spill response measure depending on several other factors. For any marine oil spill response, the basic objectives are to contain the spill offshore by preventing it from spreading to shorelines, minimize the effects of the spill on the marine ecosystem, and speed up the degradation of the unrecovered oil [9]. The existing oil spill response methods include mechanical containment and recovery, in-situ burning, use of sorbent materials, bioremediation, and dispersants application [9].

In an event of a spill, prior to the selection and application of any of the oil spill response methods, the response team must undertake a quick Net Environmental Benefit Analysis (NEBA) to determine the best response method to use for a particular kind of spill. This must be done because not every traditional response method can effectively remove every form of oil spill in the marine environment. NEBA takes into rigorous account the effects of the spill against that of the response method on the ecosystem before deploying the most suitable method [10]. In NEBA, both advantages and disadvantages of the potential response techniques on the environment and workers should be considered.

The aim of this paper is to shed light on the potential application of smart and bio-based dispersants as substitute for chemical dispersants used to remove oil from water surface. This review covers oil and its impact on spill response methods, oil spill simulation, traditional oil spill response methods emphasizing on dispersant usage for marine oil spills, comparison between traditional spill response methods for large marine oil spills, potential dispersant formulations, and way forward for dispersant application.

2. Oil

Oil pollution in the marine environment spans across a wide range of products from vegetable oil, marine diesel oil, lubricating oils, fuel oils, crude oils, and other hydrocarbon-oriented products [11]. These different types of oils have different impacts on the marine environment when spilled. In view of this, emphasis shall be placed on crude oil and other hydrocarbon-based products in this section.

Crude oil in principle is liquid, made of a complex mixture of hydrocarbon compounds with dissolved gases, and little amounts of suspended water, mineral salts and trace metals such as nickel, vanadium, iron, and chromium [7, 12]. The composition of crude oil varies and it influences the characteristics of each type of crude oil or petroleum product. The type of crude oil or hydrocarbon-based product primarily determines the properties of the oil and is a forehand influencing factor in how it behaves when spilled into marine environment [13].

Crude oil spills can have adverse social, economic, and environmental impacts. The short and long-term effects of oil spills is largely dependent on the persistence of the oil in the environment [7]. The persistence of oil in the environment also has a gross influence on the method of clean up.

2.1. Physical properties of crude oil

The behavior and fate of crude oil and other hydrocarbon-based products in the ocean are very dependent on the initial physical properties such as density, viscosity, the specific gravity, pour point, flash point, distillation and interfacial surface tension [7, 11]. Oil spill response teams must rapidly access the oil and consider the physical properties in preparation for a response because the physical properties of crude oil change rapidly at sea due to weathering effects.

Density. The buoyancy of oil in water is determined by the density, which is the mass per unit volume of the oil [13]. Typically, crude oil densities range from 0.7 g/cm^3 to 0.99 g/cm^3 and that of fresh water is 1 g/cm^3 at ambient temperature. The density of marine water is 1.03 g/cm^3 hence oil, regardless of its molecular weight, typically will float on water [14, 15]. When crude oil is released into marine water, it is impacted by weathering which results in the evaporation of volatile hydrocarbons. As a result of this, there could be a significant increase in the density of the remainder of oil [13, 15]. This affects the buoyancy of the oil and can cause it to sink due to the increase in oil density, possibly exceeding that of fresh water [15]. The density of oil increases with decreasing temperature. It is to be noted that when oil has a higher density, it spreads faster at the early stages of a spill, which makes it very

difficult to contain when using spill response methods like in-situ burning, and mechanical containment and recovery [13]. This can increase the cost of spill remediation drastically. The liquid densities for hydrocarbons are usually stated in terms of specific gravity or relative density.

Viscosity. Viscosity of oil can be defined as the resistance to the flow of oil caused by internal friction [15, 16]. Viscosity is expressed in mPa.s or centipoise (cP). The higher the viscosity of crude oil, the more hesitant it is to flow and vice versa [14]. The viscosity of crude oil is largely dependent on the amounts of large, polar molecules in its composition [15]. The quantity of saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes present in the oil largely influences its viscosity. The viscosity of crude oil is lower if the content of saturates and aromatic hydrocarbons are higher than resins and asphaltenes [13, 15]. As weathering of oil progresses, the volatile components in oil evaporate resulting in increased viscosity. Oil viscosity is also significantly affected by temperature. Higher temperatures result in lower viscosity and vice versa [15]. Hence, oil viscosity increases with the weathering and with decreasing temperature. With respect to oil spill remediation, viscous oils spread at slower rate and form more stable emulsions. Highly viscous oils are very difficult to disperse both naturally and chemically. It also has a negative response to the use of mechanical tools [14].

Interfacial Tension. It is a measure of the surface forces that exist between the phases of the oil and water and the oil and air [13, 14]. Interfacial tension is an indicator of the rate at which oil will spread on the surface of water. Spreading of oil increases with a decreasing interfacial tension with water [14]. Interfacial tension increases by weathering; affects emulsion formation and stability [13].

In terms of spill remediation, chemical dispersants are applied to reduce the surface tension at the oil – water interface so that by application of hydrodynamic energy, oil slicks will break into smaller droplets for degrading microorganisms to feed on [11]. When oils have higher interfacial tensions, chemical dispersion becomes difficult thus increasing the cost of clean-up [13].

2.2. Chemical properties of crude oil

Crude oil is made up of several compounds of varying sizes and classes. It is a complex mixture of hydrocarbons, other volatile and non – volatile constituents [13, 14]. Basically, crude oil is composed of about 83–87% carbon, 10–14% hydrogen, 0.05–6% sulphur, 0.05–1.5% oxygen and 0.1–2% nitrogen with hydrogen and carbon being the main constituents [12]. The chemistry of oil influences the fate and behaviour

after spill. It contributes largely to the effects the spill has on the marine life as well as its social economic impact. The chemical composition of spilled oils has great influence on the efficiency of response methods.

3. Oil behaviour in the environment

When oil spills into an aqueous environment, the manner in which it ends up is determined by its behaviour in the environment [14]. The behaviour of oil in an environment is a term that describes the transformational processes oil undergo when spilled into the environment [14]. These transformational processes dictate the overall fate and effects of the spill thus, they determine the short-term and long-term effects of the oil in the environment as well as influence the type of response method required to clean up a particular spill [17, 18].

Typical of oil spills, there are two basic transformational processes and these are weathering and oil movement (Transport of oil in the environment) [18]. Weathering and oil transport depend greatly on the oil type, weather, and other prevailing climatic conditions during and after a spill event [19]. Weathering and oil movement after a spill are overlapping processes in which weathering influences how oil moves in an environment [10, 20].

3.1. Oil weathering

Weathering encompasses a wide variety of biological, chemical, and physical processes that spilled oil undergo which leads to changes in its physiochemical properties [2, 11]. Figure 1 illustrates the weathering processes at sea after a spill event. In marine environments, weathering commences as soon as an oil spill occurs and at varying rates throughout the spill period [10]. The weathering processes occurring at varying onset times and different rates lead to changes in oil behaviour [2]. The rate at which weathering occurs in an aqueous environment is greatest at the earliest stages of the spill event and slows down relatively as weathering progresses with time [17]. During weathering, the physical and chemical make-up of the oil changes significantly throughout the period of the spill [2, 13].

The rate at which weathering processes occur is greatly influenced by the type of oil spilled. Many other environmental factors such as temperature, physical forces at sea (wind, wave and currents), microbial activities, and position of slick and suspended sediments in water also contribute to the rate at which weathering occurs [14, 17]. For instance, weathering increases with increasing temperature and decreases as temperature approaches zero degrees Celsius [14]. Considerably, the
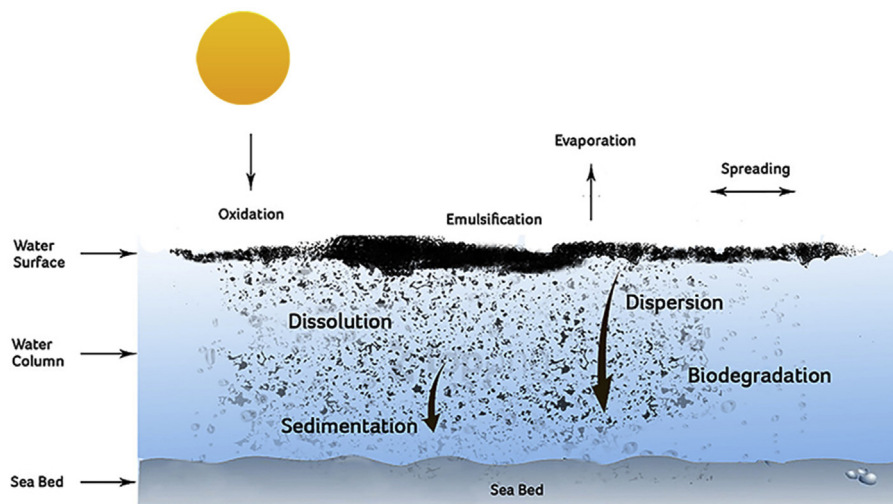

Figure 1. Oil Movement and Weathering at sea [22].

composition and chemistry of oil (type of oil) has a greater influence on the rate and type of weathering as compared to the influence of other environmental factors on weathering [21]. The processes of weathering affects most of the physical properties of the spilled oil [10, 21]. The density of oil increases typically of about 5–10% during weathering. Viscosity increases with increasing weathering. There is also a slight increase in surface and interfacial tension as weathering rate increases [13].

Weathering in the marine environment occurs at the surface of the water, within the water column or in interaction with nearby shorelines [2, 17]. It differs at different areas of a spill site. Oil weathering on the surface of water may differ vastly from oil weathering in the water column or nearby shorelines [2, 17].

The types of weathering processes have varying impacts on oil in the environment in terms of time, behaviour, fate, chemical characteristics, and the total mass balance of the spill [19]. In terms of losses to the total mass balance, weathering processes may be listed in order of importance as evaporation, emulsification, natural dispersion, dissolution, photo-oxidation, sedimentation and adhesion to materials, interaction with mineral fines, biodegradation, sedimentation and the formation of tar balls [14].

3.2. Oil spill simulation

Oil spill models are tools that are used to predict oil behaviour and fate in the marine environment and also aid in responding to and mitigating real-time oil spill accidents [23]. They are used to simulate the evolution of oil slicks when oil is released into the marine environment [24, 25]. Oil spills are events that race against time whenever they occur, hence modeling tools are used for contingency planning which supports spill responders in rapid decision making [26]. By running a series of likely to occur hypothetical spill scenarios, decision makers are most likely to be informed about suitable counter measures, strategic locations and logistics preparations required [23, 26]. This gives room for more efficient use of emergency response resources and proper spill response management.

According to Zafirakou 2018, oil spill models have been designed since the 1960s to simulate weathering processes and forecast the fate of oil spills [24].

Several types of model technologies have been developed but they differ based on their modes of operation, dataset required for application, varying complexities, ease of use and applicability to location [26]. According to Industry Technical Advisory Committee (ITAC) for oil response as stated in Zafirakou 2018, the types of oil spill models can be classified into two groups namely; Oil weathering process models and Oil transport, fate, and transformation models [24].

I. Oil weathering models determine how the properties of spilled oil undergo various physical and chemical changes overtime but does not predict the potential motion of the oil slick on the surface of water [27]. Weathering predictions usually depend on the databases of the chemical and physical characteristics of different oils, research and observations of oil behaviour [26].

II. Transport, fate and transformation models include deterministic or trajectory models, stochastic or probability models, hind cast and 3-dimensional models [24, 28]. These are used to predict the likely destination of an oil on sea water and how soon it may get there. Models under this category simulate the evolution of oil slick overtime as well as the weathering processes efficiently [24, 26].

Some oil spill models are developed to specifically predict the suitability of applying certain oil spill counter measures for spill events. For instance, a study conducted by Liu and Callies 2020 indicates the probability of using Bayesian Network, a comprehensive, decision centered oil spill model to predict the suitability of using chemical dispersants to combat oil spills in the German Bright [29]. Thrift-Viveros et al. 2015 through a study

developed an algorithm which combines ADIOS and GNOME into one suit to predict biodegradation processes of an oil spill accident [30].

Some common types of oil spill models used for both operational and academic purposes include MEDSLIK, MEDSLIK II, PISCES 2, GNOME, OILFLOW20, TRANSAS, ADIOS, OSCAR, and OILMAP.

In oil spill modeling, key factors contribute to the motion and transformation of oil slick at sea surface, these are marine and meteorological conditions which include wind strength, wind direction, waves, sea surface temperature, chemical characteristics of oil, initial volumes and release rate, air, marine currents, location and time scales [31]. Model predictions are generally validated by comparing the modelled results with real-time observations and data [32].

4. Common types of oil spill models

4.1. MEDSLIK

It is an oil spill trajectory 3-D model which is capable of predicting the transport, fate and weathering processes of oil spills and the movement of floating objects in the Mediterranean sea and worldwide [33]. MEDSLIK is capable of both forecast and hindcast trajectories of oil spills [34]. Input data required includes oil type, oil characteristics, wind field, sea temperature, and 3-dimensional sea currents [33, 35]. It is capable of predicting oil slick at sea surface, dispersed in water column, evaporated, emulsified, oil slick viscosity, oil density and oil stack at coast [36].

MEDSLIK has been verified successfully during the Lebanon oil spill in 2006 [37].

4.2. MEDSLIK-II

MEDSLIK-II is an oil slick model developed based on parent oil spill model MEDSLIK and is a freely available oil transport and transformation community model [31]. It has been designed to provide relevant and timely information on oil spill advection-diffusion and weathering after oil is released [31, 32].

MEDSLIK-II works by simulating the transport and weathering processes of oil released on water surface using Lagrangian model formalism coupled with Eulerian circulation model [38]. In addition, MEDSLIK-II has a representation of high frequency currents and wind fields in advection components of the Lagrangian trajectory model, the introduction of drifts stoke velocity, and coupling of remote sensing data [32, 39].

Input data required by MEDSLIK-II to simulate the transport and transformation process of spilled oil are oil spill data (location, time, area of spill, age of spill from initial time of release), sea surface temperature, the wind field, and three dimensional sea current [31, 40].

MEDSLIK-II has the potential to become part of an operational-prediction system using observed oil slicks as initial conditions and prediction of their motion and weathering processes to guide oil spill activities [32]. It is used to predict the physical and chemical transformation of oil on the surface of water [40].

According to CMCC 2022, MEDSLIK-II has been used to forecast the possible spill of about 2500 tons of oil from the Costa Concordia, assuming a continuous oil release [39]. It indicates that the bulletin with these forecasts have been released to the relevant authorities.

4.3. GNOME (general NOAA operational modeling environment)

GNOME is an oil spill modeling tool for spill trajectory simulation which estimates oil movements due to winds, currents, tides and spreading in the ocean [30, 36]. It predicts the fate and transport of spilled oil in water. GNOME estimates the trajectory of oil release on the surface of water by processing input data such as winds, weather conditions, circulation patterns and oil spill data [41]. It can also predict the trajectories that may result from uncertainty in current and wind observations and forecasts [42].

4.4. ADIOS (automated data inquiry for oil spills)

ADIOS is another NOAA developed model but with a different function from GNOME. ADIOS is an oil spill weathering model. It simulates how different types of oils undergo physical and chemical transformations in the marine environment [43]. The weathering processes simulated by ADIOS include spreading, evaporation, sedimentation, dispersion and emulsification [44]. ADIOS is a smart database software and simulation system which contains properties of more than a 1000 different oils and products integrated with the weathering model [45, 46].

The software requires data input on wind, wind speeds, wave heights, water salinity, water temperature, rate and duration of oil release and quantity and type of oil spilled [43, 44].

Based on data provided to and information existing in ADIOS database, it predicts the physical and chemical changes that occur in oil properties such as density, viscosity, water content in oil, evaporation rate, dispersion into water column and emulsification [44, 47]. The ADIOS software has models to estimate the effects of oil spill counter measures such as chemical dispersion, mechanical skimming and burning in-situ [43, 44].

4.5. OILMAP/OILMAP deep

OILMAP is a state-of-the-art oil spill model response software system used for real-time oil spill response and contingency planning at various spill locations [25, 48]. OILMAP has been designed in a modular framework which incorporates different types of spill models and other tools such as oil database, and environmental data tools in one system [49, 50].

OILMAP provides rapid and instantaneous predictions of the movement of spilled oil and can be used to predict all five models namely trajectory, hindcast, oil weathering, stochastic and 3-D models [28]. The 3-D model is capable of tracking hydrocarbon components in the air, water surface, and water column.

The basic features of OILMAP as described by Toz et al. 2018 and Spaulding et al. 1994 include;

  I. Algorithms for spreading, evaporation, emulsification, entrainment, oil shoreline and oil reed
 II. Surface and subsurface oil movement can be animated to identify shoreline impacts
III. Bed and oil-ice interaction
 IV. Output graphical and tabular listings of weathering, mass balance results and display of GIS resources impacted by the spill
  V. Simple graphical procedures for specifying the spill scenario and entering both wind and hydrodynamic data.

OILMAP usage has been verified by simulating the Braer oil spill [48].

4.6. OILMAP deep

It is a special model integrated into OILMAP for seamless simulations of both near-field and far-field environment [51, 52]. OILMAP Deep is a tool for well blowout response planning, well blowout response decision support, spill drill exercises and contingency planning [53].

It is made up of five integrated model components namely pipe release, blowout plume, dispersant treatment, oil droplet size and fountain and extrusion [53, 54]. The purpose for putting together these components is to predict the dynamics of the release of the oil and gas from subsea blowout with or without dispersant application [53, 55]. It is used to predict the dynamics of the plume and resulting intrusion layer, the dissolution of gas, formation of hydrates and oil droplet size distribution and concentrations [53, 55].

OILMAP Deep was used to predict the near-field transport and fate of the oil spill during the 2010 Deep Water Horizon wellhead blowout accident in the Gulf of Mexico [53].

In general oil spill simulation enhances spill response training by virtue of using simulated spill scenarios with varying circumstances for preparation towards actual spill events. It gives spill responders relevant information for advance preparation and decision making. However, modeling oil spills cannot give perfect predictions of the changes oil in the marine environment undergo but can indicate to a larger extent the fate of the oil [26]. Oil spill modeling although informative, has limitations and cannot replace actual observations, hence in response operations, model predictions should be verified by shoreline surveys, aerial surveillance, advanced technological monitoring and observations for real oil distribution and behaviour [26].

5. Oil spill clean up techniques

One primary aim of emergency response is to control the movement of oil as much as possible in order to prevent it from moving to nearby shorelines/habitats as well as minimize the toxic impact of the oil on the marine environment [56]. In principle, the method deployed to combat an oil spill is dependent on the type of oil spilled (light, medium, or heavy), quantity of oil spilled, affected area, type of life at the spill location, environmental conditions, and time at hand. Dependent on these factors, there are several traditional methods the response team can resort to; thus, a quick analysis is required to determine the most suitable option to consider to fully reduce the impact of the spill, comparing to a no spill environment. These methods include the use of mechanical containment and recovery, sorbent materials, application of dispersants, in-situ burning and bioremediation.

5.1. Sorbent materials

Sorbent materials for oil spill cleanup functions by means of sorption, a phenomenon which can be described as absorption and adsorption

Table 1. Types of sorbent materials [58, 60].

Organic Vegetable Sorbents	Inorganic Mineral Sorbents	Synthetic Sorbents
• These include milkweed, straw, coconut husk, wood fiber (saw dust), corn hub, cotton fiber and bird feathers • These exist abundantly in nature, cheap, and have a high affinity for oil • They are environmentally benign • Have high absorption capacities comparatively • They can absorb oil up to 3–15 times their weight • They have low buoyancy, low hydrophobic properties hence the tendency to absorb water as well.	• Vermiculites, organic clay, pearlite, graphite, and zeolites are few examples. • They have low buoyancy and low sorption capacity • They can absorb oil up to 4–20 times their weight • They are not biodegradable • Very expensive and low rate of re-usability • High density and sinks therefore	• These include polystyrene, polypropylene, polyurethane foams and polyvinyl chlorides. • Low density and high buoyancy • High sorption capacity • Highly hydrophobic and oleophilic. • They can absorb oil up to about seventy times their weight • However, not biodegradable, and hazardous to the environment

fused as a single process [57, 58]. Adsorption is a process in which a material or substance is able to attract liquids, in this respect oil, by means of adhesion onto its surface without necessarily penetrating it [22]. Absorption can be described as a process whereby a material or substance allows liquids to penetrate into its porous spaces by means of capillary action [57]. It is worth noting that sorbents use both mechanisms to soak-up or remove oil from the surface of water.

The motive behind the usage of sorbent materials as a spill cleanup method is to draw the oil from the environment onto/into the material then dispose off the material in the end [57, 59]. Introducing sorbent materials to spill sites promote the conversion of liquid oil into semi-solid state. At the semi-solid phase, the oil can be removed from the surface of the water by just removing the sorbents [60, 61]. For a material to be considered as a good sorbent material for oil spill remediation, it should possess several characteristics that include being hydrophobic in nature; being oleophilic in nature; having a great uptake capacity; having a good oil retention capacity; having a good oil recovery; being able to be reused; and being biodegradable [22, 62].

According to studies, there are basically three major types of sorbent materials (summarized in Table 1) that can be used as a means of oil spill cleanup and these are organic vegetable products, inorganic mineral products, and synthetic organic products [60, 61]. Organic vegetable sorbents have a high affinity for oil, high absorption capacity but tends to absorb water, and they include milkweed, coconut husk, kenaf fiber, cotton fiber, and feathers [58]. Inorganic mineral sorbent materials have low sorption capacity and they include organic clay, perlites, fly ash, vermiculite, and zeolites [58, 59]. Synthetic organic sorbents often used are artificial or man-made to serve the purpose. They are highly hydrophobic and oleophilic but are not biodegradable, and they include polystyrene, polypropylene, polyurethane foams, and polyvinyl chlorides [58].

Sorbents with high hydrophobicity are known to be the most efficient in terms of sorption (spill cleanup) but an absolute hydrophobicity of a material cannot be achieved naturally. Regardless, the material has a little tendency to take up water [62]. Sorbents are usually deployed for cleanup exercises because under ambient conditions, they work as a very effective technique [63]. Also, they are usually required for spills of small volumes or to complete cleanup exercises at shorelines where other methods are less applicable [22].

Generally, the application of sorbents as an oil spill remediation method is not suitable for large spills [59]. In open marine environments, sorbent material usage is not suitable for locations far away from onshore. At high sea energy conditions, the materials would be carried further away from the spill location to other places resulting in further pollution as well as other secondary problems and extra cost for logistics [22, 59].

Finally, over usage of sorbents for oil spill remediation exercises create disposal problems after materials have been recovered from the water surface. Incineration is a very expensive method to get rid of the materials whiles landfill usage is an undesired procedure in the environment [61, 62].

5.2. Burning in-situ

In-situ burning is the process of burning spilled oil under restrained conditions at the area of the spill incident [64, 65]. In-situ burning is often deployed at snow and ice-filled conditions as an emergency response technique [66, 67]. It is also known to be an old practice very potent for land spills, inexpensive and very effective [64, 65]. Per reports based on various field operations and experiments, burning removes about 95% of the crude oil mass of ignited oil on the water surface (when all conditions required for burning are met) [56, 65, 68]. Bullock et al. 2019 reported that the Exxon Valdez spill that occurred on 25th March 1989 released 11 million gallons of North slope crude oil in Prince William Sound, Alaska. About 12,000 to 15,000 gallons of the spilled oil was

burned on calm seas achieving a 95–98% burn efficiency. The burning procedure was done a day after the spill [69].

According to Mabile 2012, over 400 burns were conducted during the 2010 Deep water Horizon incident to remove about 35–49 km^3 Louisiana sweet crude in open water which represents about 99% burn effectiveness of oil ignited [70].

Considering a spill on open marine environment, it is a surface phenomenon where by oil is collected and contained by means of fire-resistant booms and quickly removed by combustion [64]. For crude oil on the surface of water to burn in-situ, it requires the presence of oxygen, fuel, and a source of ignition [68, 71]. Fuel in this regard does not mean the mere oil on the surface of water but in the form of oil vaporization which leads to ignition and subsequent sustenance of burning when adequate [71].

Burning in-situ in the marine environment requires that the movement of oil is restrained to obtain a minimum slick thickness for ignition and sustenance of the burning process [68, 71]. There should be at least a 1 mm slick thickness of fresh crude oil before it can be burnt in open water [64]. It also requires at least a 2–3 mm thickness of oil slick to burn oil that has undergone some form of weathering in water [68].

Ignition will not happen if vaporization of oil is not adequate and in a situation whereby it does, it shall go off as quickly as possible [71, 72]. It is relevant to provide adequate heat that will vaporize the oil to ignite. Heating the oil adequately leads to vapour formation and subsequent burning [68, 71]. Some common sources of ignition include the use of helitorch from helicopter to set the oil ablaze. Other methods such as the use of road flares and diesel-soaked rags have been improvised to ignite the oil [68]. When in-situ burning commences, the oil burns at an average rate of 1 mm per minute [71]. In open waters or marine environment, burning of oil immediately after a spill removes a large amount on the surface of the water considering that when the spill is fresh, most of the volatile and flammable components are available [71].

At optimal conditions, burning can remove about 100–300 tons of spilled oil on water surface within 60 min [73].

5.3. Challenges associated with burning in-situ

It is reported by Fingas 2011 [4] that about 45 successful burns or tests occurred between the periods of 1958 and 2008. Regardless of this, in-situ burning comes with various limitations and its own effects on the environment and hence mostly serve as the last option to consider when all other clean up methods are not suitable for a particular incident [65].

In-situ burning in open marine water is affected by oil submergence, weathering, emulsification, and spreading [68]. Emulsification and weathering results in removing the combustible components of oil within a short time after a spill incident whereas spreading of the oil results in the formation of thin oil slicks that are insufficient for ignition [64, 71]. This makes burning in-situ a very complicated phenomenon in open waters after 24 h of a spill occurrence [64]. For weathered and emulsified oil, it requires a minimum slick thickness of about 10 mm to ignite the oil [68]. Therefore, in order to efficiently burn in-situ on an open marine environment, the spill must be in such a way that oil is continuously released from the source like that of the Deepwater Horizon incident which occurred as a result of a wellhead blowout [71].

In-situ burning leads to atmospheric pollution due to the production of soot and toxic gases which cover near and far neighboring atmosphere, presenting potential health threats to human lives (including response teams) and other organisms as well as habitats [71]. In view of this, burning in-situ does not imply that oil is completely removed from the environment but rather transformed into other harmful products [68].

Open water surface burning kills surface flora and fauna thus rendering this habitat potentially lifeless [65]. Removing oil on the surface of water by burning also presents a potential risk of fire spreading unintentionally to other combustible materials and areas causing additional damage and cost [56].

In conclusion, in-situ burning is best on land and is not as difficult as on open water because oil will not spread into thin layers, emulsify nor submerge on land [64]. However, in open seas, burning in-situ is considered when there is no viable option because of its high risk nature and rapid but careful risk analysis must be conducted before the final decision to employ burning is taken [56, 65]. It is however recommended for emergency response in ice field environments.

5.4. Mechanical containment and recovery

The use of mechanical methods for remediation of oil spills in the marine environment or on water surfaces involves two basic phases [74, 75]. The first phase is described as containment and the second phase is known as recovery [75]. In every containment and recovery process, the utmost goal is to collect as much oil as possible for storage [76].

Containment is the process where physical barriers are used to restrain the movement of oil on the surface of water [74, 75]. Preventing oil from spreading wide on water surface by this means gives room for recovery of the oil and shields other clean, sensitive, and nearby habitats and shorelines from the oil pollution [76]. The commonest of these physical barriers are in the form of booms. Booms are devices basically designed to float on the surface of water [59]. They serve as barriers around oil on the surface of water, preventing it from spreading and assists in accumulating thicker oil slicks to enhance collection into recovery tanks [74, 75].

According to Wadsworth 1995 [77], the basic design of booms consists of a free board above the water surface for oil containment and to prevent oil loss by splash over. It is also made of a below-water skirt component which prevents water loss from beneath. Booms have a longitudinal support along the bottom for stability and strength. The floatability of booms on the surface of water is due to its flamboyant material make-up. Commonly used booms can be categorized into two basic groups namely curtain booms and fence booms.[76]There is a third category that is uncommon because its expensive. This third category is the non-rigid inflatable booms [74]. Notably, the usage of booms in the marine environment is largely affected by mechanical energy at sea [76].

Recovery of the oil contained is the second phase of the mechanical equipment method of remediation. Recovery of oil contained in the boom can be done by using skimming equipment commonly known as skimmers or sorbent materials [74]. Skimmers are devices used to collect the oil from the surface of the water after containment for storage [77]. Skimmers can be used by vessel attachment or can be self-propelled [77]. There are several types of skimmers available and they include oleophilic skimmers, weir skimmers, vortex skimmers, and suction skimmers [78].

In selecting an appropriate skimmer for a particular spill clean-up exercise, factors to be considered include the type of oil and its viscosity, degree of weathering and emulsification of oil, amount of debris present, and the present weather conditions on the water surface [78]. For sorbent materials deployed for recovery, they recover the oil through adsorption, absorption or both mechanisms at a go [74]. Sorbent materials are both hydrophobic and oleophilic in nature and thus aid in the process of oil recovery. [74]. It is worthy of note that sorbent materials are involved in mechanical containment and recovery process when skimmers cannot be deployed efficiently in certain areas of a spill, usually at the final stages of oil recovery [74].

In the selection of this method for a major open water clean-up, it must be considered that mechanical containment and recovery is highly dependent on the climatic conditions in the marine environment, thus requires a calm sea to work effectively. The application of mechanical containment and recovery procedure often results in a collection of oil-water mixture from the water surface. In situations like this, the absorbed oil-water mixture can be squeezed or pumped through a pipe hose into a storage tank for disposal or recycling [74]. This method is however, the most utilised means of spill response because most spills are small and close to shore [79].

5.5. Role of chemical herding agents in spill response

Chemical herders, also known as surface collecting agents as stated on the U.S EPA National Contingency Plan (NCP) product schedule, were first designed in the 1970s and commercialized during the 1970s & 1980s to aid in oil spill clean-up exercises [69, 80]. Chemical herders can be a single surface active agent or a combination of two or more surface active agents which are specifically made with capabilities to compress or draw together oil to form thicker slicks on the surface of water [81]. The surface-active agents which make up the chemical herders possess high spreading pressures or coefficients (mid 40 m.N/m at best) greater than that of most oils (10–20 m.N/m range) [82, 83]. The high spreading coefficients of herders facilitate a quick spread across the surface of water and they form a monomolecular film or layer on the water surface [69, 84]. Surface collecting agents basically float on water, are slowly soluble in oil and thus, are less soluble in water [81].

Chemical herders are designed to mix up with water surrounding the oil and not the oil [80]. Therefore, surface collecting agents are applied at the periphery or edge of the oil (in between the area of spilled oil and the surrounding water) [85]. When the surfactants are applied at the periphery of the oil on the water surface, it quickly creates a monomolecular surface layer which causes clearing and containment of oil on the surface of water [86].

The herding agents applied cause an alteration in the acting interfacial forces at the oil perimeter on the water surface [69, 85]. There occurs a drastic decrease in surface tension of the surrounding water which is noticeable from about 70 m.N/m to about 20–30 m.N/m [80]. The reduction in surface tension of the surrounding water leads to the oil moving towards itself to amass into thicker slicks [81]. The oil contracts to form smaller and thicker slicks over a small coverage area due to intermolecular forces of attraction within the oil [85].

These intermolecular forces are peculiar to the type of oil and its composition [85]. In view of this, the magnitude of the effectiveness for a surface collecting agent depends on the type of oil spilled. It is reported that the more viscous and dense the oil, the higher the effectiveness of the surface collecting agents [84, 85]. Using surface collecting agents on the surface of water can amass an average oil slick thickness of around 3 mm which is suitable for ignition [81].

Silsurf A004D, USN herder, and Silsurf A108 are examples of herding agents used in various spill response studies [81]. Corexit OC-5, oil compress/binder, oil herder, and oil spill remover are also chemical herders that were once listed on the NCP product schedule but removed.

However, there is currently only two commercial surface collecting agents listed on NCP product schedule as of October 2021 and these are Siltech OP-40 (silicon based herder) and Thickslick 6535 (hydrocarbon based herder) [87, 88]. Comparing the two commercially available surface collecting agents, Thickslick 6535 is slow to reach maximum oil thickness when used but can sustain slick thickness for a longer period of time as compared to OP-40 [85]. Thickslick 6535 coagulate at -2 °C and freezes at -24 °C [80]. Siltech OP-40 results in a rapid increase of oil slick thickness and within 300 s of application, maximum slick thickness is achieved [85]. However, it does not hold elevated slick thickness as long as Thickslick 6535 does [85]. OP-40 coagulates at -59 °C and freezes at -71 °C [80].

The above comparison indicates that temperature is an influencing factor for herder effectiveness and thus must be considered in the selection of chemical herder to use for a particular oil spill response. It is reported that 0P-40 increases oil slick thickness better in cold environment as compared to Thickslick which has a better performance in warm conditions [69].

Surface collecting agents can be applied around the oil on the surface of water by means of vessel and aerial application [80, 89]. For surface vessel application, the vessel moves slowly without mixing the herding agents in the water column whiles applying it around the perimeter of the target oil [82]. In terms of the aerial application method, the aircrafts that are used for operations work at suitable speeds and altitudes which

regulates the rotor downwash on the application of the surface collecting agents and on the target oil [80, 90].

5.6. Using surface collecting agents to aid in spill response

In principle, the formed monomolecular film on the surface of water by herders serves as a barrier around the oil to prevent spreading into thin sheens [91]. One of the aims of emergency spill clean-up exercise is to prevent oil from moving to sensitive areas as well as locations that are not affected by a particular spill incident. In view of this, several means possible are used to contain the oil at a small area and this includes the use of mechanical tools such as booms and sweeping arms. However, surface collecting agents can be deployed in place of physical barriers in some conditions at sea [91].

Surface collecting agents can be used in the containment and recovery response exercise, dispersant applications, as well as aid effective in-situ burning process in both ice fields and open water [80, 84, 88].

5.7. Chemical herders and dispersant application

Surfactant herders can be applied at the oil spill perimeter to enhance the effectiveness of dispersant application [91]. Due to inconsistent slick thickness of spilled oil in open sea as a result of spreading, dispersant application faces a big challenge of under dosage or excessive application [83, 84]. When dispersants are released onto thin sheens of oil slicks, the surfactant content herds the oil by contracting it to itself and hence, leads to increased dispersant-water contact during application [83, 84]. This results in excessive application and wastage of dispersant when efforts are being made to increase the dispersant-oil contact rate. This, to an extent, can be resolved by using surface collecting agents as oil slick thickeners and as anti-spread agents [90]. When surfactant herders are applied at the periphery of the oil on the surface of water, thicker slicks are achieved by herding oil on the surface of water together, as a result, an increased dispersant-oil contact is obtained [84]. In view of this, the quantity of dispersant applied is well controlled. Dispersant application effectiveness is enhanced by increasing the overall precision of the application process [91]. By this means, targeting oil slicks on the surface of water with dispersants becomes relatively easy and efficient.

Considering the mode of application of dispersants on herded oil slicks on the surface of water, vessel application of dispersants improves dispersant efficiency [84]. Aerial application of dispersants onto herded oil slicks reduces operational dispersant efficiency due to large amounts of dispersants going waste by coming in contact with surface water [84].

Chemical herding of oil can be beneficial to dispersant application in the sense that when environmental conditions at sea is very calm, making it impossible for mechanical energy to be present, chemical herders can be applied at the oil periphery to confine oil at a particular area until sea forces are active to necessitate dispersant applications [83, 84].

5.8. Using surface collecting agents for containment & recovery

These surface-active chemicals can be used in place of mechanical barriers such as booms and sweeping arms attached to vessels in the containment and recovery process [91]. When oil on the water surface forms thicker slicks and do not spread to form thin sheens, it enhances the use of skimmers making it easier and more effective at the collection phase [80].

5.9. Using surface collecting agents for burning in-situ

As already recounted in this paper, oil on the surface of water will burn in the presence of oxygen, fuel and an ignition source [56, 91]. Chemical herders can be used for open sea and in-situ burning on icefield environments per studies and experiments conducted by researchers like Buist et al. 2011, Buist et al. 2014, Aggarwal et al. 2017 and Bullock et al. 2019. Ignition can only occur if adequate slick thickness is obtained [73].

For fresh crude oil on water, slick thickness required for ignition is 1 mm whereas slick thickness of range 2–5 mm is required for aged and unemulsified oil to ignite and sustain burns [85]. In view of these, chemical herders can be used in place of mechanical barriers to induce adequate oil thickness for ignition [69].

Usage of surface collecting agents have shown great potential of achieving great burning efficiencies [69, 88]. Per studies, application of surface collecting agents as a means of oil confinement method for burning can yield about >90% of oil removal from the surface of water[71] Buist et al. 2010 reports that for an in-situ burning field scale experiment in the Barent sea (Norway), the USN Herder was used to achieve a maximum burn efficiency of 90% [92]. Bullock et al. 2019 report that for an in-situ burning field test trial using Thickslick 6535 and OP-40 in the UAF poker flats, Alaska, USA, a maximum burn efficiency of 94% was achieved. They also report that at the Frigg field, North seas (Norway), thickslick 6535 was used to herd Grane blend crude in open water and the result was 95% maximum burn efficiency [69].

5.10. Challenges associated with chemical herder usage

Reports and data on surface collecting agents indicate that the negative effects of applying these chemical agents are much less on the ecosystem as compared to that of spilled oil [69, 93]. However, the use of surface collecting agents come with its own barriers and challenges and hence must be taken into critical consideration whenever herders are to accompany any spill response method for an exercise.

Generally, herders can only be used under calm conditions at sea since breaking waves and other forces at sea disrupt the herding monomolecular layer formed on the water surface to confine oil [81]. Reports also indicate that surface collecting agents on the average can hold up oil slick together for at most a 60-minutes period, and can amass a maximum of 3 mm oil slick thickness only. This implies that for some particular oils such as bunker "C" which require more thickness to ignite, herder application is less relevant [67]. There is a possibility of chemical herders mixing up with oil when applying at oil perimeter most especially via aerial operation, this reduces herder effectiveness because surfactant will herd the oil instead [80, 90]. Per reports, not much is known about the abilities of surface collecting agents to thicken emulsified and weathered oil, hence, might not be appropriate to consider for oil that has undergone much weathering and emulsification [88].

5.11. Bioremediation

The natural phenomenon whereby microorganisms change and break down organic molecular compounds into fatty acids, carbon dioxide and other non-toxic substances is known as biodegradation [94, 95]. Bioremediation method involves introducing other materials to oil spill sites to enhance the natural process of microbial biodegradation [96, 97]. To enhance the process of natural degradation, the spill site should not be low in microbial activity-enhancing nutrients such as phosphorous and nitrogen [95]. This means that nitrogen and phosphorous rich substances can be introduced to spill locations to enhance biodegradation [94]. Materials rich in nitrogen and phosphorous were used as a catalyst to enhance microbial activities on the Exxon Valdez oil spill which occurred in Alaska, 1989 [97].

Biodegradation is the final fate of any oil not collected or entirely redeemed during spill response [98]. Research shows that there are more than 170 genera of bacteria identified as sources of hydrocarbon degradation whereas fungi can boast of a similar number of genera. These microbes are ubiquitous in the ocean and other spill environment, and can degrade oil under both non-aerobic and aerobic conditions [94, 98]. There is a huge dynamism in the microbial communities. In this sense, different species of these organisms inhabit in different locations of the marine environment with each species having their specialty in contributing to the degradation process [94, 99].

These microorganisms are oleophilic by nature, thus feed on and metabolize liquid hydrocarbons as a source of energy for their life cycle activities [80]. Throughout this alteration of oil process, oil degrading microorganisms change per time and per component available for consumption [95, 99]. As biodegradation progresses, organisms that do consume compounds die off and the process is continued by other microorganisms that depend on the remains of these compounds to consume [94]. This process takes a very long time to complete. Bioremediation is known to be the best method in terms of achieving a near natural environment after a spill but takes an unknown period to be completed, making it unsuitable for the purpose of emergency response [100].

5.12. Dispersants

For marine oil spill clean-up exercises, one of the traditional methods available is dispersant application and they are basically chemical agents which are introduced onto the spill in order to break the oil into large quantities of tiny droplets into the water column by means of sea energy as shown in Figure 2 [101]. The fate of these large quantities of the tiny oil droplets is to remain in the water column and disperse naturally [101]. Within the water column, further processes such as biodegradation, dissolution, and possible sedimentation occur to these small droplets of oil of which biodegradation also known as microbial degradation is dominant [101]. Microbial degradation is a natural process whereby microorganisms consume and breakdown oil [79]. These microorganisms such as bacteria exist in all areas within the water column in unlimited numbers [79].

Chemical dispersants are a uniform mixture of solvents and surface active agents commonly known as surfactants and other additives [102]. Dispersants, like detergents and soaps contain surface active agents [14]

that are basically dissolved in solvents [102]. Dispersants can be applied to spill sites at the surface by vessel or aerial operations and also at subsurface by means of subsea injection or point source application [103].

The reason why dispersants application to spilled oil works is because it contains surfactant molecules which consists of two parts; a lipophilic part that gets attracted to the oil, and a hydrophilic part that gets attracted to the water [104]. They orient or align themselves at the oil-water interface and reduce interfacial tension between the oil and water [79]. The interfacial tension often used interchangeably with surface tension can be described as the free energy change in relation to the change in contact area at the interface between the oil and water [101]. When the interfacial or surface tension is reduced in this regard, it leads to a rapid break-up of oil slick into million quantities of small droplets in the presence of mixed energy in the marine environment [14]. These droplets are so tiny that their diameter is less than 100 microns on the average [79]. With a diameter as small as this, it implies that there is little or no possibility for these oil droplets to resurface to form coalescence [14]. The mixing energy or hydrodynamic energy at sea in the form of wave action, winds, tides and currents transfer oil droplets into the water column within 10 m approximately [79]. Due to the very small nature of the oil droplets, there is an increased surface area to volume ratio which is enough for microbes to attack the oil droplets [104].

Mathematical expression for minimum energy required for dispersing oil droplet into the Water Column [101, 105].

$$W_K = \gamma_{o/w} \, A_{o/w} \qquad (4)$$

where, W_K = mixing energy [measured in ergs or g-cm^2-s^{-2}; 1 erg = 10^{-7} J (kg-m^2-s^{-2})] $\gamma_{o/w}$ = oil-water interfacial tension (measured in dynes-cm^{-1}, where 1 dyne = 1 g-cm-s^{-2}; equivalent to ergs-cm^{-2}).

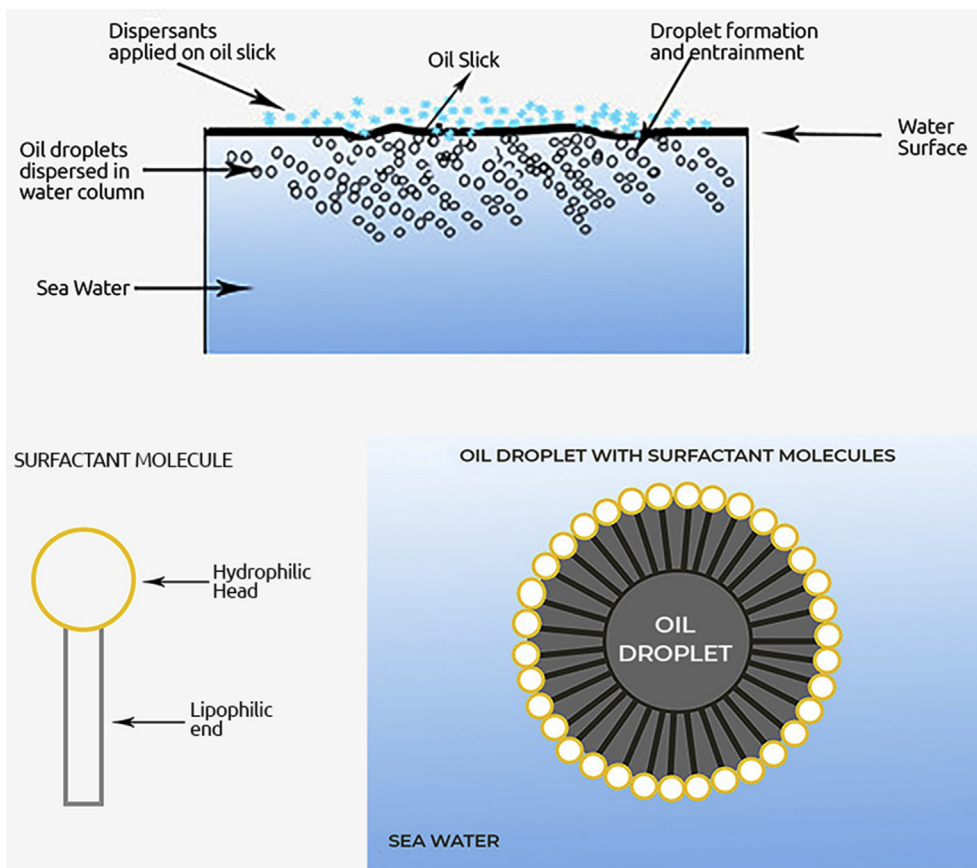$A_{o/w}$ = area of oil-water interfacial (measured in cm^2).

Figure 2. Chemical dispersion mechanism [81].

Microorganisms are ubiquitous within this depth of the water column and will therefore colonize, consume, and degrade the oil droplets as their source of food [102]. By these processes, it can fairly be concluded that dispersants clean-up spill from water surface via enhanced micro-organism degradation.

According to T. Coolbaugh 2011 [103], the primary objective for dispersant application is to reduce environmental impacts associated with oil on water surface, enhance the removal of oil from the water surface through biodegradation and rapidly reduce toxicity through dilution. Therefore, dispersants application is said to be effective if the primary objective is accomplished. To achieve an effective dispersant application, the three categorized sections below must be ensured;

I. The effectiveness of the operation. This can be interpreted as how well the dispersant is applied and introduced onto the spilled oil
II. The effectiveness of the chemical dispersant. This covers the amount of treated oil that is submerged or entrained as tiny droplets in the water column.
III. Effectiveness of hydrodynamic energy. This entails the presence of adequate turbulent energy at sea and its ability to transfer dispersed oil droplets and its dilution through vertical and horizontal processes.

The effectiveness of dispersant application in a marine environment can further be described as a measure of the quantity of oil dispersed into the water column as against the quantity of oil which is left on the surface of water [106, 107].

With respect to the above effectiveness measuring parameters, several factors combine to determine how effective a dispersant application for a particular spill can be and these include; oil composition, energy at sea (mixed energy), quantity and type of dispersants (surfactant) applied, dispersant-oil contact rate, degree of weathering, temperature and the salinity of water [108].

5.13. Factors influencing dispersant effectiveness

The most important factor influencing dispersant effectiveness is the quantity of dispersant added to oil [108]. When dispersants are applied in the right proportion, adequate dispersant-oil contact rate is achieved, this reduces the quantity of dispersants that gets wasted and thus enhances the effectiveness of the chemical dispersant. On the other hand, if the quantity of dispersants applied is not adequate, the oil on the surface of the water with no contact with the chemical dispersants undergoes further weathering and spreading which makes the clean-up exercise more difficult to accomplish. This sums up the effectiveness of the operation which intends impacts the effectiveness of chemical dispersants as described by T. Coolbaugh 2011.

Hydrodynamic energy such as waves, currents, tides, and wind actions at sea adds a lot of energy to mixing of dispersants and the oil [106]. When the conditions at sea is very rough, mechanical energy is high and provides the best results for dispersion [108]. The effectiveness of hydrodynamic energy at sea enhances transfer of dispersed oil droplets into the water column.

Considering the composition of oil, for example, dispersants are less effective on heavy oils as a result of the high asphaltene and resin content of these oils [14, 109]. These oils have high viscosities which impedes the effectiveness of dispersants [13]. Therefore, the type of oil as well has an influence on dispersion effectiveness, hence must be considered when dispersants are to be used as a spill clean-up method.

Temperature is also an influencing factor in the effectiveness of dispersants in a marine environment [106]. High temperature enhances the effectiveness of dispersants in the sense that oil viscosity which impedes effectiveness reduces at high temperature [106]. Hence, lower temperature limits dispersion effectiveness as it causes both dispersant and oil to increase viscosity [106].

When oil spills into the marine environment, it undergoes different degrees of weathering as time passes by. Oil on the surface of water over time undergoes evaporation, formation of water-in-oil emulsions, increased density and increased viscosity [105]. When these happen, the overall effectiveness of dispersants is negatively affected since weathered oil requires higher mixing energy to disperse [110]. Hence, dispersants are more effective when applied immediately after a spill incident.

The salinity of water is another important factor that contributes to the effectiveness of dispersants. Dispersant effectiveness increases with high water salinity [111]. Most commercially available dispersants are designed for regular marine salinity of 30% and above [106]. High water salinity daunts the migration of surfactant molecules into the water phase of the oil-water interface and this influences the contact between the surfactant molecules and oil at the oil-water interface [106]. It is reported that high salinity minimizes dispersant solubility in water, thus increasing the dispersant-oil contact [107].

Low salinity waters result in the production of very little energy from hydrodynamic mixing, therefore the use of dispersants in such waters will not yield the desired effectiveness [112].

However, to achieve an overall effective dispersion process, the National Response Centre (NRC) has seven laid down requirements [101] and these as stated are;

1. The dispersant must hit the target oil at the desired dosage.
2. The surfactant molecules in the dispersant must have time to penetrate and mix into the oil.
3. The surfactant molecules must orient at the oil-water interface with the hydrophilic groups in the water phase and the lipophilic group in the oil phase.
4. The oil-water interfacial tension must decrease due to the presence of surfactant molecules at the oil-water interface, thereby weakening the cohesive strength of the oil film.
5. Sufficient mixing energy must be applied at the oil-water interface (by wind/or wave action) to allow generation of small oil droplets (with concomitant increase in interfacial surface area).
6. The droplets must be dispersed throughout the water column by a combination of diffusive and advection processes to minimize droplet-droplet collisions and coalescence to form larger droplets (which can resurface in the absence of continued turbulence).
7. After entrainment, the droplets must be diluted to nontoxic concentrations and remain suspended in the water column long enough for most of the oil to be biodegraded.

The application of dispersants is most effective within the first 72–96 h of a spill incident [101]. A coffee-coloured plume seen within the water column is an indication that chemical dispersants are successfully working [14]. However, chemical dispersants do not work perfectly for all compositions and types of spilled oil [103]. Light oils and medium oils disperse with relative ease as compared to that of heavy oils. Oils with larger quantities of asphaltenes and resins tend to disperse quite poorly [14]. Reports also indicate that effectiveness of dispersants vary for different dispersant formulations, hence in selecting dispersants, the relevant factors like oil type, temperature and salinity must be well considered in order to select the product that will give the highest effectiveness for a particular spill condition [113].

Application of dispersants is one of the first response methods for major offshore oil spills [114]. Dispersants have been deployed in quite a number of marine oil spills across the world. After the Torey canyon incident which occurred in March 1967, dispersant applications have been improved and widely utilized in the USA (approximately 20 times) [115]. It has also been well used outside the shores of the United States.

Taking into account a few spills that utilized dispersants for remediation, approximately 9000 metric tons of chemical dispersants were used in the south-western Gulf of Mexico to combat the Ixtoc-I spill off the Campeche, Mexico which occurred in June 1979 due to marine blowout that lasted about 9 months [115, 116]. Also, during the Montara wellhead

Table 2. How dispersants and other traditional remediation methods compare in terms of crude oil spill in open sea.

Parameter	Dispersant	Burning	Mechanical Containment & Recovery	Sorbents	Bioremediation
Response time	The best response time since dispersants can be deployed via aircrafts at top speeds to far and obscure locations within the shortest possible time. It can also work on the slimmest forms of slicks.	Good response time because oil can be removed from the surface of water quickly if and only if all conditions required for ignition and sustenance are met. Torching of oil can be done by aircrafts	Not suitable for large spills, and at locations very far from shore since it requires a lot of time to transport materials and form such barriers around a large spill.	Not suitable for large spills, and at locations very far from shore because it will present logistics difficulties which runs against time	Cannot be used as a rapid response method
Environmental effects	Removes oil from the surface of water into the water column to save surface species. Prevents water-in-oil emulsions and promotes natural dispersion.	Kills surface organisms, leads to atmospheric pollution and a potential hazard to humans	At higher sea energy, the use of mechanical barriers poses logistic problems leading to secondary pollution of clean sites	For open sea major spills, it presents its own logistic difficulties such as secondary pollution of clean sites, retrieval, storage, and disposal	Environment friendly
Prevailing weather conditions	Works better in rough environmental conditions prevalent at sea	Difficult to form physical barriers to amass required oil slick for ignition under rough sea conditions	Physical barriers can only be used at calm environmental conditions at sea	Suitable for calm environmental conditions at sea	Prevailing weather conditions at sea do not necessarily have impacts on bioremediation. It requires suitable temperature and nutrients to succeed
Spill location & size	Appropriate for large scale spills and spills which are very far from shore	Can be used for large scale spills and spills very far from shore	Usually used for minor spills and shoreline clean-up	Usually used for minor spills and shoreline clean-up	Can be used in conjunction with other countermeasures for both major and minor spills. It can be used near and far from shore
Team safety	Dispersant application does not require large response team hence reducing human risk involved. However, chemicals can pose some degree of health risks to humans	Response teams at risk of respiratory health problems	Response teams come in contact with oil during and after collection (disposal or recycling phases) and could be exposed to a potential health risk	Response teams come in contact with oil during and after collection (disposal or recycling phases) and could be exposed to a potential health risk	Safe method

blowout that occurred in western Australia in 2009, forty-eight thousand gallons of dispersants were used to combat the spill [115]. Likewise, in October 2009, dispersants were applied to oil spilled from the Krynsk tank ship on the coast of Galveston, Texas [117]. Lastly, during the Deepwater horizon oil spill incident which occurred in the northern Gulf of Mexico in 2010, an unprecedented amount of about 1.84 million gallons of dispersants were used to combat the oil spill in the marine environment [118, 119].

Dispersant-treated oil spills have exhibited that oil dispersion has the ability to minimize environmental impacts at large because it reduces the destruction at the sea surface and shorelines [108].

6. How dispersants compare with other remediation methods

When major crude oil spills occur in the marine environment, prior to the response, Net Environmental Benefit Analysis is quickly done by spill responders to select the most suitable response method. This process involves possible trade-offs. However, modern oil spill modelling tools help spill responders with information for contingency planning and swift decision making. Some of the factors considered during Net Environmental Benefit Analysis are location of spill, volume of spill, type and composition of oil, time, aquatic species present at spill location and prevailing environmental conditions in the marine environment [14]. Comparatively, the strengths and weaknesses associated with the traditional remediation methods in terms of major factors to consider for spill applications in the marine environment are broken-down and summarized in Table 2.

Sorbent material application is good at removing oil from the surface of water due to its generally good wettability properties such as good hydrophobicity and high adsorption capacity [62]. However, they are generally not a suitable spill remediation method for large scale spills in the marine environment because they do not function appropriately when turbulent energy at sea is high or environmental conditions are unstable [59, 120]. Usage of sorbent materials for open sea major spills presents its own logistic difficulties such as secondary pollution of clean sites, retrieval, storage, and disposal [41]. They increase the cost of clean-up in this regard.

Sorbent materials however do not function appropriately on more viscous oils such as heavy crude as well as much weathered oil [22]. The application of sorbents for spill clean-up is mostly effective for small scale oil spill recoveries and also at the completion stages of clean-up operations at shoreline as a means of polishing [22, 61].

Burning (In-situ) of oil on open water surface is a very rapid means of removing large amounts of oil [68]. It has a high efficiency rate. It reduces the quantity of oil that requires disposal and does not need more hands and equipment [71].

However, removing oil by in-situ burning from the surface of water does not mean the spilled oil has been completely removed from the environment [68]. The burned oil transforms into large black smoke, gases such as carbon dioxide, volatile organic compound and carbon monoxide together with other harmful products [64, 71]. These by-products of burning may have adverse effects on atmospheric species, nearby habitats as well as humans who inhale them [68]. They present major health risk to response teams and other humans in nearby habitats because particulate matter, a product of burning oil in-situ, when inhaled into the alveoli of the lungs can cause severe respiratory tract problems [64].

Emulsification and weathering affect in-situ burning processes by removing combustible components from oil within a very short time [64, 71]. This implies that emulsified and weathered oil are very difficult to ignite as well as a low tendency to burn and sustain [71]. In view of this, burning in-situ is very difficult after the first 12- to 24-hour period of a spill incident [64]. There should be at least 1-millimetre slick thickness for fresh crude oil before it can burn on water [64]. It requires at least 2–3 mm of oil slick thickness to burn oil that has undergone some form of weathering in open water [64, 68]. For heavy oils, there should be a minimum slick thickness of 10 mm before it can burn [71].

With in-situ burning, there is also a high risk of surface biota being destroyed by fire as well as spreading to other combustible materials in nearby habitats [71]. Also, fire-resistant booms like any form of booms lose stability which results in entrainment of contained oil under high sea forces [67].

In view of oil slick thickness requirements, thus, weathering and emulsification of oil on water within a very short period and climatic conditions, in-situ burning for a major spill in open marine environment must be considered under special circumstances whereby there is a continuous release of oil from its source such as that of the BP Deepwater horizon wellhead-blowout incident in 2010 [68, 71]. Without this, ignition and sustenance of burn is extremely difficult. As compared to that of open water, in-situ burning is more efficient on land due to no emulsification of oil on land [71] and also on ice as a result of the ice serving as natural barriers to contain oil [71].

Bioremediation is known to be the safest and most appropriate remediation method because it has the capacity to restore the environment to almost its natural state [94]. However, it does not serve the immediate needs of the environment due to the unknown amount of time required for bioremediation to be complete [100]. This does not make it a considerable emergency spill response method for a major marine spill.

Mechanical containment and recovery is highly dependent on the weather conditions at sea and therefore requires a stable climate to work effectively [77]. At sea, mechanical energy greatly affects the efficiency of boom usage. These sea forces such as wave action, winds and current together with other forms of turbulence disturbs containment of oil by booms which results in entrainment as well as splash over [75]. Unstable weather conditions can cause damage to recovery systems especially single ship systems [77]. Many factors such as the degree of emulsification, rate of spreading and oil type affects recovery processes [78]. Emulsified and viscous oils are very difficult to recover by skimmers due to its water contents whereas spreading also reduces oil encounter rate because thin sheens of oil resulting from spreading are difficult to scud [78].

According to T. Wadsworth [77], not more than 10% of oil that spills on the surface of water is recovered usually. This is a clear indication that mechanical containment and recovery is not the most appropriate when it comes to emergency major spill response at sea. However, very suitable and recommended for shoreline clean-up exercises [77].

Dispersants application has many advantages over other oil spill response methods in terms of major spills in the marine environment. Dispersant usage can be deployed for a broad range of conditions which includes large spills far offshore, subsurface spills and spills in ice-filled environments [79]. Dispersants command a variety of application methods which is very beneficial in terms of gaining time and can also be applied to slicks as thin as 0.1 mm on the water surface [79, 103].

With dispersants, far from shore spills can be quickly attended to by means of aerial dispersant application, small spills can be dispersed by means of boat application whereas subsurface sources of spills can be dealt with by virtue of subsea injection [103, 114, 121]. It can be applied in large volumes within a very short time to cover a vast area of spill on the surface of water [114].

Dispersants remove oil from the surface of water which curtails physical contact between species such as sea birds and the oil [9, 14]. By this, these organisms are protected from the surface contaminated oil. Dispersants applied in modern times are biodegradable and also promote natural microbial degradation activities [14, 79]. Dispersants can be deployed when weather conditions are forecasted to become severe, when conditions at sea do not permit the usage of other spill countermeasures [79]. It is worthy to also note that dispersants perform more effectively at sea when mixed energy or sea forces are high [9, 14].

In view of the above description on all the traditional methods of spill response in relation to major spills at sea, it can be summarized that dispersant application is the most suitable response method for major spills at sea considering that it can work on the slimmest form of slicks, performs better at rough sea, can be applied to oil by different means to save some time, the location and volume of spill does not matter and enhances natural biodegradation. However, it can be said that a common deficiency runs across majority of the methods and that is in dealing with weathered and emulsified oils.

Moreover, comparison between the use of chemical dispersants and other response methods is non-holistic in the sense that dispersants are chemicals and differ vastly in terms of time and area scales [71]. However, they can be applied hand-in-hand after critical considerations and Net Environmental Benefit Analysis for a particular spill incident.

7. Dispersant formulation

Chemical dispersants on the market are a typical mixture of surfactants and solvents and sometimes with additives [101, 102]. Commercial chemical dispersants usually consist of 2 or more surface-active agents and carbon-based solvents [122].

Solvents are a component of chemical dispersants that dissolve the surface-active agents and additives into a uniform mixture [79]. Solvents control the extent to which dispersants may be premixed with water for some spraying applications due to the fact that aqueous-based solvent systems freeze in spray nozzles at surrounding temperatures below 0 °C [101]. Solvents also play a vital role in dispersant solubility, keeps surface active agents in solution and aids in the reduction of dispersant viscosity [123]. It enhances the coverage and distribution of surface-active agents onto the oil spill.

Generally solvents used in producing dispersants are either neutral such as water, or organic (hydrocarbon-based) [102]. Solvents used in formulating commercial chemical dispersants available on the market include 2-Butoxyethanol, water, propylene glycol, paraffin and ester based solvents [124].

Surface-active agents are compounds which consist of both lipophilic groups and hydrophilic groups [101, 102]. These groups have a high affinity for oil and water respectively. Surfactants are amphipathic in nature and hence orient itself appropriately at the oil-water interface to influence dispersion. It is the most important component of dispersants as well as aid in the formation and stabilization of emulsions [102, 125].

Surface-active agents can be anionic, cationic, amphoteric, and nonionic. These classifications are based on their dissociation in water (thus the charge at the hydrophilic part) and all these types are available on the market [126, 127]. Surfactants used in making commercial dispersants include sorbitan esters such as Span™ series, ethoxylated sorbitan esters such as Tween™ series and Sodium di-iso-octyl sulphosuccinate [102, 126].

Additives, usually the final component of dispersants are present to prolong stability of dispersants and also to enhance dissolution of surface-active agents into an oil slick [101]. It is worthy to note that blending surface-active agents usually results in a dispersant with predominant hydrophilic characteristics which tends to promote oil-in-water dispersion and can be one of the few reasons why commercial dispersants are made of two or more surfactants [101].

8. Blending surfactants

Several studies report that blending surfactants (being it a nonionic, anionic, or zwitterionic combination) have a higher potential for surface activity as compared with the individual surfactants which make up the mixture [128, 129]. When surface active agents are combined, they undergo strong intermolecular interactions which enhance the rate of natural dispersion [113, 130].

The surface active potential of a surfactant depends on its hydrophilic characteristics and structure [131]. By virtue of their structure, surfactants have different solubilities and can be characterized by their hydrophilic-lipophilic balance usually referred as HLB which ranges from zero (0) to twenty (20) [101]. The 0 indicating the highest lipophilic concentration and the 20 being the highest hydrophilic concentration [101]. This implies that a specific HLB value for a mixed surfactant

indicates whether it has low HLB which means more soluble in oil or has high HLB which means more soluble in water [127, 131]. Dispersants made by surfactants blending have a usual HLB range of 9–11 [113]. However, HLB alone cannot be used to determine the effectiveness of a surfactant blend [113].

For an instance, anionic surfactants have high HLB due to high solubility in water whiles nonionic surfactants have low HLB thus soluble in oil. When nonionic and anionic surfactants are mixed to form dispersants, they interact in synergy to improve upon the effectiveness of dispersion [131]. Nonionic surfactants have good ability to reduce interfacial tension and in the presence of salt, they have constant properties as compared to anionic surfactants. These lead to low critical micelle concentrations and better performance of the mixture [132].

Another parameter to be considered when studying the effectiveness of surfactants in a dispersant is the critical micelle concentration (CMC), the lowest concentration at which any addition of surfactants form micelles and above this concentration, surface tension remains constant [127]. The lower the CMC, the less surfactants is needed to form stable emulsions, solubilize and disperse oils [133].

It is reported that a mixture of anionic and nonionic surfactants show a critical micelle concentration lower than that of anionic component only and further addition of the nonionic surfactant into the mixture will only decrease the CMC to the level of the nonionic surfactant component only [132]. This depicts that nonionic surfactants naturally have lower CMCs compared to anionic surfactants. Anionic surfactants due to high CMCs in aqueous solution sorbs less at the oil-water interface [132].

When different surfactants are mixed at optimum ratios, the surfactants interact to promote synergistic adsorptions which improve interfacial characteristics and stability of emulsions [129]. Athas et al. 2014 reported that, a combination of 60 wt.% Lecithin and 40 wt.% Tween 80 had an interfacial synergy which effectively formed stable emulsions for a long period without droplet coalescence. Nyankson et al. 2020 also reported that a surfactant mixture of 50 wt.% Dioctyl Sulfosuccinate Salt (DOSS) and 50 wt.% binary saponin resulted in 87% and 83% dispersion effectiveness for light crude and Texas crude samples respectively in their study.

It can be said that blending surfactants yield an enhanced oil droplet dispersion because the surfactant molecules in the mixture, based on their structure, align appropriately at the oil-water interface. This is to promote intermolecular interactions which keeps the surfactants densely packed together at the oil-water interface resulting in reduced interfacial tension and emulsion stability [101, 134]. The surfactants can stay at the interface for longer periods without desorbing whiles the hydrophilic head groups within the surfactant blend cause steric stabilization of the emulsion [101, 134]. In summary, blending surfactants to formulate dispersants are more effective as compared to the individual surfactant components of the blend because the surfactant interacts at the oil-water interface in the following three ways.

a) Synergy in the effectiveness of surface tension reduction (this is when the surface tension of the mixture obtained at CMC is lower than that of the individual surfactants which make up the mixture) [131, 133, 134].
b) Efficiency in surface tension reduction synergy (in this case, a given surface tension attained at a total mixed surfactant concentration is less than that of each individual surfactant making up the mixture) [131, 133, 134].
c) Mixed micelle formation synergy (in this, the CMC of the mixture is lower than that of the individual surfactants making up the mixture) [131, 133, 134].

Per the above breakdown, surfactants can be blended to improve upon their dispersion effectiveness, however, being it a combination of two or more biosurfactants or a combination of biosurfactants and synthetic surfactants, the structure of the individual surfactant components must be considered to ensure they interact synergistically at the oil-water

interface when combined. In conclusion, combining surfactants show synergism in surface tension reduction, foaming effectiveness and micellization behavior, hence provides a more effective dispersion performance than the sole surfactants of the mixtures [133].

9. Mode of dispersant application

Depending on the kind of spill and identified dispersant to be used, it can be applied neatly or undiluted [27]. Dispersants can be administered onto oil spills by means of aerial application, vessel or boat application, and subsea injection or point source application, depending on the location or source of incident, quantity of oil spilled, time required and proximity to shore [14, 103].

The most important aspect of dispersant application is to distribute adequate dispersants to a specified spill area in droplets of correct size whiles ensuring that the chemical comes into contact with the spilled oil [14]. This implies that slicks must be overdosed with dispersants to ensure effectiveness [110]. Inappropriate dispersant droplet sizes greater than 1000 microns usually leads to the chemical breaking through the oil slick which results in a process called herding [14]. However, it is imperative to ensure that systems used in administering dispersants are purposefully designed for it.

9.1. Aerial application

Spray systems to administer the dosage and tanks to store dispersants are specially designed and installed on specifically associated aircrafts for aerial application of the dispersants [14, 114]. These aircrafts and its associated systems are of a wide range of sizes from small, medium to large as well as helicopters [114]. A common aerial spraying system used for administering dispersants is the Aerial Dispersant Deployment System such as the Rapid Installation and Deployment Spray systems which can be installed on the C-130 Hercules aircraft specifically designed for it [121, 135].

Before dispersants are released from the aircraft, a person known as spotter identifies the location of the dispersible surface oil and conducts the aircraft to such sites. The person in this position is in charge of coordinating the operation [114]. The spotter indicates to the pilot when to put on and/or off the dispersant spray to ensure accuracy and avoid over spraying and wastage [114].

When dispersants are released in the air towards the oil spill, it spreads and appears as a form of carpet before it finally lands on the oil [102]. Spray aircrafts do dispersant application operation averagely at 125–145 knot (speed range) at relatively low altitudes ranging between 15- 30 m [121, 135]. Spray systems are specially designed to release spray of particular droplet sizes to cover the oil slick and enhance contact between dispersants and oil [14]. The use of aircrafts provide rapid response within 2–4 h thus reducing spreading rate of oil [114]. Also, dispersant applications via air covers very large areas and can treat a large volume of oil within a single day. The use of aircrafts makes arrival at spill sites far offshore possible within the first day of the incident [95].

According to Radpour (2015), disadvantages of aerial application are not necessarily associated with the aircraft but the operational logistics such as lack of many readily available aircrafts fully fitted with dispersant application systems [110]. To apply dispersants aerially, there must be pilots who can fly at relatively low altitudes at top speeds and without this, dispersants applied may not come in contact with the oil on the surface of the water [110]. Spotters serving as conductors must be 100% focused to minimize dispersant-water contact and wastage during application [135].

9.2. Marine vessel application

Vessels of varying sizes are deployed for such exercises at sea. Vessels required for dispersant application are fully equipped with standard

equipment for this purpose and these are of four components namely storage tanks (for dispersants), delivery pumps, volumetric metering device and spray system [110].

The spray systems are specially designed to release a particular droplet size at a particular rate [14, 114]. This enables an enhanced dispersant-to-oil contact for rapid degradation [136]. Vessel application of dispersants are used to suppress volatile organic compounds in order to protect spill response teams especially in areas where aircrafts cannot be operated [114, 137]. It is also for the purpose of small-scale operations aiding in proper clean ups of spills close to shorelines [14, 114]. The easy accessibility of marine vessel to resource them for dispersant applications are also vital for emergency responses [110].

There are associated disadvantages to marine vessel application of dispersants for spill response. Vessel operations are relatively slow thus travels at an average speed of 7 knots [14, 114]. Using vessels to apply dispersants over a large spill can be very difficult and will lead to loss of time due to the travelling speed of the vessels [101]. Also, for vessel operators to know the overall magnitude of the spill as well as the effectiveness of the dispersant application, they require an aircraft to assist them visualize the reality by means of instructions and directions [110].

9.3. Subsea application

The Deep water Horizon wellhead blowout incident which occurred in 2010 can be said to be the first of its kind – a large scale wellhead blowout incident that required subsea application of dispersants [138]. Applying dispersants by subsea injection reduces the oil quantities that surfaces as well as the potential exposure of spill response teams to volatile organic compounds [101, 118]. Less amounts of dispersants are required for subsea injection as compared to the quantity required for surface dispersion process [139]. Atmospheric and weather conditions at sea surface do not play a role in this process [129].

For a subsea dispersant application operation, a remotely operated vehicle (ROV) or hard pipe into the blow-out preventer (BOP) can be used to administer dispersants from storage tanks on the sea floor or from a surface vessel to the point of oil release directly [121]. ROVs and other subsea assemblies use nozzles to directly deliver dispersants into the oil released as done with the 2010 Deepwater horizon incident which occurred in the Mexican Gulf [121].

For subsea operations, dispersants-to-oil contact rate can be 100% [121]. When dispersion happens in deeper waters, oil droplets rarely move to the water surface [14]. Subsea injection can be applied directly at the source of a spill and it is known as point source application of dispersants [121]. Subsea injection and point source application of dispersants is a safe method to practice because it reduces the need for surface recovery which exposes teams to volatile organic compounds and also prevent the spreading of oil to shores [137, 139].

However, not much data is gathered on the fate of subsurface dispersant application, but based on a few experiments it can be said that dispersant compounds, hydrocarbons and other associated compounds dissolving in deep waters have the potential to impact adversely on local organisms as well as surrounding ecosystems [110, 138].

It can safely be concluded that dispersant application is very versatile and allows room for diverse means of attacking oil slicks on the surface and subsurface of a marine environment.

10. Limitations of dispersants application and effects

It is known that both the use of dispersants and effects of dispersed oil in the water column are generally less harmful compared to the effects of oil left on sea surface and allowed to migrate to shoreline habitats [140]. However, there are various discussions on chemical dispersants having a potential toxic effect on biodiversity. The question of toxicity of dispersants and its sublethal effects on biodiversity has not been clearly answered [115, 140, 141]. However, it appears that expert debates about

toxicity will carry on until a conclusion is drawn on the subject for now and the future of chemical dispersant usage.

There are other challenges associated with the use of chemical dispersants and these have to do with dispersant solubility and the effects of oil weathering in the marine environment.

10.1. Dispersants solubility and weathering effects influence excessive dispersant application

To recap this statement, during the Deepwater horizon oil spill incident which occurred in 2010, an unprecedented amount of about 1.84 million gallons of dispersants were used to combat the oil spill in the marine environment [118, 119]. Critical thinking may lead to attributing the higher amount of dispersant application to two possible causes and these are the behaviour of oil in the marine environment (mainly weathering and emulsification) and aqueous solubility of dispersants.

I. Dispersants are known to perform very poorly on oil that has undergone much weathering and emulsification [14]. When oil undergoes weathering and emulsification, they become highly viscous due to loss of lighter oil components and leaving residues of mainly asphaltenes and resins [13].

This therefore requires that, for a particular type of dispersant to work effectively on such viscous oils, the slicks must be overdosed [14, 124].

According to M. Fingas [14], the amount of dispersants in oil decreases as time progresses and thus 50% of dispersants applied gets depleted in the course of a day. This means that dispersants application is done repeatedly on daily basis until slicks disperse within the water column. In cases where white plumes form on the surface of water, it indicates that the chemical is not working appropriately, hence the dispersants are re-applied to the oil. These timely monitoring and re-application dispersants on the water surface to ensure that the dispersants function appropriately leads to the larger quantities of dispersant application being released into the environment.

II. Solubility of dispersants in water leads to large quantities of dispersant being applied to oil spills in a marine environment. Dispersants are made of surfactants and solvents with the surfactant molecules consisting of a lipophilic portion and a hydrophilic portion [14]. This means that dispersants are soluble in oil and water at the same time [101]. However, water in the ocean is much abundant compared to any volume of oil spilled and hence gives dispersant enough room to dissolve into it at the slightest opportunity. In this regard, if dispersants are not applied appropriately to the target oil and there exists a limited encounter rate of the dispersant with the spilled oil, much of the dispersants applied encounters the water and dissolves.[131]This is usually seen by a white plume at the surface of the water, indicating that the dispersants did not function appropriately [14].

In view of this, more dispersants are re-applied because the earlier application did not come in contact with substantive oil on the sea and hence have gone to waste via aqueous solubility [131]. If this series of events keeps happening, then it means more dispersant dissolution in water and hence, more dispersant application. This indiscriminate act of applying dispersants into the oil spill obviously increases remediation cost.

11. Way forward in dispersant usage

There is the potential need to move from typical chemicals to the usage of smart dispersants and bio-based surfactants that are biodegradable, biocompatible as well as great oil-in-water emulsion stabilizers. Using bio-degradable dispersant formulations to an extent, may bring a closure to the discussions around the potential toxicity of chemical dispersants.

Also, there is a substantial need to find accurate and appropriate means of delivery for dispersants onto target oil spills in the marine environment. By so doing, the primary challenge of excessive application due to aqueous solubility can be drastically minimized. This shall increase dispersant effectiveness, save time, and protect sensitive habitats and shorelines from pollution.

11.1. Bio-based formulations

Biosurfactants are naturally existing surface active compounds possessing both lipophilic and hydrophilic portions and have the tendency to lower interfacial tension for surface activities [142]. These substances are biodegradable, biocompatible and/or do form nontoxic emulsion-based formulations that can be used in food, medicinal and pharmaceutical industries [143]. Biosurfactants are multi-purposeful due to their anti-adhesive, anti-microbial and emulsifying characteristics and can be found in both plants (saponins) and animals (proteins) [143]. However, there are synthetic surfactants such as sorbitan esters and their ethoxylates and sucrose esters that have been approved by the Food and Drug Administration for use in food emulsion formulations as well [143].

Few studies have been conducted by researchers on the possibility of deploying bio-based dispersants for a marine spill response. A study by Nyankson et al. 2015 [144] delved into the possibility of using soybean lecithin, a food grade surfactant to disperse crude oil spills. In this study, fractionated soybean lecithin into phosphatidylinositol (PI) was used to formulate dispersants and the test results of the 'functionalized' fractionated soybean lecithin (FPI) showed that FPI solubilized in water recorded a higher dispersion effectiveness when compared to Dioctyl Sulfosuccinate Sodium Salt (DOSS) and Tween solubilized in propylene glycol solvent. It is reported that the FPI recorded 74.7 vol.%, DOSS recorded about 71 vol.% and Tween 80 recorded about 65 vol.% at high surfactant-to-oil ratio.

For a dispersant formulation to be listed on the U.S. EPA National Contingency Plan product schedule, it should be able to disperse at least 50 ± 5 vol% of oil used in the standard laboratory test (using U.S. EPA's Swirling Flask Test or Baffled Flask Test, a revised protocol) [144]. It should have a dispersion effectiveness value of 45% or more in a standard laboratory test. FPI has a greater potential of dispersing oil spill in the marine environment effectively compared to DOSS and Tween 80 which are already used in formulating commercial dispersants.

Nyankson et al. 2016 [145] also reported that dispersants synthetized from hydroxylated lecithin soybean is an effective oil-in-water emulsifier and that emulsions formed are stable over a long period of time. It was stated that this type of formulation can be used to replace the commercial chemical dispersants.

In this study, it is reported that hydroxylated soybean lecithin recorded a dispersion effectiveness of 85.4 vol%. Considering that a dispersant must record dispersion effectiveness value of 50 ± 5 vol% of oil used in a laboratory test before it can be listed on the National Contingency Plan product schedule, hydroxylated soybean lecithin should be highly considered in future dispersant formulations and applications on large scale.

Another study conducted into the potential of using a combined DOSS and saponin dispersant in oil spill remediation was done by Nyankson et al. (2020) [131]. In this study, it is reported that the combination of DOSS, an anionic surfactant, and Saponin, a nonionic surfactant, to formulate a dispersant resulted in an enhanced interfacial activity and stable emulsion formation. This resulted in droplets averagely smaller in sizes compared to that of only DOSS dispersant formulated.

It is however worthy to note that combining two or more surfactants result in an enhanced interfacial activity [145]. Therefore, to increase dispersion effectiveness, dispersants should be formulated with a combination of anionic surfactants and nonionic surfactants.

Nyankson 2015 reports on usage of a blend of solid water-insoluble paraffin wax particles carrying Dioctyl Sodium Sulfosuccinate Salt (DOSS) as surfactants for dispersion of oil in a study [146]. He reports that for this mixture, the DOSS surfactant was only released at the point where the paraffin wax dissolved in the oil. The paraffin wax microparticles tend to stick to the oil-water interface and can promote direct continuous release of surfactants when required [146]. To a large extent, this minimizes surfactant wastage by increasing its oil contact rate for effective dispersion. The use of composite particle dispersant formulation can replace the use of petroleum-based solvents [146]. In view of this, blending surfactants to form smart dispersants enhances dispersion efficiency.

With regards to addressing the issue of dispersants' lack of efficiency on viscous oils, a study was conducted by Hajimohammadi et al. 2016 [147] on the use of saponins, a nonionic surfactant, to upgrade the physical properties of heavy crude oil. In the study, it is reported that saponins have the potential to reduce the viscosity of heavy oil and improve upon its API gravity.

The initial API of the heavy oil per the study is 19 and that of viscosity is 2350 mPa s. After application of the saponin surfactant into the oil, it is reported that the API of the oil increased from 19 to 27 whiles the viscosity of the oil reduced from 2350 mPa s to 900 mPa s.

In view of the findings of this study, it means inculcating bio-saponins in the formulation of dispersants has the potential of improving upon dispersant effectiveness on viscous oils resulting from weathering and emulsification. This chapter of environmentally benign formulations must be highly considered in preparing dispersants for marine oil spills.

11.2. Smart dispersants: a controlled delivery of dispersants onto oil spills

As discussed earlier, aqueous solubility mainly causes excessive application of dispersants onto marine oil spills, however certain studies have been conducted into using accurate delivery media in smart dispersants to administer surfactants onto oil spills to minimize wastage. An example of such medium of delivery is the use of nano vehicles, which is widely used in the pharmaceutical industries for drug delivery [148]. Nano-vehicles such as iron-oxide carbon particles and halloysite clay nanotubes can be used to transport dispersants accurately onto target spills in the marine environment. Using nano vehicles to deliver surfactants increases oil encounter rate and hence, increases dispersion effectiveness, cutting down the number of times dispersants are to be applied.

One study by Owoseni et al. 2014 [148] described halloysite clay nanotubes as a natural mineral, effective stabilizers of oil-in-water emulsions and a potential delivery mechanism of dispersants at the oil-water interface. In the study, they indicated that halloysite nanotubes are absorbed at the oil-water interface and aid in the formation of oil-in-water emulsions that are stable for over a period of three months when surfactants were distributed onto the oil through it without using petroleum-based solvents.

The study further asserts that, in addition to loading surfactants onto the halloysite nanotubes, it can be constructed to contain hydrophobic fluorescent markers to partition into the oil phase to aid identification of spilled oil especially during night operations. The loading of surfactants onto the halloysite nanotubes for delivery increases the oil encounter rate as well as dispersion effectiveness.

In a study to use surfactant-loaded halloysite clay-nanotubes as dispersants for crude oil spill remediation, 99 vol% dispersion effectiveness was recorded by loading the halloysite nanotubes with ternary food grade surface-active agents Tween 80, Span 80 and Lecithin PI [149].

This is a clear indication that there was an almost perfect oil contact when the surfactants were loaded and delivered into the oil by means of the halloysite nanotubes.

According to a study Owoseni et al. 2016 [150] on the release characteristics and interfacial adsorption of magnetically functionalized halloysite nanotubes for a responsive emulsion, halloysite nanotubes supported by super-magnetic iron-oxide nano particles at the oil-water interface causes magnetic responsiveness to emulsions and provides a steric barrier to droplet coalescence, thus hold the formation of stable emulsions over a long period of time.

Surfactants released onto oil spills via this medium have a great potential of forming stable emulsions. The magnetically supported halloysite nanotubes holds-up and stabilizes the oil-water interface and makes it sensitive to released surfactants to reduce interfacial tension at the oil-water interface leading to break down of oil into droplets of sizes less than 20 microns.

However, it can be concluded that using nano vehicles to transport dispersants onto spilled oil in the marine environment increases dispersant-oil contact and thereby shall reduce excessive applications caused by aqueous solubility.

Generally, smart dispersant formulations can be used to control dispersant delivery onto oil spills for enhanced effective dispersion. As stated earlier, Nyankson 2015 reports on usage of a blend of solid water-insoluble paraffin wax particles carrying Dioctyl Sodium Sulfosuccinate Salt (DOSS) as surfactants for dispersion of oil in a study [146]. The DOSS surfactant was only released at the point where the paraffin wax dissolved in the oil. The paraffin wax microparticles tend to stick to the oil-water interface and can promote direct continuous release of surfactants when required [146]. Release of surfactants is well controlled, this minimizes surfactant wastage by increasing its oil contact rate, promotes reduction in interfacial tension for stable emulsion formation and enhances effectiveness of oil dispersion. It was reported that the paraffin wax particles-DOSS composite dispersant recorded high dispersion effectiveness of about 60 vol.% and 62.6 vol.% on heavy Texas crude and light crude oils respectively.

In view of the above studies, more research can be conducted to exploit more smart dispersant media of surfactant delivery to broaden the spectrum of operation.

12. Conclusion

Dispersants are chemical agents most suitable for offshore major spill applications due to its wide variety of applications regardless of the source of the spill. Dispersants as discussed can be applied on the surface of water by using aircrafts which can travel at top speed to far offshore spill locations and by vessel application for small scale spills that are near shore. It can also be applied subsea by means of injection. When subsea injection application is done effectively, the possibility of oil migrating to the water surface is reduced, hence protecting spill teams from the harmful volatile organic carbons in oil.

Dispersants can be used to combat oil spills irrespective of the prevailing climatic conditions at sea because dispersants function better at rough sea in the presence of high mixed energy. In the presence of mixed energy, dispersants break up surface slicks into small droplets and disperses them into the water column for further microbial degradation. This implies that dispersants are basically microbial activity catalysts. The possibility of requiring further treatment on the environment after dispersant application is quite low because microbial organisms, ubiquitous in the marine environment feed on the oil droplets dispersed [9]. Dispersants if administered rightly, is the best emergency response method for large marine spills.

However, dispersants are said to be very effective on light to medium oils but struggles to disperse heavy oils.

Dispersants can also be made from naturally existing surfactants and solvents that are biocompatible, biodegradable, and great emulsifiers. Studies are constantly being conducted into the production of potential environmentally friendly dispersants from these biosurfactants and/or food grade surfactants. However, dispersants made from these natural sources have the potential to be listed on the U.S. EPA National Contingency Plan product schedule to replace the chemically made dispersants and must be highly considered.

To reduce the problem of dispersant over application, employing smart dispersants is the now and future. Dispersants can be applied onto oil spills by means of nano vehicles and other smart surfactant combinations to reduce the aqueous solubility which often leads to over application and wastage of dispersants in the marine environment.

However, it can be concluded that dispersants serve the purpose of emergency response in terms of large-scale spills in the marine environment and usually requires no extra after work on the environment after application.

Declarations

Data availability statement

No data was used for the research described in the article.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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