

A Report of Oil Spill Recovery Technologies

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Abstract

Consequences of oil spill disasters from waterway accidents, the oilrig, and the acts of wanton vandalism usually affected so seriously the environment, marine creatures, plants, life of other animals, and human in a long time. The ever-developing and advanced technologies should be used to meet treat and recover fast, efficiently oil spills and oil slicks. The overviews of as-using technologies such as physical, chemical, in-situ burning and bioremediation method were presented in this work. A large efficiency of oil recovery from physical method was shown although it was only suitable for application before oil emulsified. Meanwhile, chemical method might be concordant with all oil types but the chemical residual caused perniciously to marine environment. The relationship between safety distance and square of burnt oil area was investigated and established for thermal/in-situ burning method that was denoted as a restricted and inefficient one for oil slick treatment. Among introduced methods, the bioremediation was considered the most efficient and safest. The variation, transformation process of oil; the interaction between oil and seawater under the nature conditions such as the wave, wind, sunshine; the efficiency of oil spill recovery and treatment technologies were considered and analyzed comparatively. Finally, a key summarization for each technology was presented by showing their applicability and influence in specific situation.

Keywords: Oil spill, oil slick, recovery technology, treatment efficiency, oil pollution

INTRODUCTION

Physical smothering in a long time and toxic components due to oil spill disasters not only affected very seriously marine creatures, plants and life of other animals, but also polluted the air environment and reduced the health of human. Among the toxic substances discharged into the environment, it was certain to mention the environmental pollution caused by the oil spill and the appearing oil on the water surface [1]. Marine oil pollution might be from ships or vessels accidents, the operation of the ships and vessels, the shipwreck, and the incidents at the oil exploration well, the oil rig, the illegal bilge discharges of water [2, 3]. From 1970 - 2010, there were about 5.71 million tons of spilled oil due to tanker incidents [4]. Physical and chemical properties of oil spill and oil slick affected significantly marine life, natural structure of ocean or water source, tourism and entertainment activities [5,6]. The formation of slick oil after spilling oil depended on many different factor such as weather, speed of spreading on the

water surface, drifting in the sea water, evaporation into the air, biodegradation and emulsions between water and oil that effect dramatically on the change of viscosity, density, the force of interfacial tension [7, 8]. Furthermore, some contents of oxygenated oil spill and oil slick such as aromatic contents, acids, alcohols caused the pollution of water in long time [9]. Several developing techniques were use to recovery the oil spill such as mechanical recovery or burning, especially using bioremediation, solidifiers or dispersants was considered as useful methods [10]. Any selected methods were based on the oil spill type and quantity, the conditions of weather and environment [11]. The variation, transformation, alteration process of oil after spilled into the sea and interacted to the seawater under the nature conditions was shown in Figure 1.

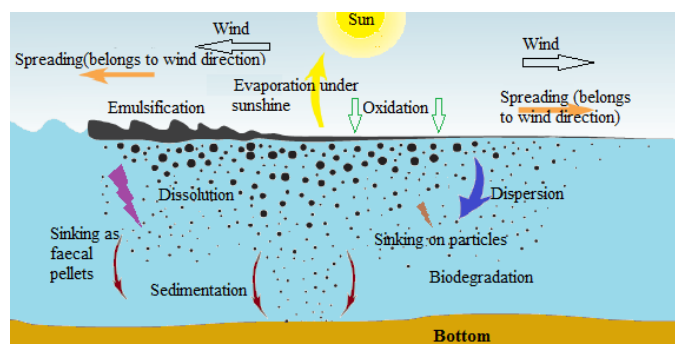


Figure 1. The variation, transformation, alteration process of oil after spilled into the sea

Oil spill and oil slick in marine environment were classified in three classes as following:

The first class, small oil spill and oil slick were related to berthing, ships or vessels operation in port, and discharges of oil-water-mixtures from machinery spaces.

The second class, oil spill and oil slick were associated with shipping incidents such as collisions, fires or other damage. The oil spills related to damage of oil tanker, offshore structures tend to occur on large area and result in damaging the ocean environmental.

The third class, oil spill and oil-slick were considered as the "unacceptable actions" or "degenerationers" who dump sneakily the waste oil into the marine environment aiming at saving their money. These intentional dumping actions of oil into marine environment were ultra criminal ones and different from maritime accidents.

In the world, the statistics showed that from 1900 to now, there were two to four large oil spills in the world each year

[12]. The most notable incidents included: The Amoco Cadiz spilled 231.000 tons of crude oil into Brittany Bay, Northwestern France, in 1978; In 1989, the Exxon Valdez ship spilled 40.000 tons of oil into Alaska (USA) offshore; In 2002, the Prestige ship spilled 77.000 tons of oil into the North-Western Spain offshore; In 2007, the Hebei Spirit ship spilled 2.7 million gallons of oil into the South West Sea of Korea [13]. Most of the oil spills have been catastrophic, with serious ecological, economical, and social losses [14]. Thus, finding a solution to absorb oil spill and slick on the water surface was an urgent issue to protect the marine environment [15].

This work presented the overview results of remediation techniques such as physic, chemical, thermal or in-situ burning and bioremediation methods for recovering and treating oil spill and slick. Based on comparative analysis, some solutions of technical oil remediation depending on the level of oil spill, the conditions of wave or wind, available equipment, physicochemical properties of oil were suggested.

PROPERTIES OF OIL SPILL AND OIL SLICK

A. Physical characteristics

The oil physical properties such as surface tension, density, pour point, solubility in water and viscosity dramatically effected on the spreading speed of oil or oil slick [16]. Density of most oils, that was an important factor in order to predict, determine the behavior in water, was lower and smaller than that of water so the oils floated and lied flat on water surface and tented to spread, expand horizontally [17]. Lower density of oils resulted in increasing the evaporation of lighter materials and substances and they have left the heavier materials, which sank in water column, interacted with water or others in seawater to form the dangerous sedimentation on seawater body [18]. Oil viscosity was also an index of evaluating the rate of oil spreading. The information about the chocolate mousse was formed due to higher viscous oil and leads to the difficulty in degradation or treatment [10]. Furthermore, the increase in temperature resulted in reducing oil density and viscosity and increasing the horizontal spreading ability. Oil pour point was considered as a function of temperature, the oil spill becoming a semi-solid at temperature higher than that of freeze point caused the cleanup strategy difficultly and complicatedly [19]. Solubility of oil in water related to form the pollutant and bioremediation was low and depends on temperature and chemical structure of hydrocarbon, solubility of oil in water was about 28-31 mg/l [20]. On the other hand, oil surface tension was inversely proportional to temperature, hence oil spread more easily in warmer waters, this index effected directly, quickly on the ability of spreading even in case of disappearing the wind or water currents.

B. Chemical characteristics

The hydrocarbons with 50 to 98% of oil total components dominated complex chemical properties of oil. Furthermore, oil also included non- hydrocarbon compounds such as

oxygen, nitrogen, sulphur, and trace metals [21]. Hydrocarbons listed in oil components and classified following nomenclature by The International Union of Pure and Applied Chemistry (IUPAC) were given in Table 1.

Table 1. Primary classes of hydrocarbons

Primary class	Compounds
Straigh chain alkanes, n-alkanes	Propane [C ₃ H ₈] n-Hexane [CH ₃ (CH ₂) ₄ CH ₃] n-Dodecane [CH ₃ (CH ₂) ₁₀ CH ₃]
Straigh chain alkenes, n-alkenes	Cis-but-2-ene [CH ₃ CH=CHCH ₃] Pent-1-ene [CH ₂ =CH(CH ₂) ₂ CH ₃] Trans-hept-2-ene [CH ₃ CH=CH(CH ₂) ₃ CH ₃]
Cycloalkanes, a ring with single bond	Cyclohexane [C ₆ H ₁₂] n-Propyl-cyclopentane [CH ₃ CH ₂ CH ₂ C ₅ H ₉] Ethyl-cyclohexane [CH ₃ CH ₂ C ₆ H ₁₁]
Cycloalkenes, a ring with double bonds	Cyclopentene [C ₅ H ₈] 3-Methyl-cyclopentene [CH ₃ C ₅ H ₇]
Branched chain alkanes	2-Methyl-propane [CH ₃ CH(CH ₃)CH ₃] 2,2-Dimethyl-butane [CH ₃ CH(C-H ₃) ₂ CH ₃ CH ₃] 2,2-Dimethyl-propane [CH ₃ CH(CH ₃) ₂ CH ₃] 2-Ethyl-hexane [CH ₃ CH(C ₂ H ₅)(CH ₂) ₃ CH ₃]
Branched chain alkenes	2-Methyl-but-1-ene [CH ₂ =C(CH ₃)CH ₂ CH ₃] 4,4-Dimethyl-cis-pent-2-ene [CH ₃ CH=C-HC(CH ₃) ₂ CH ₃]
(Alkyl) benzenes	Benzene [C ₆ H ₆] Methyl benzene [CH ₃ C ₆ H ₅] Ethyl benzene [C ₂ H ₅ C ₆ H ₅] (o-Xylene) o-Methyl-toluen [CH ₃ C ₆ H ₄ (o-CH ₃)] (m-Xylene) m-Methyl-toluen [CH ₃ C ₆ H ₄ (m-CH ₃)] (p-Xylene) p-Methyl-toluen [CH ₃ C ₆ H ₄ (p-CH ₃)] 1,2-Dimethyl-3-ethyl-benzen [(1-CH ₃)(2-CH ₃)C ₆ H ₃ (3-C ₂ H ₅)] 1,2,3-Trimethyl-benzen [(1-CH ₃)(2-CH ₃)C ₆ H ₃ (3-CH ₃)] n-Propyl-benzene [CH ₃ CH ₂ CH ₂ C ₆ H ₅]
Other aromatic hydrocarbons	Phenol [C ₆ H ₅ OH] Crezol [RC ₆ H ₄ OH], R is anky Hexachloro-cyclohexane [C ₆ H ₆ Cl ₆]
Polycyclic aromatic hydrocarbons	Acenaphthene with 2 rings of benzene and a ring of cycloalkane [C ₁₂ H ₁₀] Naphthalene with 2 rings of benzene [C ₁₀ H ₈] Athracene with 2 rings of benzene, a ring of cycloalkane and a ring of cycloalkene [C ₁₄ H ₁₀] Chrysene with 3 rings of benzene, a ring of cycloalkadiene [C ₁₈ H ₁₂] Coronene with 4 rings of benzene, a ring of cycloalkene and 2 ring of cycloalkadiene [C ₂₄ H ₁₂] Pyrene with 3 rings of benzene, a ring of cycloalkene [C ₁₆ H ₁₀]
Straigh chain alkanes, n-alkanes, -C-C-C-C-	Propane [C ₃ H ₈] n-Hexane [CH ₃ (CH ₂) ₄ CH ₃] n-Dodecane [CH ₃ (CH ₂) ₁₀ CH ₃]

Straigh chain alkenes, n-ankenenes	Cis-but-2-ene [$\text{CH}_3\text{CH}=\text{CHCH}_3$] Pent-1-ene [$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}_3$] Trans-hept-2-ene [$\text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3$]
Cycloalkanes, a ring with single bond	Cyclohexane [C_6H_{12}] n-Propyl-cyclopentane [$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}_5\text{H}_9$] Ethyl-cyclohexane [$\text{CH}_3\text{CH}_2\text{C}_6\text{H}_{11}$]

Oils might be divided into saturated and unsaturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes, refined products [22]. Saturated hydrocarbons were also considered as alkanes with the simplest hydrocarbon form and only consist of carbon and saturated hydrogen atoms. Alkanes were little chemical reactive, flammable, contain from 1-40 carbons atoms in carbon chains and were no-polar compounds, thus they were difficult to solute in sea water [23]. Aromatic hydrocarbons were compounds with at least one aromatic ring, in which six carbons were contained in a carbon-hydrogen ring. Aromatic hydrocarbons included monopolycyclic, and two or more polycyclic aromatic rings. Aromatic hydrocarbons were serious pollutant because they were considered as potential carcinogens. The aromatic hydrocarbons degradation went on most sharply under aerobic conditions [24]. Average crude oil contained about 30% of alkanes; 50% of cycloalkanes, alkenes, alkynes or dialkenes; 15% of aromatics; 5% of nitrogen, sulphur and oxygen and others. Resins and asphaltenes with complex structure were considered as insusceptible biodegradation were difficult to analyze [24]. Refined oil products included unsaturated hydrocarbons that were formed and created out by the process of catalytic cracking depended on the type of crude oils and the treatment method.

OIL SPILL AND OIL SLICK RECOVERY METHODS

Oil spill and slick cleanup was one of the matters with the most debatable due to impossible cleanup all the discharged and dumped oil into the seawater [25]. Recent recovery methods were: physical techniques, chemical techniques, thermal (or in-situ burning) techniques and biological techniques (or bioremediation).

A. Physical methods

Physical methods were mainly used as the barriers to control and prevent the oil spill and oil slick from spreading but oil physical and chemical characteristics were not changing. Many barriers were used such as booms, skimmers, adsorbent materials aiming at controlling oil spills and oil slicks [26, 27].

Booms: Boom was a normal type of equipment used to prevent oil spill and slick from spreading [28]. However, the effective operation of booms not only depended on the boom design, but also was strongly affected by the characteristics of the currents, wind direction, velocity, and wave height. In case of current velocity over 0.4 m/s, wind velocity over 5.5 m/s or the height of waves over about 1m will carried spilled oil and oil slick underneath the barrier [26]. Based on taking barrier for oil movement, the oil spills and slick could be recovered through skimmers or other techniques. Figure 2 and Figure 3 showed three types of booms such as fence boom, curtain boom, and resistant boom of fire [29, 30].



Figure 2. Boom types

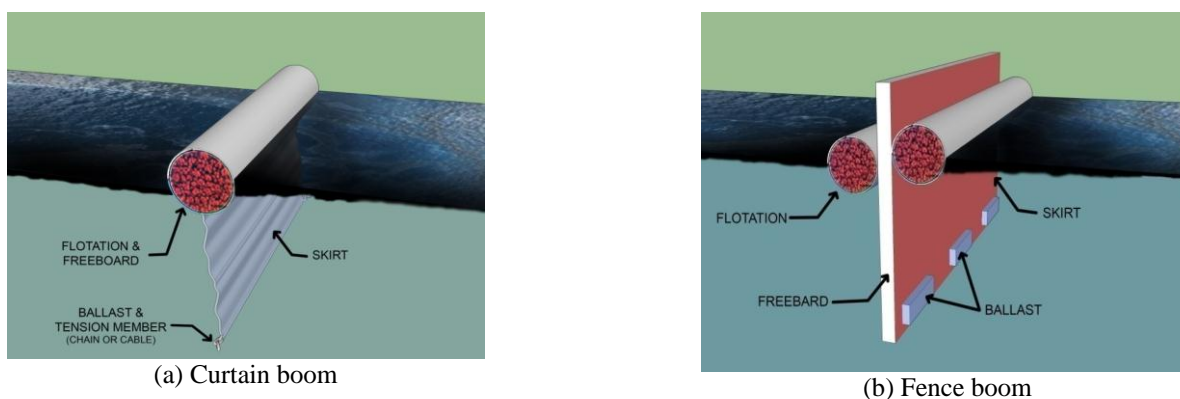


Figure 3. Boom types

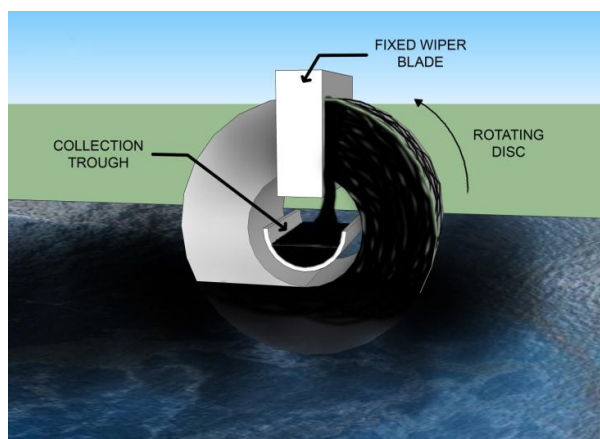
Fence booms were floating structures that were made of rigid or semi-rigid materials. They were used to prevent floating oil vertically with normally 60% of fence boom under the water [31]. Boom sections with 15 meters of length and 300, 600 or 800 millimetres of height were usually used. Multiple booms were connected together through special connectors [29]. The advantages of fence booms were included: lightweight, minimal space for storage, resistible corrosion, and easy treatment, highly reliable on quiet waters [32]. Besides, low stability in case of strong winds and currents, low flexibility were their main disadvantages.

Curtain booms with large circular and filled chamber of foam aiming at remaining on the water surface although a flexible skirt under the water were the floating structures without being pervious and absorbing. Curtain booms were usually made of polyurethane, polystyrene, bubble wrap [31]. The diameter of curtain booms chambers were from 100 to 500 meters and from 150 to 800 meters of the skirt length. Although curtain booms were reliable, high flexibility, and realize better than fence booms but the difficulty in cleanup and storage of curtain booms was higher than that of fence booms [33].

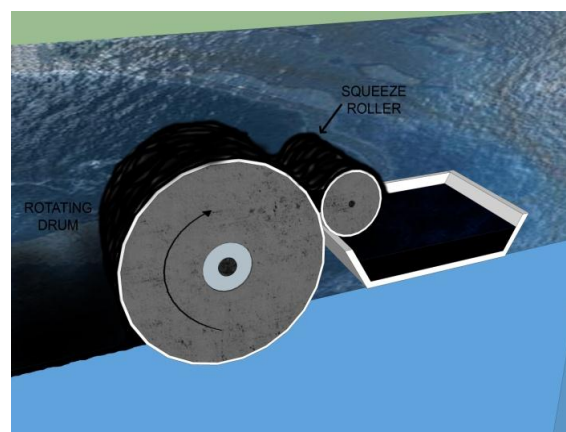
Resistant booms of fire were fabricated from the fireproof materials. This equipment could collect and concentrate oil

spill and slick to the most suitable temperature and burn enough at that temperature and used coherently with burning [34]. Practically, about 1.500 m² of burn area was corresponding to 200 meters of fire boom in length [35]. Resistant boom of fire were reliable, great potential in preventing the bad impact from an oil fire due to oil spills or oil slick on seawater surface. However, high cost and difficulty in towing due to high weight and size were the disadvantages of fire-resistant booms.

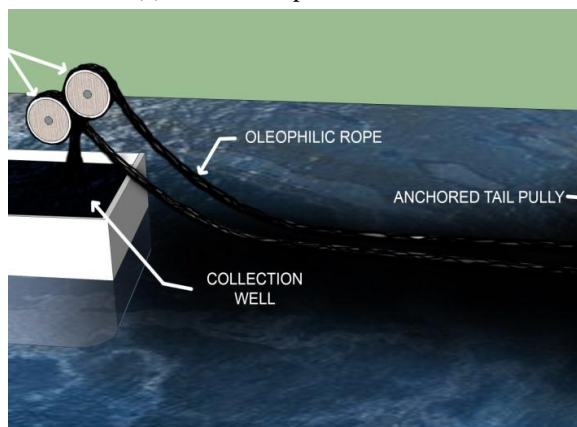
Skimmers: After using booms to limit the effective area of spilled oil, skimmer equipments were used with booms in order to recover oil spill and slick from the surface of seawater but changing oil properties were maintained hence recovered oil spills can be reused [36]. The characterized disadvantages of skimmers were depending on the factors of weather condition and the thickness of floating oil [37, 38]. Moreover, the current, wave and wind characteristics were the same as for booms. However, self-propelled, towed from the shore, and operated by vessels were the advantages of skimmers in comparison with booms. Skimmers shown in Figure 4 to Figure 9 might be classified as oleophilic skimmers, weir skimmers, elevating skimmers, submersion skimmers, suction/vacuum skimmers and vortex/centrifugal skimmers [35, 39]. The spilled oil recovery capacity of skimmers was given in Table 2.



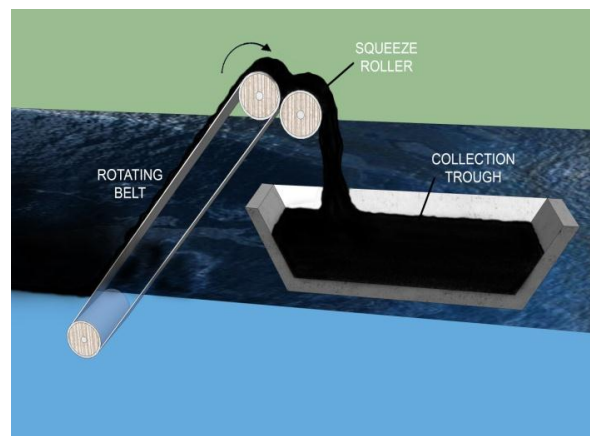
(a) Disc - Oleophilic skimmer



(b) Drum - oleophilic skimmer



(c) Rope - oleophilic skimmer



(d) Belt - oleophilic skimmer

Figure 4. Oleophilic skimmers

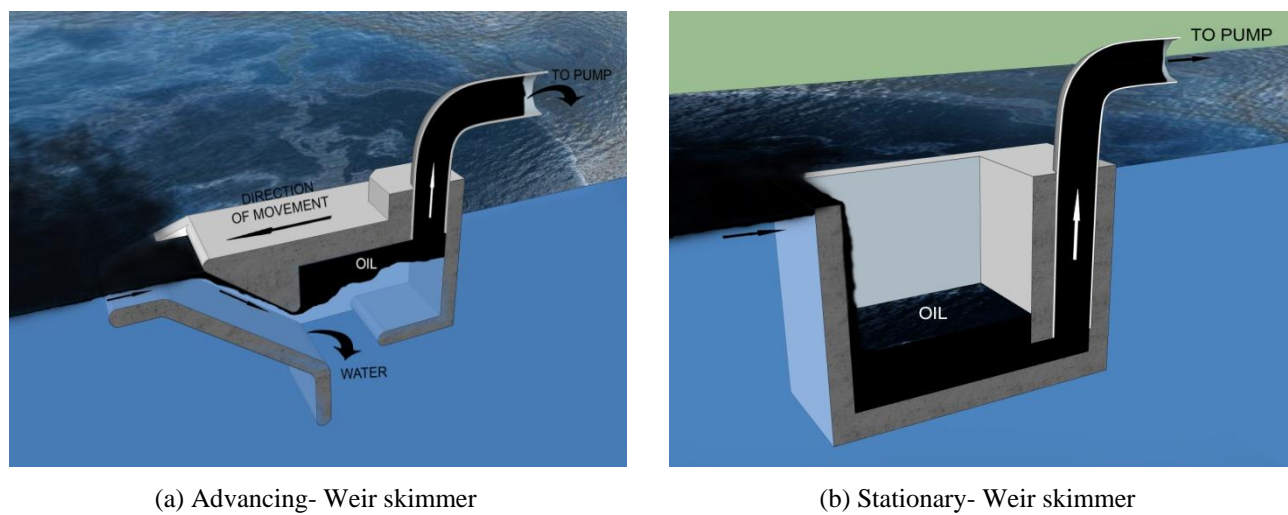


Figure 5. Weir skimmers

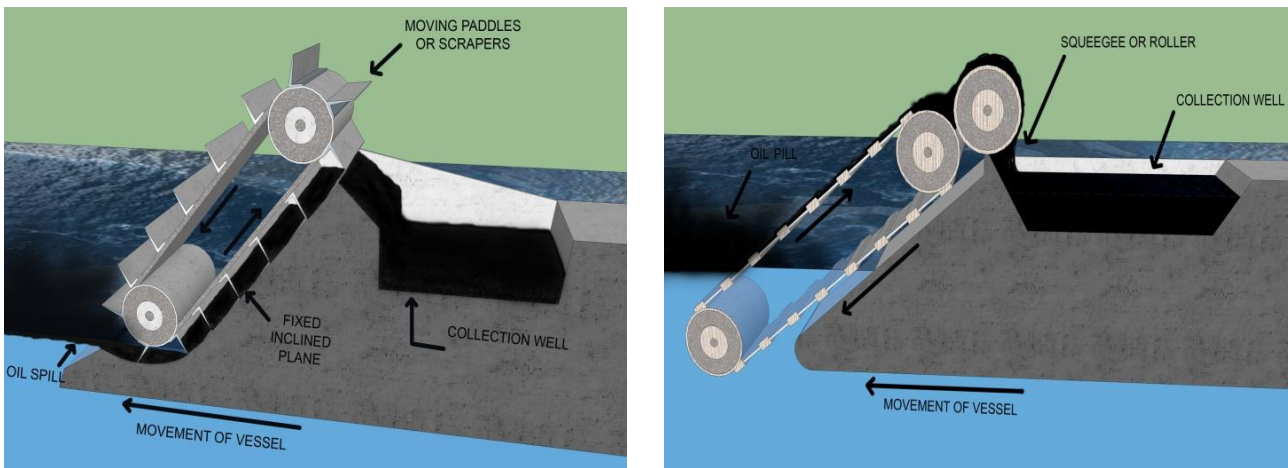


Figure 6. Elevating skimmers

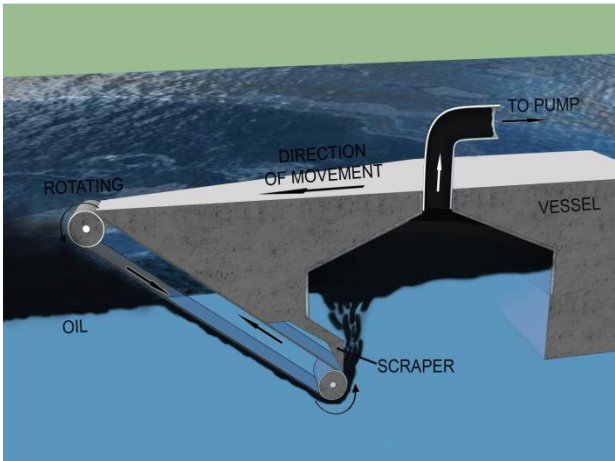


Figure 7. Submersion skimmers

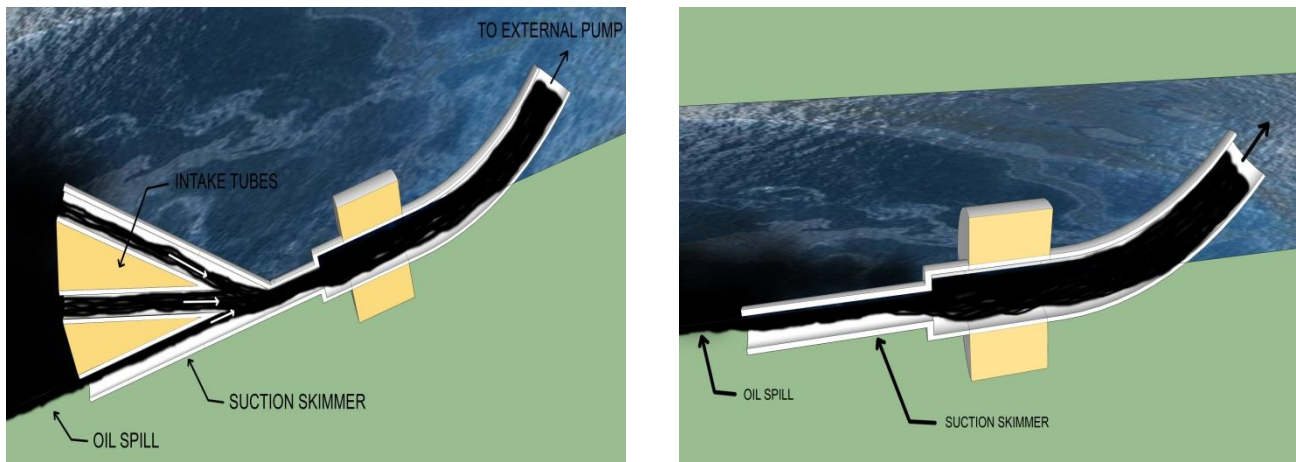
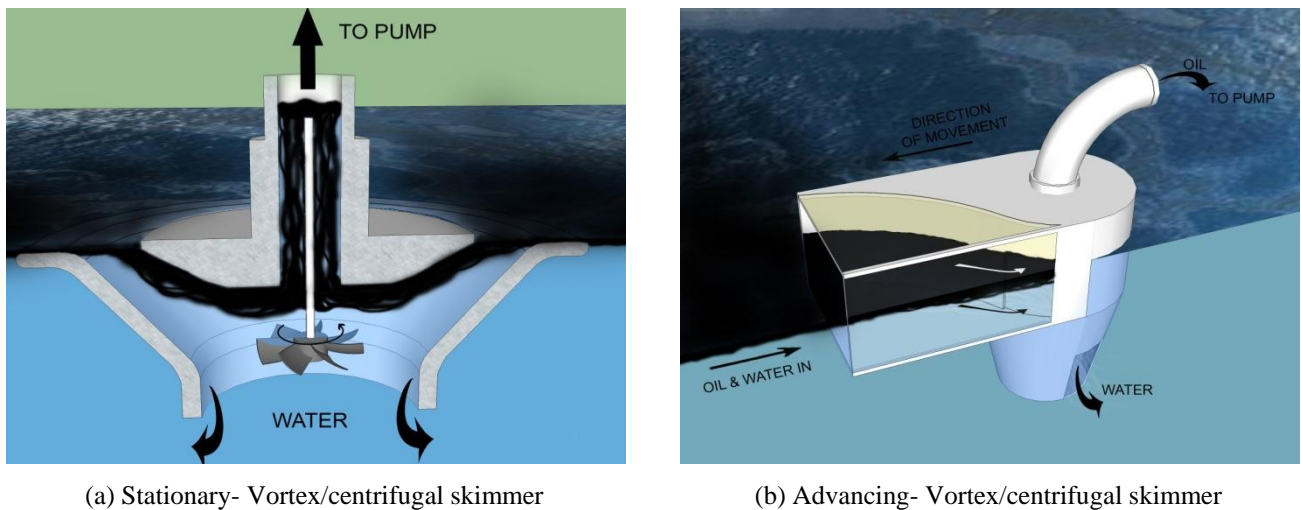


Figure 8. Suction/ vacuum skimmers



(a) Stationary- Vortex/centrifugal skimmer

(b) Advancing- Vortex/centrifugal skimmer

Figure 9. Vortex/centrifugal skimmer

Table 2. Classification, oil recovery potential of skimmers

Skimmer types	Operational principle	Range of oil recovery rate (m ³ /h)*	Percent of oil recovery (%)
Oleophilic	A surface was used to oil spill or slick adhere in order to remove the oil from the surface of water	0.2 - 50	75-95
Weir	A skimmer groups based on the gravity aiming at draining the oil on the water surface into a submerged tank	0.2-100	20-90
Elevating	Conveyors was used to lift oil spill on the water surface to the recovery area	1-20	10-40
Submersion	A belt combined with inclined plane to force the oil under the surface and push oil into a tank	0.5-80	70-95
Suction/ vacuum	The principle of changing pressure was use to create the vacuum or pressure difference in order to remove oil spill or slick from the water surface	0.3-40	3-90
Vortex/centrifugal	Based on the oil density was smaller than that of water, hence water was separated from mixture by vortex force, then most of oil was removed.	0.2-10	2-20

*Depends on oil type such as diesel oil, light or heavy crude oil, bunker and other conditions

Adsorbent materials: Adsorbent materials were considered as the interest for recovering oil spills at final cleanup step after using skimmers with a high capacity of adsorbing the oil and repelling water [5]. The purpose of using adsorbent materials was to convert the liquid into semisolid in order to remove oil spill and oil slick [40]. There were 3 types of adsorbent materials such as natural organic products (materials) and inorganic sorbent materials, synthetic materials [37, 41]. The sorbent material was given into the oil slick aiming at adsorbing and collecting oil [42]. Depending on the kind of sorbent, the sorbent was usually wringed in order to remove

oil and reused or disposed safely. The efficient usage of sorbent materials was evaluated by the factors such as recyclability, sorption capacity, sorption rate because they conclude the required time for spreading and harvesting the sorbents [16]. For all sorbents, the spreading on/over the oil spill before increasing of oil viscosity to the impossible sorbent point was an ultra important requirement [43]. Using sorbents were recorded as the most effective materials and cheapest solution of oil spills and slick cleanup [44-46]. Classification and oil absorption capacity of adsorbent materials was given in Table 3.

Table 3. Classification, oil absorption capacity of adsorbent materials

Adsorbent materials	Classification	Characteristics	Range of oil recovery rate (g/g)*	Percent of oil recovery (%)
Inorganic sorbent materials	<ul style="list-style-type: none"> - Treated chalk - Treated silicone - Pulverized fly ash - Zeolite - Graphite - Activated carbon - Clay - Treated perlite - Treated vermiculite - Vermiculite - Silica, Silica gel 	<ul style="list-style-type: none"> - Sea bed contamination - Harmful impact on aquatic habitats - Retention capacity is low - Expensive - Some of them are friendly 	<ul style="list-style-type: none"> - From 2-9 - Functionalized silica aere gel with 237 g/g - Expanded graphite with 86 g/g 	≈70
Natural organic sorbent materials	<ul style="list-style-type: none"> - Bark or wood fiber - Bird feathers - Collagen sponge - Peat moss - Treated peat moss - Silk-floss fiber - Kapok - Silkworm cocoon - Acetylated rice straw - Rice husk - Acetylated sugarcane bagasse - Cellulose, Cellulose fiber - Raw cotton 	<ul style="list-style-type: none"> - High cost with agricultural sorbents because of high cost in store and transportation - Lower sorption capacity - Limited recyclability - Retrieval by hand labor is time consuming - Effective use in small areas or residual spill cleanup after using in-situ burning 	From 1 – 40, some of them with oil absorbent are higher such as silk-floss fiber, cotton lint	≥75
Synthetic organic materials	<ul style="list-style-type: none"> - Polyester foams - Polyethylene foams - Polyolefin foams - Polypropylene foams - Polyurethane foams 	<ul style="list-style-type: none"> - Nonbiodegradability - Ability of recovering, cleaning, reusing. - High sorption capacity. - Expensive and not friendly 	7-45	≥ 90

Physical methods were able to recover most kinds of oil, inflammable, effective as final cleanup, simple. However, they were expensive, complex, not able to use without being assisted by technological devices, necessary to treat collected oil, used before emulsified, depending on the weather conditions, especially they were difficult to biodegrade with the synthetic sorbents.

B. Chemical methods

These methods treated oil spills due to the capabilities of changing the oil spill physical and chemical properties were used in combination with physical methods. The chemical methods used the main chemicals to control oil spills such as dispersants and solidifiers.

Dispersants: Dispersants might be used in larger areas and consist of different surfactants. A part of surfactants solutes in both of oil and water because the interfacial surface tension between the oil and water was reduced as sprayed surfactants on the surface of oil spill [47]. This promoted the dispersion and increased biodegradation of oil in water. The study of [7] showed the results about the sprayed dispersant on oil slick as a 15m³ of oil slick treated by helicopter, and oil slick disappeared after 10 minutes of spraying in comparison with 0.5-1h of treated oil slick by boat [37, 48]. However, some studies showed the impacts of dispersants to the ecological. Dispersants might be using restrictedly under the deep water because of fast dilution in the water body and form the toxic that affected the ecological at the seabed [49]. Nowadays, the available dispersants were being used widely such as Slickgone NS with 1/25 of dispersant/oil, Corexit 9500 with 1/10-1/50 of dispersant/oil, Corexit 9527 with 1/20-1/30 of dispersant/oil, Corexit 9550 with 1/20 of dispersant/oil, Tergo R-40 with 1/20 of dispersant/oil, Ardrex 6120 with 1/25 of dispersant/oil, Shell VDC with 1/20-1/30 of dispersant/oil [50] [51, 52]. The application ratio in treating and controlling depended on the level of medium and heavy oil, light oil [53]. The method of treating oil spill and oil slick by using dispersants in combination to helicopter was shown in Figure 10.

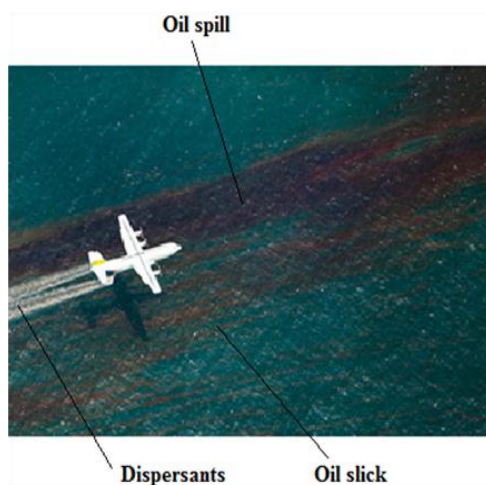


Figure 10. Sprayed dispersant on oil slick by Helicopter

Besides the advantages of dispersants such as: cleanup 90% of spilled oil, ability of operation on rough seas, rapid treatment, slowing down the oil-water emulsion formation, acceleration of natural biodegradation rate [54]. Their disadvantages were containing toxic compounds, ineffective in calm seawater, difficult operation in thinner oil slicks because of easy losses, and expensive.

Solidifiers: Solidifiers were considered as dry granular materials, which functioned as reacting with oil compounds aiming at changing liquid oil into solid state and they were able to be removed easily [55]. Solidifiers were used and contained in booms, pillows, pads in order to convert oil spill into solid or semi-solid materials [56] and shown in Figure 11.

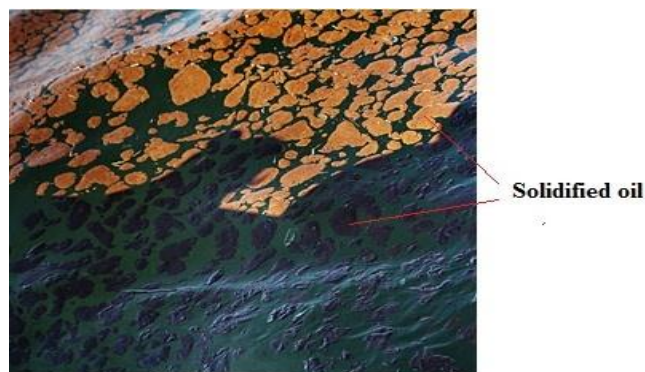


Figure 11. Oil is solidified after being treated by solidifiers

The advantages of solidifiers were usable on rough seas although the solidifier efficiency relies on the oil spill and slick type and composition. In the past, solidifiers have not been used because of lower efficiency in comparison with dispersants [57]. Some solidifiers such as Spill Green LS with 43, Petro Lock with 44, SmartBond HO with 45, Oil Bond100 with 33, Molten wax with 109, Powdered wax with 278 of percent to solidify were usually used [58-60].

Chemical methods were considered using quickly in all of weather conditions with high efficiency on many kinds of oil. Besides, chemical methods did not need much manpower and were cheaper than those of physical methods. However, their big disadvantages such as no any oil recovered, recovery of oil with high viscosity not effectively were shown. The natural break-up of oil was promoted by dispersants but they were not suitable for oil spill with high viscosity or stable emulsions, and oil slick.

C. Thermal or in-situ burning methods

Thermal or in-situ burning method was a simple and quick one that relates to oil spill or thick oil slick that was burnt on the surface of water and was shown in Figure 12.



Figure 12. Oil burning and emission components

This method was used to reduce the risks and the impacts of the oil slick and oil spill on the in-water ecosystem and the sea environment [61]. A 100-300 tons of oil spill and slick could be removed per hour by thermal or in-situ burning method [62]. Since 1960s, this method has been widely used aiming at removing the oil spill, oil slick in/on ice, water, snow resulted by the accidents from broken pipeline, punctured/ broken storage tank or ship accidents in the USA, Canada, Europe [63]. To overcome oil spill using this method, a Heliport equipment was used for ignition, a type of flamethrower hanged under the helicopter; or an oiled rag with diesel fuel thrown from the helicopter. Generally, this method might be used in many large oil spills although it has to be subject to the ratification of government [64]. Several oil spill and slick such as in northern Canada in 1958; Spitsbergen, Norway in

1988, Exxon Valdez in 1989; Newfoundland, Canada in 1993 was successful in using this method to control the oil spill and slick [65]. However, thermal or in-situ burning method was only effective as: the oil slick on the water was wide enough to burn a oil volume at the same time; the thickness of oil slick was also enough to maintain the combustion; the seawater condition was calm; and the place of oil slick was far from sensitive zones, facilities, equipments [61, 66].

An in-situ burning promoted its advantage in oil spill cleanup while used in ice, cold water conditions or snow because of maintenance ability of conditions favouring combustion for a long time [67]. Although this method was an effective one to recovery the oil spill, however the main constraints of this method were the ability of occurring secondary fires, the impact on the human health, the impact of burnt by-product on the environment [35, 68]. Safe distances based on PM 2.5 concentrations considered as the most dangerous, harmful emission to human health were determined as equation:

$$y = 0.75x \quad (1)$$

where: y was safety distance (m); x was square or burning oil area (m²)

The main chemical components of burnt by-product formed from this method, the CO_x, SO_x, NO_x, PM, VOCs, PAH emission quantity in the in-situ burning [69, 70]. The impacts and the safety distance of in-situ burning method in spilled oil treatment were given in Table 4.

Table 4. Emission components from an in-situ burning of oil spill treatment

Emission components	Emission quantity (g.kg ⁻¹) (g emission in comparison with kg burned oil)	USA Standard (g.kg ⁻¹) (g emission in comparison with kg burned oil)	Characteristics	Minimum safety distance
CO ₂	3.000	-	An increased concentrations around an in-situ burning with normal atmospheric levels are about 300 g.kg ⁻¹ in comparison with 500 g.kg ⁻¹ of near in-situ burning.	Wind velocity from 2 to 5 m/s was not considered.
CO	20 - 50	35 over 1 hour, 9 after 8 hours	Low detection levels and not harmful to humans	
SO _x	3	14 after 24 hours, 3 annual average	Low concentrations and a part reacted with water to convert into sulfuric acid.	
NO _x	5	0.05 annual average	Low concentrations and not harmful to humans	
PM	50 - 200	0.5	Most of health professionals consider PM as the main combustion product affecting to human health.	
VOCs	5	-	The VOCs concentrations in in-situ burning are lower than that of oil slick	
PAH	0.04	-	Polyaromatic hydrocarbons (PAHs) appear under the fire with low concentrations	

Thermal or in-situ burning methods used quickly but with high efficiency if supported by specialized devices, cheap were shown, but it was only suitable for the area of open water, snow or ice. However, these methods showed many disadvantages such as no any oil recovered, emission of many polluting components to air and marine environment, threat for marine creatures, human life, other resources.

D. Bioremediation

Biodegradation was a natural process that microorganisms like bacteria, yeasts, and fungi degrade, breakup and metabolize the complex compounds and the chemical substances into their food in order to restore and overcome the environmental quality [64, 71]. Main microorganisms for degrading the oil spill and slick were given in Table 5.

Table 5. Main microorganisms of oil degradation

Microorganisms		Description	Ability to degrade compounds
Bacteria	Arthrobacter spp	Arthrobacter grown on mineral salts is commonly found in soil with Gram-positive and exponential growth. Notable characteristics are able to use pyridine as its only carbon source.	Phenanthrene (C ₁₄ H ₁₀) Methyl-tert-butyl ether, or 2-Methoxy-2-methylpropane ((CH ₃) ₃ COCH ₃) Ethyl-tert-butyl ether (C ₂ H ₅ OC(CH ₃) ₃) Tert-amyl methyl ether (C ₂ H ₅ C(CH ₃) ₃ OCH ₃)
	Brevibacterium	Brevibacteria is short life, asporogenous, aerobic, gram-positive with optimum growth from 30 to 37°C.	Asphaltenes, Petroleum oil
	Dietzia	Dietzia is considered as promoting the activities of HC-degrading aiming at increasing the hydrogenase and catalase for degrading and speeding up the oil biodegradation process.	n-Alkanes with number carbon from 12 to 38 and branched alkanes
	Flavobacterium	Flavobacterium is a Gram-negative, used engine-oil as a carbon source, isolate capable up to 80 and 90% of oil with 30–37°C of optimal temperature.	Chlorophenols (HOC ₆ H _{5-x} Cl _x ; 1≤x≤5) include from Monochlorophenol to Pentachlorophenol
	Mycobacterium	The Mycobacterium is degrading hydrocarbon with the highest rate of C12 and C13	Polycyclic hydrocarbon Pyrene (C ₁₆ H ₁₀) Phenanthrene (C ₁₄ H ₁₀) Diesel oil
	Pseudomonas spp	Pseudomonas show high potential for degrading hydrocarbon because of the metabolic diversity, the abundant microorganisms, the chemical remediation resistance.	4-chlorobenzoate (C ₇ H ₄ ClO ₂)
	Rhodococcus	Rhodococcus are potential producer, high emulsifying index of diesel-water, suitable for light oil	Polychlorinated-biphenyl (C ₁₂ H _{10-x} Cl _x ; 1≤x≤10) Hexadecane (C ₁₆ H ₃₄) Trichloroethane (CH ₃ CCl ₃) Polycyclic hydrocarbon contain only C, H with many aromatic rings
Fungi	Aspergillus	Aspergillus show the highest biodegradation extent with 98% of degradation efficiency for aromatic hydrocarbon	Pyrene (C ₁₆ H ₁₀) Benzo(a)pyrene (C ₂₀ H ₁₂)
	Candida	Candida shows a high potential in biodegradation of oil spill and some hydrocarbons.	Toluene (C ₇ H ₈)
	Fusarium	Fusarium has ability in degradation hydrocarbons up to C31 with high efficiency.	Methyl tert-butyl ether (CH ₃) ₃ COCH ₃) Tert-butyl alcohol (C ₄ H ₁₀ O)
	Phanerochaete	Phanerochaete has the ability in catabolizing oil spill to carbon dioxide.	Benzo(a)pyrene (C ₂₀ H ₁₂) Phenanthrene (C ₁₄ H ₁₀) Fluorene (C ₁₃ H ₁₀)

The biodegradation application in recovering and cleaning-up oil spill related to give native or non-native microorganisms aiming at speeding up the natural biodegradation process and therefore they helped to protect the affected areas by oil spill risks and prevent environment from being damaged further [72, 73]. Many enzymatic microorganisms showed the ability of degrading hydrocarbons in petroleum, crude oil or diesel fuel [74]. Alkanes, aromatic contents, and other hydrocarbons might be degraded by some of enzymatic microorganisms [75]. Alkanes from 10 to 26 of the carbon number were degraded the fastest, besides aromatic contents like benzene, toluene or xylene with low-molecular-weight were also biodegraded very fast by [76]. However, complex or complicated structures were difficult to degrade because fewer small organisms could biodegrade those structures. The higher the hydrocarbon structure complexity was, the slower the biodegradation rates were [26]. The oil spill biodegradation was affected by many factors such as nutrient bioavailability, the oil concentration, temperature [77]. Nutrients such as nitrogen, dissolved oxygen and phosphorus were necessary for the metabolic activity of microorganisms in marine environment [78]. Hence, it needed about 2-4 weeks for biodegradation process if the concentration of oil spill was high [79]. The biodegradation needed at least a week in order to microorganisms acclimate to the marine environment, and to complete the whole process of bioremediation, it might take several months, even years [73].

Biodegradation method was suitable for all of weather conditions, efficiency with cheap cost, and the product after biodegrading only including CO₂, H₂O. Although this method was also no any oil recovered but the residues were continuously biodegraded by multi- microorganisms.

The summarized methods for recovering and treating the oil spill from accident, disasters were proposed. Each method also included advantages and disadvantages. Hence, it was necessary to carry out the criteria to evaluate aiming at choosing the most suitable oil spill recovery methods [75] [80]. The criteria should be reliability, efficiency, recovery and treatment time, charge, marine life effect, difficulty level, ability of oil recovery, level of depending on weather conditions, level of effect on oil characteristics of oil, level of further treatment after recovering.

CONCLUSIONS

Some technical results of oil spill, oil slick recovery and remediation was concluded as based on this study following:

Physical methods were used as the first ones to recover the huge oil spill as oil spill incidents was found early with not large area. Booms should be used to zone and self-contain the oil spill area. After that, oleophilic, weir or submersion skimmers were considered as the main first equipment for thick oil layer with large range of oil recovery rate. The rest skimmers were useful with thin oil layer such as oil slick. As reported and experience, the recovered oil spill was up to 80 m³/h while used skimmers in Figures 4a, 4b, 4d, 5a and 7 in good weather conditions.

Chemical methods only were considered in small area such as bay without tourism or aquaculture because of unrecovered oil after treatment by chemicals. Moreover, the residual chemicals as after spraying into oil spill or oil slick were still exist with long time in the seawater and difficult decomposition. Thus, they affected the marine creatures and ecology system. The experience showed that, it should not use chemical methods for treating high viscosity or with stable emulsion oil spill, and oil slick. Using chemical methods after recovering by physical methods to restrict the negative effects on the marine environmental should be done.

In case of oil spill occurred in open water such as very large area on the seawater surface, snow or ice, thermal or in-situ burning methods were only used because emission of many pollution components into air and marine environment threatened marine creatures, human life, other resources. The pollution level from thermal or in-situ burning methods was very serious.

Although no any oil spill products recovered after treating by biodegradation methods, but this methods were considered as the most advanced and efficient one because CO₂, H₂O was the last products of biodegradation process by multi-microorganisms. However, the specification of oil types was extremely necessary to choice the most suitable microorganisms due to each microorganisms only favoured one specific oil. This method might be the safest solution for oil spill, oil slick remediation though it took long time.

Based on the level of oil spill and oil slick, kind of oils, weather conditions at each area, the reality condition of each countries, the choice of suitable methods, solution or remedies were necessary to recover the oil the most efficiently.

ACKNOWLEDGMENT

The authors acknowledge Ho Chi Minh city University of Transport, Vietnam Maritime University for supporting this research.

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