Remediation Technologies for Marine Oil Spills: A Critical Review and Comparative Analysis

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Abstract: Problem statement: Anthropogenic activities pollute the oceans with oil through land run off, vessels accidents, periodic tanker discharges and bilge discharges. Oil spills are environmental disasters that impact human, plants and wild life including birds, fish and mammals. Approach: In this study, the International Guidelines for Preventing Oils Spills and Response to Disasters were reviewed and the characteristics of oil spills were discussed. The advantages and disadvantages of various oil spill response methods were evaluated. A comparative analysis were performed on the currently available remediation technologies using 10 evaluation criteria that included cost, efficiency, time, impact on wild life, reliability, level of difficulty, oil recovery, weather, effect on physical/chemical characteristics of oil and the need for further treatment. The advantages and disadvantages of each response method were used to determine the score assigned to that method. Results: There are many government regualtions for individual countries that serve as prevention mesures for oil spills in the offshore environment. They have to do with the design of equipment and machinery used in the offshore environment and performing the necessary safety inspections. The primary objectives of response to oil spill are: to prevent the spill from moving onto shore, reduce the impact on marine life and speed the degradation of any unrecovered oil. There are several physical, chemical, thermal and biological remediation technologies for oil spills including booms, skimmers, sorbents, dispersants, in-situ burning and bioremediation. Each technique has its advantages and disadvantages and the choice of a particular technique will depend on: type of oil, physical, biological and economical characteristics of the spill, location, weather and sea conditions, amount spilled and rate of spillage, depth of water column, time of the year and effectiveness of technique. Conclusion: Based on the comparative analysis, oil recovery with mechanical methods and the application of dispersants followed by bioremediation is the most effective response for marine oil spill.

Key words: Marine oil spill, spill prevention, response to spill, booms, skimmers, dispersants, in-situ burning, bioremediation, aesthetic appeal, oil recovery

INTRODUCTION

Marine oil pollution results from land runoff, vessels and pipelines accidents, offshore petroleum exploration and production operations, shipping activities and illegal bilge water discharges (Lucas and Macgregor, 2006). Approximately 5.71 million tones of oil were spilled due to tanker incidents during the period of 1970-2010 (ITOPF, 2010). Marine oil spills affect marine life, tourism and aesthetic appeal and leisure activities. Significant physical and chemical changes of oil occur after the spill (Annunciado et al., 2005). A slick formation after oil spill undergoes various weathering processes including spreading, drifting, evaporation, dissolution, photolysis, biodegradation and formation of water-oil emulsions which cause significant changes in oil viscosity, density and interfacial tension (Daling and Strom, 1999). Numerous oxygenated products such as aromatic, aliphatic, benzoic and naphthanoic acids, alcohols, phenols and aliphatic ketones result due to the photolysis of oil (Hussein et al., 2009).

Several techniques are developed for the oil spill response including mechanical recovery, use of dispersants and solidifiers, burning and bioremediation. Davis and Guidry (1996) estimated the average cost of cleaning a crude oil spill to be $2730 per barrel. The selection of the most effective technique depends on the type and quantity of oil spill, weather conditions and surrounding environment (Choi and Cloud, 1992;
Marine oil spills include crude oil, refined petroleum products (gasoline, diesel and other by-products), heavier fuels (bunker fuel) and any oily waste oil (API, 2002). The severity of the impact of an oil spill depends on the type of the oil and its chemical and physical properties (Holakoo, 2001). The physical and chemical properties of oil affect weathering/transformation processes (evaporation, spreading, emulsification, dissolution, sedimentation and photolysis). These processes collectively may lead towards the formation of chocolate mousse and tar balls as well as the formation of numerous oxygenated products which make it difficult to recover the oil (Daling and Strom, 1999).

**Physical characteristics:** The physical properties of oil include: colour, surface tension, specific gravity and viscosity. The physical properties of oil spills vary depending on the type of oil introduced into the ocean environment. Generally, the dark brown or black colour of oil may change to yellow, green or red color (Holakoo, 2001). The ability of oil spill to spread depends on surface tension, specific gravity and viscosity. Oil with a lower surface tension have the ability to spread very quickly even in the absence of wind or currents. Oil surface tension is related to temperature and oil spreading tendency increases in warmer waters than in cold waters. Since the density of most of oils is lower than the ocean water, oils tend to float on the surface and spread out horizontally. However, the evaporation of lighter substance of oil can increase the specific gravity of oil allowing heavier oils to sink and form tar balls that may interact with rocks or sediments on the bottom of the water body. Highly viscous oil has less tendency to spread out (USEPA, 1999a). Payne and Philips (1985) reported that higher viscosity of an oil spill leads to the formation of chocolate moss which is not easy to degrade or treat. Nordvik et al. (1996) reported that a temperature increase of 10-50°C decreased the fuel oil density from 0.88-0.855 kg dm³ and the viscosity from 5000-200 cSt which reduced oil resistance to flow and increased its ability to spread horizontally.

**Chemical characteristics:** Chemical properties of oil include: molecular weight, melting point, boiling point, partition coefficient, flash point, solubility, flammability limits and explosivity limits. These chemical characteristics vary based on type of oil (ASTDR, 1995). Oil has a complex chemical composition that is dominated by the hydrocarbons it contains. Oil may also include sulphur, nitrogen, oxygen and some metals. The International Union of Pure and Applied Chemistry (IUPAC) classify hydrocarbons by nomenclature as shown in Fig. 1 (Olah and Molnar, 2003).

Alkanes are the simplest form of hydrocarbon, consisting of only saturated carbon and hydrogen atoms. Alkenes and Alkynes are unsaturated molecules, containing only carbon and hydrogen, with one or more double or triple bonds. Cycloalkanes are carbon-hydrogen structures that form a ring. Aromatic hydrocarbons contain at least one aromatic ring structure, a carbon-hydrogen ring containing six carbons, each with one double bond (McMurry, 2004).

Oil groups can be divided into four main groups having different compounds such as saturated, unsaturated, aromatic and polar compounds (Clayton, 2005). An average crude oil will contain 30% paraffins or alkanes, 50% naphthenes or cycloalkanes, 15% aromatics, 5% nitrogen, sulphur and oxygen containing compounds. The primary groups of hydrocarbons found in gasoline are paraffins, olefins, naphthenes and aromatics. Represented classes of these contaminants Table 1 are straight chain alkanes, branched alkanes, cycloalkanes, straight chain alkenes, branched alkenes, cycloalkenes, alkyl benzenes, other aromatics and polycyclic aromatic hydrocarbons (PAHs) (Netwpec, 2003).

**GUIDELINES FOR PREVENTION AND RESPONSE TO OIL SPILLS**

**Prevention of oil spill:** There are many government regulations for individual countries that serve as prevention measures for oil spills in an offshore environment. Many of these regulations have to do with design of equipment and machinery used in the offshore environment and performing necessary safety inspections. Among these regulations, those of the USA, Canada and UK are the most comprehensive.
Table 1: Examples of the primary classes of hydrocarbons (NEIWPCC, 2003)

| Primary class            | Representative compounds                                                                 |
|--------------------------|------------------------------------------------------------------------------------------|
| Straight chain alkanes   | Propane, n-hexane, n-dodecane                                                             |
| Branched alkanes         | 2-methyl-1-butene, 4,4-dimethyl-cis-2-pentene                                            |
| Cycloalkanes             | Cyclohexane, 3-methylcyclopentene                                                         |
| Alkyl benzenes (includes BTEX compounds) | 1,2-dimethyl-3-ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4,5-tetramethyl benzene, 2-methyl-1-butene, 4,4-dimethyl-cis-2-pentene |
| n-propylbenzene          | Naphthalene, acenaphthene, acenaphthylene, anthracene, benz[a] anthracene, benzo[a] pyrene, chrysene, coronene, dibenz(a,h) anthracene, fluorene, fluoranthen, fluorene |
| Other aromatics          | 1,2,4,5-tetramerhylbenzene, 1,2,3-trimethylbenzene, 1,2,4,5-tetramethyl benzene, 2-methyl-1-butene, 4,4-dimethyl-cis-2-pentene |

**Fig. 1: IUPAC classification of hydrocarbons (Olah and Molnar, 2003)**

- (a) Alkanes
- (b) Alkanes
- (c) Alkanes
- (d) Cyloalkanes
- (e) Aromatic hydrocarbons

The development plan must also include the production rate, evaluations of the area, potential recovery amounts of oil and gas, recovery methods, monitoring procedures, costs, technical proposals and environmental factors. The National Energy Board is responsible for reviewing the safety of the study in question before it begins. The National Energy Board consults the Chief Safety Officer and makes a decision on whether or not the proposed oil pool or field will be safe for both workers and the environment (DJC, 2010).

**USA prevention regulations:** The US Clean Water Act (USCWA) Sec. 311 authorizes US Environmental Protection Agency (USEPA) and the US Coast Guard to prevent, prepare for and respond to oil spills. According to Federal Water Pollution Control Act, a facility has to be covered by the Spill Prevention, Control and Countermeasure (SPCC) Regulations if it has: (a) more than 5000 L (1320 gallons) of aboveground oil storage capacity; (b) more than 158,988 L (42000 gallons) of underground storage capacity and (c) a reasonable expectation of an oil discharge into or upon navigable water of the US or adjoining shorelines. A facility that meets these criteria must prevent oil spills by developing and implementing an SPCC Plan. The prevention actions include using suitable oil containers, providing overfill prevention of oil containers, periodically inspecting and testing pipes and containers, providing adequate secondary containment and catching of oil spills where transferring of oil happens. The SPCC Plan should describe oil handling operations, spill prevention practices, discharge or drainage controls, personnel, equipment and resources at the facility that are used to prevent oil spills from reaching navigable waters or adjoining shorelines (US Senate, 2002; USEPA, 2010a).

**UK prevention regulations:** In United Kingdom, every harbour authority, operator of an oil handling facility and operator of an offshore installation must have an oil pollution emergency plan according to The Merchant Shipping (Oil Pollution Preparedness, Response and Co-operation Convention) Regulations 1998 (UK Government, 1998). According to The Offshore Petroleum Activities (Oil Pollution Prevention and Control) Regulation 2005, the discharge of oil by the offshore installation should apply for a permit that include information about the offshore installation, the oil to be discharged and the measures planned to monitor the discharge. The violation of the regulation will be fined not exceeding the statutory maximum (UK Government. 2005). According to The Control of Pollution (Oil Storage-England) Regulations 2001, the
installation and capacity of oil container have been regulated in order to ensure that it is unlikely to burst or leak in its ordinary use (UK Government, 2001).

**Response to oil spill:** There are many government regulations for individual countries that serve as response measures for oil spills in an offshore environment. Among these regulations, those of the USA, Canada and UK are the most comprehensive.

**Canadian response regulations:** According to the Canada Oil and Gas Operations Act Sections 24-28, oil spills are prohibited, meaning no person can cause or allow an oil spill to happen. However, if an oil spill does happen accidentally, it must be reported by the workers on duty immediately to the Chief Conservation Officer. Also, according to the act, those who reported the spill must do everything possible to contain the spill, prevent further spillage and mitigate harmful environmental impact. The Chief Conservation Officer has the authority to take emergency environmental measures to clean up the spill and allow management to be taken over in order to prevent further impact. The company that caused the spill will then have to pay any costs for remedial measures along with the possibility of being sued for damages and negligence as decided in court (DJC, 2010). Other Canadian Governing Bodies and Organizations will also be involved in the response to the oil spill. The Canadian Coast Guard should also be notified immediately about any oil spill, especially if the spill is from an oil tanker (TC, 2010). Canadian Wildlife Services (CWS) will also be involved with an oil spill to determine the effect of the spill on migratory birds and marine life in the area and the precautions necessary to ensure there is as little effect as possible on the wildlife of the area (CWS, 2000).

**USA response regulations:** In USA, if an oil spill happened, any person in charge of the related facilities must notify the National Response Center (NRC) immediately and provide necessary information of the spill to the Regional Administrator. Reporting to State and Local Agencies may also apply. If more than 3785 liters (1000 gallons) of oil are discharged to water body in a single event or more than 159 L (42 gallons) of oil in each of two discharges to navigable waters or adjoining shorelines occur within any 12 month period, the owner or operator of the facility must report to USEPA (US Senate, 2002; USEPA, 2010a).

**UK response regulations:** In UK, regardless of volume, any accidental or unplanned discharges of oil to sea must be reported using the Petroleum Operations Notice No. 1 as soon as possible. If the source of the oil spill is in doubt, sample of the oil should be taken for analysis (Oil and Gas UK, 2011). According to The Merchant Shipping (Oil Pollution Preparedness, Response and Co-operation Convention) Regulations 1998, ship owners or operators, a person who is in charge of an offshore installation or an oil handling facility and a harbour master must report any event involving discharge of oil at sea from another ship or from an offshore installation without delay to Her Majesty’s (HM) coast guard or to the nearest Coastal State. Any person who failed to make the report will be fined not exceeding the statutory maximum (UK Government, 1998).

### OIL SPILL REMEDIATION METHODS

Marine oil spill control and clean up is the most debatable issue because it is not possible to clean up all the oil introduced into the marine water. Current remediation techniques are: (a) physical (b) chemical (c) thermal and (d) biological (Larson, 2010).

**Physical remediation methods:** Physical methods are commonly used to control oil spills in a water environment. They are mainly used as a barrier to control the spreading oil spill without changing its physical and chemical characteristics. A variety of barriers are used to control oil spills including: (a) booms (b) skimmers and (c) adsorbent materials (Fingas 2011; Vergetis, 2002).

**Booms:** Boom are a common type of oil spill response equipment which are used to prevent spreading of the oil spill by providing barrier to oil movement which can improve the recovery of oil through skimmers or other response techniques. There are three categories of booms as shown in Fig. 2: (a) fence boom (b) curtain boom and (c) fire-resistant boom (Potter and Morrison, 2008).

**Fence booms:** They are floating fence-like structures made of rigid or semi-rigid materials and provide a vertical screen against floating oil as 60% of the boom remain under the water and 40% remain above the surface of water. Boom sections are usually 15 m in length and 300, 600 or 800 mm in height. Multiple boom sections can be connect together with special connectors. Fence booms are light weight, take up minimal storage space, resist abrasion, are easy to handle, clean and store are highly reliable in calm quiet waters. However, they have several disadvantages including low stability in strong winds and currents, low flexibility for towing and low efficiency in high waves (Ventikos et al., 2004; Potter and Morrison, 2008; OSS, 2010).
Fig. 2: Types of booms (OSS, 2010) (a) Fence boom (b) Curtain boom (c) Fire resistant boom

Curtain booms: They are impervious, non absorbent, floating structures. They have a large circular, foam filled chamber that remains over the water and a flexible skirt that remain under the water. They are made up of polyurethane, polystyrene, bubble rap or cork. The chamber diameter ranges from 100-500 mm and the skirt length ranges from 150-800 mm. They are reliable in offshore situation in clam water, have high flexibility in towing and perform better than fence boom but are more difficult to clean and store (Ventikos et al., 2004; OSS, 2010; GPC, 2010).

Fire-resistant boom: They are made up with the fire proof metal which can concentrate sufficient amount of oil to burn efficiently at 1093°C (2000°F). They are used in combination with in situ burning techniques (Ventikos et al., 2004). They are available in several types: Water-cooled booms, stainless-steel booms, thermally resistant booms and ceramic booms. Generally, the length of 200 m of fire boom will provide about 1,500 m² of burn area (ARPEL, 2006). They are reliable in clam water and have great potential to protect the shoreline from the impact of an oil fire at sea. They are very expensive and difficult to tow due to their weight and size (GPC, 2010).

Skimmers: These devices can be used in conjunction with booms to recover oil from water surface without changing its properties so it can be reprocessed and reused. Skimmers consist of disks, belts, drums and brushes (Larson, 2010; Hammoud, 2001). They may be self-propelled, used from shore or operated from vessels. Skimmers are three categories as shown in Fig. 3: (a) weir, (b) oleophilic and (c) suction (Nomack and Cleveland, 2010). The success of skimming depends on the type and thickness of the oil spill, the amount of debris in the water, the location and the weather conditions. They are generally effective in calm waters and subject to clogging by floating debris.

Wier skimmers: They act like a dam and collect the floating oil from the water surface via gravity action. The collected oil is transferred from the weir central sink by gravity or by a pump to storage tanks. They have high static stability in waves and high efficiency in recovering oil quickly (Hammoud, 2001). They work well with less viscous, low density oil and non emulsion oil. However, they have significantly low efficiency with oil emulsion and are frequently jammed and clogged by floating debris (Jensen et al., 1995).

Oleophilic skimmers: They include drums, ropes, disks, brushes and belt type skimmers. All types of these skimmers are made up from oleophilic properties materials. The oil adhere to the surface of the material which can be scraped or squeezed from the surface and collected in a storage tank. They can recover 90% of oil in the water due to their oleophilic nature (OSS, 2010). Flexible oleophilic skimmers are effective on spills of any thickness, work well with debris or rough ice and are less influenced by waves (Nomack and Cleveland, 2010). However, they are not able to deal with oil mixed with dispersants and trash separation is performed with hand (OSS, 2010).

Suction skimmers: They are vacuum pumps as well as air venture system that suck up oil through wide floating heads and transfer it into storage tanks. They are very efficient in handling a wide range of oil viscosity but can also be clogged by debris and require skilled operators. However, they are efficient in collecting oil residue and are most widely used for the recovery of oil from beaches, confined areas or removal of oil from land surface. In off shore areas, they work efficiently in conjunction with boom in clam water. They are not advisable for use with inflammable oil products that lead to explosion (Ventikos et al., 2004; OSS, 2010).
Adsorbent materials: Hydrophobic sorbents are of great interest for controlling oil spills as they serve as a final step of cleanup for the remained oil after skimming operation. They facilitate conversion of liquid to semisolid phase for complete removal of oil (Adebajo et al., 2003; OSS, 2010). The adsorbent materials for oil spill clean-up include: (a) natural organics (b) natural inorganics and (c) synthetic materials.

Natural organic adsorbents: They include peat moss, kapok, saw dust, vegetable fibers, milkweed and straw (Karakasi and Moutsatsou, 2005). Choi and Cloud (1992) reported that the milkweed and cotton fibers adsorbed 74-85% of crude oil from the surface of an artificial sea water bath containing crude oil. Banerjee et al., (2006) reported that sawdust achieved a maximum adsorption capacity of 3.6 g/g sawdust while oleic acid grafted sawdust achieved 6 g/g sawdust within 5 min. Ghalb et al. (1999) reported a maximum adsorption of 6.7 g g⁻¹ peat moss. Natural organic adsorbents are less expensive, readily available and their adsorbing capacities are 3-15 times their weight. The major disadvantages for their use are that they are labor intensive, adsorb water along with oil which lead to their sinking, are very difficult to collect adsorbents after spreading on the oil spill water and must be disposed off (USEPA, 1999b; Nomack and Cleveland, 2010).

Natural inorganic adsorbents: They include clay, glass, wool, sand, vermiculate or volcanic ash (Holakoo, 2001). Ding et al. (2001) reported that clay minerals such as smectites and pillared interlayer clays (PILCs) are used as adsorbents for organic compounds in liquid phase in the controlled release of agrochemicals. Teas et al. (2001) showed that hydrophobic perlite had comparable absorption capacity with synthetic organic materials used for oil spill cleanup. Alther (2002) reported that modified clays with quaternary ammonium cations have better performance in adsorption of 50 types of oil than activated carbon. Natural inorganic sorbents are less expensive, readily available and their absorbing capacities are 4-20 times of their weight. The major disadvantages of their use are that they are not advisable for water surface, many natural inorganic adsorbents such as clay and vermiculite are loose material and very difficult to apply in windy conditions and they are associated with potential health risk if inhaled (USEPA, 2011a).

Synthetic adsorbents: They are the most widely used commercial sorbents. They include polypropylene, polyester foam and polystyrene. They are available in sheets, rolls or booms and can also be applied on to the water surface as powders (Teas et al., 2001). Jarre et al. (1979) reported that ultralight, open-cell polyurethane foams were capable of absorbing 100 times their weight oil from oil-water mixtures. Teas et al. (2001) reported that polypropylene had the highest oil adsorption (4.5 g g⁻¹ light cycle oil or light gasoline oil). Synthetic adsorbent have adsorbing capacity 70-100 times of their weights in oil due to their hydrophobic and oleophilic nature. Some types of synthetic adsorbents are reusable several times. The major disadvantages are their storage and nonbiodegradability after their use (Choi and Cloud, 1992; Deschamps et al., 2003; USEPA, 2011a). Application of synthetic adsorbents for oil spill response is shown in Fig. 4.

Chemical remediation methods: Chemical methods are used in combination with physical methods for marine oil spill remediation as they restrict the spreading of oil spill and help to protect the shorelines and sensitive marine habitats.
Table 2: Functions and classes of chemical dispersants (Sitting, 1974)

| Component   | Function                                                                 | Classes                                                                                           |
|-------------|--------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
| Surfactants | Decreases formation of an oil in water emulsion, to spread and increase surface area for microbial decomposition | Ionic: colloidal electrolytes work similarly to soaps examples are: Ammonium lauryl sulfate, sodium lauryl sulfate, Alkyl aryl ether phosphate Non-ionic: weak solubilizing groups such as ether linkages or hydroxyl groups. Examples are: cetyl alcohol, stearyl alcohol, taethylene glycol monododecyl ether |
| Solvents    | Reduces viscosity of surfactants, dilute compound of dispersant, depress freezing point of dispersant, optimize concentration of dispersant | Petroleum hydrocarbons: mineral spirits, kerosene, #2 fuel oil, heavy aromatic naphthas with boiling points above 300°F Alcoholic or hydroxyl group: Alcohols, glycols, glycol ethers Water-used as solvent |
| Stabilizers | Adjust pH, adjust color, stop corrosion, increase hard water stability    | Polycarboxylates, Triton™, LTSA-35 MIL                                                             |

Fig. 4: Application of synthetic adsorbents for oil spill response (USEPA, 1999b)

Fig. 5: Mechanism of dispersing oil (Lessard and Demarco, 2000) (Application of dispersant on oil) (b) Surfactant locates at interface (c) Oil slick disperse into the small droplets with minimal energy

Various chemicals are used to treat the oil spills as they have capabilities to change the physical and chemical properties of oil (Vergetis, 2002). The chemicals used to control oil spills include: (a) dispersants and (b) solidifiers.

**Dispersants:** Dispersants consist of surfactants (surface active agents) dissolved in one or more solvents and stabilizer Table 2. Dispersants have capabilities to break down the slick of oil into smaller droplets and transfer it into the water column where it undergoes rapid dilution and can be easily degraded (Lessard and Demarco, 2000). The mechanism of dispersing oil is shown in Fig. 5. Dispersants are usually applied by spraying the water with the chemical and ensuring that it is well mixed either by wind or the propeller of a boat (Sitting, 1974).

The dispersants available today are less toxic and more effective compared to the compounds that were previously used (Lessard and Demarco, 2000). These concentrated types of dispersants include: Slickgone NS, Neos AB3000, Corexit 9500, Corexit 8667, Corexit 9600, SPC 1000™, Finasol OSR 52, Nokomis 3-AA, Nokomis 3-F4, Saf-Ron Gold, ZI-400, Finasol OSR 52 (USEPA, 2011b). A list of dispersants and their application ratios are shown in Table 3.

Davies et al. (1998) reported that 50-75% of No. 5 bunker oil slick (20 ton) was dispersed with the application of Corexit 9500 dispersant. Siang (1998) reported that the target oil spill in the history of Singapore (October, 1997) was cleaned up in a record of 3 weeks with the application of Corexit 9500 dispersant.

Dispersants proved their capabilities to treat up to 90% of spilled oil and are less costly than the physical methods (Holakoo, 2001). They can be used on rough seas where there are high winds and the mechanical recovery is not possible. They also allow for rapid treatment, slow down the formation of oil-water emulsions make the oil less likely to stick to surfaces (including animals) and accelerate the rate of natural biodegradation by increasing the surface area of the oil droplets. Applicability of dispersants depends on type of oil, temperature, wind speed and sea conditions (Nomack and Cleveland, 2010). However, the inflammable nature of most dispersants can cause human health hazards during applications and potential damage to marine life. They are also responsible for fouling of shorelines and contamination of drinking water sources (NRC, 1989).
Table 3: Dispersant and their application ratio (NRC, 1989)

| Dispersant             | Application ratio | Type of oil                     |
|------------------------|-------------------|---------------------------------|
| Tergo R-40             | 1: 20             | Medium and heavy oil, possibly on light oil |
| Ardrox 6120            | 1: 25             | Medium and heavy oil, possibly on light oil |
| BP-AB                  | 1: 3              | Medium and heavy oil, possibly on light oil |
| Corexit 9500           | 1: 10-1: 50       | Medium, heavy oil and light oil |
| Corexit 9527           | 1: 20-1: 30       | Medium and heavy oil, possibly on light oil |
| Corexit 9550           | 1: 20             | Medium and heavy oil, possibly on light oil |
| Shell VDC              | 1: 20 1: 30       | Medium and heavy oil, possibly on light oil |
| Slickgone NS           | 1: 25             | Medium and heavy oil, possibly on light oil |
| Corexit 7664           | Diluted 1-3 in water | Medium, possibly on light oil |

Table 4: Solidifiers and their ability for solidification of oil (Fingas and Fieldhouse, 2011)

| Solidifier          | Percent* to solidify | Toxicity *(Aquatic) |
|---------------------|----------------------|---------------------|
| A610 Petrobond (Nochar) | 13                   | >5600               |
| Rawflex             | 16                   | >5600               |
| Envirobond 403      | 18                   | >5600               |
| Norsorex            | 19                   | >5600               |
| Jet Gell            | 19                   | >5600               |
| Grabber A           | 21                   | >3665               |
| Rubberizer          | 24                   | >5600               |
| SmartBond HS        | 25                   | >5600               |
| Elastol             | 26                   | >5600               |
| CI Agent            | 26                   | >5600               |
| Gelco 200           | 29                   | >5600               |
| Oil Bond100         | 33                   | >5600               |
| Oil Sponge          | 36                   | >5600               |
| Spill Green LS      | 43                   | >10000              |
| Petro Lock          | 44                   | >5600               |
| SmartBond HO        | 45                   | >5600               |
| Molten wax          | 109                  | >5600               |
| Powdered wax        | 278                  | >5600               |

*Values are the average of at least 3 measurements, average standard deviation is 6
**Values are LC50 to Rainbow Trout in 96 h. this shows that all are insoluble and less can be measured

Table 5: Airborne emissions from an in situ petroleum fire (Buist et al., 1999)

| Components | Emitted quantity* (kg emission/kg oil burned) |
|------------|-----------------------------------------------|
| Carbon dioxide (CO2) | 3.000000 |
| Particulate matter | 0.05-0.20 |
| Carbon monoxide (CO) | 0.02-0.05 |
| Nitrogen Oxides (NOx) | 0.001000 |
| Volatile Organic Compounds (VOCs) | 0.005000 |
| Polynuclear Aromatic Hydrocarbons (PAH) | 0.000040 |

* Quantities will vary with burn efficiency and composition of parent oil

Solidifiers: Solidifiers are dry granular (hydrophobic polymers) materials that react with oil and change its liquid state into solid rubber-like state that can be easily remove by physical means. Solidifiers can be applied in various forms including dry particulate and semi-solid materials (pucks, cakes, balls, sponge designs). They are contained in booms, pillows, pads and socks or packaged forms (Dahl et al., 1996; Delaune et al., 1999). Examples of solidifier are shown in Table 4.

Solidifiers can be used on moderately rough seas as the waves provide the mixing energy which results in greater solidification (Nomack and Cleveland, 2010).

The efficiency of solidifier depends on the type and composition of oil (Fingas et al., 1990). Solidifiers have not been used extensively in the past because of the issue of recovery after solidification large amount is required (16-200% by weight of oil mass) and they have a relatively lower efficiency than dispersants (Fingas et al., 1995).

Thermal remediation method: In situ burning is a simple and rapid a thermal mean of oil spill remediation that can proceed with minimal specialized equipment (fire resistant boom, igniters) with higher rates of oil removal efficiency. Since the late 1960s, in situ burning is widely used to remove spilled oil and jet fuel in ice covered waters and snow resulting from pipeline, storage tank and ship accidents in the USA and Canada as well as several European and Scandinavian countries (Mullin and Champ, 2003; Buist et al., 1999). This method of oil spill response is effective in calm wind conditions and spills of fresh oils or light refined products which quickly burn without causing any danger to marine life. However, the residue may sink and cover up an underground water resource. Removal of the residue can be achieved through mechanical means (Davidson et al., 2008).

A successful operation of burning depends on the thickness of oil (as thick oil layer will not cool down the fire) and sufficient supply of oxygen (Buist et al., 1999). There are two agents that can be used for sustaining the combustion of the oil and providing enough oxygen to the fire: (a) burning agents who include gasoline, light crude oils and numerous commercially available products and (b) wicking agents who include straw, wood, glass beads and silica (Fingas et al., 1995). Although in situ burning is an effective method for oil spill response, the major constraints in use of this method are: (a) fear of catching secondary fires (b) human health and environmental risks due to the byproduct of burning (Buist et al., 1999). Table 5 shows the major chemical components of smoke generated from in-situ burning and their approximate proportion.

Vegetation and aquatic life adjacent to site can be affected by burning, including long-term alteration in aquatic plants and animals. However, in situ burning is the most successful remediation method if applied immediate after the oil spill has occurred.
Table 6: Major genera of oil degrading bacteria and fungi (Webb, 2005; Capotorti et al., 2004)

| Microorganism     | Ability to degrade compounds                                                                 |
|-------------------|---------------------------------------------------------------------------------------------|
| **Bacteria**      |                                                                                             |
| Arthrobacter spp. | phenanthrene, methyl-tert-butyl ether, ethyl-tert-butyl ether and tert-amyl methyl ether     |
| Brevebacterium    | Asphaltenes, petroleum oil                                                                   |
| Brachybacterium   |                                                                                             |
| Dietzia           | n-C12 to n-C38 alkane components                                                             |
| Flavobacterium    | chlorophenols                                                                               |
| Janibacter        | Polycyclic hydrocarbon                                                                       |
| Mycobacterium     | Polycyclic hydrocarbon, pyrene, phenanthrene, diesel                                        |
| Nocardia spp.     | 4-chlorobenzoxate                                                                           |
| Pseudomonas spp.  | 4-chlorobenzoxoate                                                                          |
| Rhodococcus       | Polychlorinated-biphenyl, hexadecane, trichloroethan, polycyclic hydrocarbon                 |
| **Fungi**         |                                                                                             |
| Aspergillus       | Pyrene, benzo(a)pyrene                                                                      |
| Candida           | Toluene                                                                                     |
| Fusarium          | Methyl tert-butyl ether and tert-butyl alcohol                                              |
| Trichoderma       | phenanthrene                                                                                |
| Phanerochaete     | benzo(a)pyrene, phenanthrene and fluorene                                                   |
| Mortierella       | 2, 4-Dichlorophenol                                                                         |

**Bioremediation method:** Bioremediation is a process whereby microorganisms degrade and metabolize chemical substances and restore environment quality. It aims to accelerate the natural attenuation process through which microorganisms assimilate organic molecules to cell biomass and produce by-products such as carbon dioxide, water and heat (Atlas and Cerniglia, 1995). In the case of marine oil spill, microorganisms with the ability to degrade hydrocarbons are ubiquitous in the indigenous oil spill site. Both paraffinic and aromatic hydrocarbons can be degraded by a variety of microorganisms but have different degradation rates. Alkanes with carbon train of 10-26 and low-molecular-weight aromatics are the most easily degraded hydrocarbons in petroleum. Branched alkanes and high-molecular-weight aromatics are recalcitrant to biodegradation (Atlas, 1995; Swannell et al., 1996). Major genera of oil degrading bacteria and fungi are listed in Table 6. Bacteria are the dominant hydrocarbon degraders in aquatic systems. Bacterial genera that have been reported to degrade hydrocarbons include: *Pseudomonas, Achromobacter, Acinobacter, Alcaligenes, Arthrobacter, Bacillus Brevibacterium, cornybaeaterium, Flavobacterium, Nocardia, Pseudomonas, Vibrio*. (Atlas and Cerniglia, 1995). Different microorganisms dominate at different bioremediation phases and as readily degraded hydrocarbons are eliminated, microbial populations shift from alkanes to aromatic hydrocarbons (Sugai et al., 1997).

The biodegradation of oil spill in the marine environment is mainly affected by the bioavailability of nutrients, the concentration of oil, time and the extent to which the natural biodegradation had already taken place (Bragg et al., 1994; Atlas, 1995; Zahed et al., 2010). Nutrients that are necessary for the growth of hydrocarbon-degraders such as nitrogen and phosphorus are always in low concentrations in marine environment.

Because of the scarcity of nutrients, the natural attenuation of oil spill does not processed at a practical rate (Atlas and Bartha, 1973; Atlas, 1995). Also, the high initial concentration of spilled oil has a negative effect on the biodegradation process causing a significant lag phase in the order of 2-4 weeks (Zahed et al., 2010). Even after biostimulation, at least a week is needed for microorganisms to acclimate to the environment and the entire bioremediation process may require months and even years to complete (Atlas, 1995; Zahed et al., 2010). Other environmental factor such as temperature and oxygen are important as temperature affects the viscosity of crude oil and dissolved oxygen affects the metabolic activity of microorganisms (Yang et al., 2009).

For effective bioremediation of oil spill, inoculation of contaminated seawater with hydrocarbon-degrading microorganisms (bioaugmentation) and the addition of fertilizers and/or dispersant (biostimulation) are necessary in order to accelerate the rate of the natural degradation process. Screening of petroleum hydrocarbon degrading microorganisms from previously contaminated sites and inoculating them to the contaminated sea water are one option for bioremediation of marine oil spill. However, the wide distribution of hydrocarbon degrading bacteria and fungi makes the competition between indigenous species and those in the inoculum very severe. Most studies indicated that bioaugmentation was not a promising option for the bioremediation of oil spill (Venosa et al., 1991; Atlas, 1995; Swannell et al., 1996). The application of fertilizers as nitrogen and phosphorus nutrient supplements has been shown to be effective for marine oil spills, though the efficacy is limited in the bioremediation of extensively degraded oil (Bragg et al., 1994; Zahed et al., 2010). The application of surfactants or dispersant is also reported to be successful because they increase the bioavailability of oil to hydrocarbon degraders (Zahed et al., 2010).

The eutrophication caused by the addition of nitrogen and phosphorus to the water body has been studied. Atlas and Bartha (1973) found that the use of oleophilic fertilizers would not trigger algal blooms. In the study of bioremediation of Exxon Valdez oil spill.
Table 7: Review of three large marine oil spill event (impact, clean up and cost)

| Oil Spill                     | Responsible company | Quantity of oil and area | Affected Industries | Affected Wild life | Treatments                                      | Cleanup cost | Remarks                                      |
|------------------------------|---------------------|--------------------------|---------------------|--------------------|------------------------------------------------|-------------|----------------------------------------------|
| The Exxon Valdez Disaster    | Exxon mobil Corporation | 41 million liters over 28,000 km² | $31 million         | Recreational fishing- loss of                  | Physical recovery methods (Booms and Skimmers) | US $3 billion dollars | $755.2 total lost due to ecosystem damage and depleted fish stock |
| Prince William Sound, Alaska |                     |                          |                     | Sea otters, harbor seals, bald eagles, seabirds harlequin ducks | | | |
| The Prestige oil spill       | Universe Maritime Ltd | 63700 tonnes over 2.500 km² |                     | Commercial fishing- loss of $300 million | Salmon fish | Dispersants (Corexit 7664, Corexit EC 9530, BP1100X) | Harbor seal Harlequin Duck pacific herring and guillemot still have not fully recovered |
| of north-western Spain       |                     |                          |                     | Sea birds, shark, marine mollusks, mussels, octopus, sardines, sole goose barnacle | | | |
| Gulf of mexico oil spill     | British Petroleum | 780 million liters over 11,000 km² |                     | Recreational fishing- loss of $138 million | Aquatic Invertebrates, fish, sea turtles, birds, beach mouse | Physical recovery methods (Booms and Skimmers) | US$12billion dollars | Caused pollution in the area for ten years subsequent to the initial spill |
| Gulf of mexico               |                     |                          |                     | Aquatic Invertebrates, fish, sea turtles, birds, beach mouse | | | |
| Gulf of mexico               |                     |                          |                     | Commercial fishing- loss of $18 million | | | |
|                             |                     |                          |                     | Tourist- loss of $2.8 billion | | | |

Bragg et al. (1994) and Atlas (1995) reported that the use of fertilizer did not cause eutrophication and no acute toxicity to tested sensitive species was reported. Moreover, complex components in the crude oil which are not biodegradable are always left as asphaltic residues which may cause the coating and suffocation of marine life in an area. However, the biota toxicity of petroleum hydrocarbons is removed from the environment through bioremediation (Atlas, 1995; Swannell et al., 1996).

Bioremediation has many advantages in the treatment of marine oil spill because of its environmentally friendly and economic properties. The cost of bioremediation is significantly lower than the costs of other remediation options (Atlas, 1995). The major constraints of this method are the relatively long period of treatment, low tolerance capacity of microbes to higher concentrations, the dependency on environmental factors, the biodegradability of limited petroleum hydrocarbons and the heterogeneity of marine oil spill makes it difficult to evaluate the efficiency of bioremediation (Swannell et al., 1996).

**IMORTANT MAJOR OIL SPILLS**

Major oil spills have been caused by human error, improper designs or tragic weather events. Whether on a small or a large scale, the overall effect of any oil spill or leak is highly detrimental to marine environment and the economy. There are many instances of marine oil pollution caused by unfortunate events all over the world. A review of three large oil spills is presented in Table 7.

**The exxon valdez disaster:** Just after midnight on March 24, 1989, oil tanker Exxon Valdez was trying to navigate through large pieces of ice but could not turn fast and hit Bligh Reef. Due to the impact, the oil cargo tanks were ripped causing the spilling of 41 million liters of oil into Prince William Sound, Alaska. By the third day, the oil slick had covered 161 square km (100 square miles) and was continuing to spread. It was a significant ecological disaster as the southern shore of Alaska is a home to one of America’s richest concentrations wildlife. The fishing industry and native villagers were severely affected as their ways of hunting, gathering and fishing were threatened and altered. The effect of oil was extend to inland area because the seepage of oil into local groundwater sources. Significant amounts of ocean animals including fish species, birds and coastal mammals died due to contact with oil on their skin or ingestion of oil.
Table 8: Advantages and disadvantages of booms

| Booms             | Advantages                                                                 | Disadvantages                                                                 |
|-------------------|----------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Fence booms       | Used with all kind of oil                                                  | Expensive                                                                     |
|                   | Recovery of oil is possible                                                | Low flexibility for towing                                                    |
|                   | Easy to handle, clean and store                                           | Only contain oil and must be used with other technologies                     |
|                   | Resist abrasion                                                            | Low stability in strong wind and currents                                      |
| Curtain booms     | Used with all kind of oil                                                  | Expensive                                                                     |
|                   | Recovery of oil is possible                                                | Labor intensive                                                               |
|                   | Flexibility for towing                                                    | Complex                                                                       |
|                   | Resists abrasion                                                           | Collected oil need further treatment                                          |
| Fire-resistant boom| Used with all kind of oil                                                  | Low Efficiency in high waves                                                  |
|                   | Protect the shoreline from the impact of an oil fire at sea               | Difficult to store and clean                                                  |
|                   |                                                                            | Low Efficiency in high waves                                                  |
|                   |                                                                            | Collected oil are directly burned off                                         |

Scientists are still attempting to determine the extent of the ecological damage caused by this spill (Lee, 1997; Bragg et al., 1994; Swannell et al., 1996). Treatments of oil were applied shortly after the incident which included cold- and warm-water washing, steam cleaning, manual oil recovery operation and bioremediation. However, the washing and excavation of contaminated coastal rocks was concluded to be particularly damaging to the environment and the use of chemical dispersants like Corexit EC 9580 (contains propylene glycol, 2-butoxyethanol and dioctyl sodium sulfosuccinate) to disperse oil was not applicable because of their toxicity to human. Thus, bioremediation, with the application of fertilizers as nitrogen and phosphorous nutrients to stimulate oil-degrading microorganisms, was used predominantly as the cleanup strategy. Fertilizers used were Inipol EAP 22 (7.4% N, 0.7% P) and Customblen (28% N, 3.5% P). It has been proved that the biodegradation can be stimulated 2-7 times that of natural attenuation by the addition of fertilizer (Bragg et al., 1994; Swannell et al., 1996). The economical cost of the spill on the cleanup operation and research was estimated to be about $1.9 billion dollars and used 11,000 workers (Lee, 1997).

**The prestige oil spill:** The oil tanker Prestige (containing heavy fuel no. 2-M100) caused a major oil spill as it sank off the coast of Galicia of Northwestern Spain on November 19th, 2002. About 63, 700 tonnes of the total cargo of 77,000 tonnes were discharged into the surface waters and contaminated about 2,500 km of the shorelines of Spain, Portugal and France a year later. Direct and immediate impacts included the death of marine fishes, plants and animals. The industry of tourism along Spanish, Portuguese and French beaches was also affected in the year of the accident (Jimenez et al., 2006; Diez et al., 2009). However, there were no observable effects on the macroalgae and invertebrates (Lobon et al., 2008). Only mechanical cleaning methods were only conducted and between 55,000 and 59,000 tonnes of oil were recovered either at sea or from the adjacent beaches. Bioremediation of oil was attempted in field and oleophilic fertilizer S200 enhanced biodegradation of high molecular weight n-alkanes, alkylcyclohexanes, benzenes and alkylated PAHs (Jimenez et al., 2006; Diez et al., 2009).

**Deepwater horizon drilling rig:** On April 20, 2010, an explosion occurred on the Deep Horizon drilling rig in the Gulf of Mexico which caused a leak from a pipe located 1.6 km under the sea surface. About 779 million liters (205.8 million gallons) of oil leaked before the pipe was capped (Hoch, 2010). The spill caused significant impact on the marine ecosystem and severely affected the fishery and tourism industries of contaminated region in the Gulf of Mexico (Tangley, 2010). As of November 2, 2010, 6104 birds, 609 sea turtles, 100 dophins and other mammals and reptile had been collected dead (USWFS, 2010). The habitats of various animals including aquatic invertebrates, fish, sea turtles, birds and beach mouse were still affected after 7 months of the sealing pipe (OSAT-2, 2011).

Direct in situ burning of oil on the surface of the ocean to reduce the spread of oil had resulted inremoval of 35.2-49.6 million liters (9.3-13.1 million gallons) of the spilled oil (USEPA, 2010b). Physical clean-up methods such as the use of booms and skimmer to collect surface oil were been conducted (USEPA, 2011c). Dispersant chemicals were used to break up the oil and speed its natural degradation (Jackson, 2010). By September, 2011, over $650 million have been spent on the study, services and materials related to the clean-up project (RestoreTheGulf, 2011).
Table 9: Advantages and disadvantages of skimmers

| Skimmers       | Advantages                                                                 | Disadvantages                                                                 |
|----------------|----------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Wier skimmers  | Used with less viscous, low density oil and non-emulsion oil                | Expensive                                                                     |
|                | Recovery of oil is possible                                                | Labour intensive                                                             |
|                | High stability in waves                                                    | Complex                                                                      |
|                |                                                                              | Collected oil and need for further treatment                                 |
|                |                                                                              | Jammed and clogged by floating debris                                         |
|                |                                                                              | Low efficiency with oil emulsions                                             |
| Oleophilic skimmers | Effective on spills of any thickness 90% recovery of oil is possible in relation to water | Labo...
| Suction skimmers | Used with all kind of oil except inflammable                               | Expensive                                                                     |
|                | Efficient in collecting oil residue                                        | Labour intensive                                                             |
|                | Recovery of oil is possible                                                | Complex                                                                      |
|                |                                                                              | Collected oil and need for further treatment                                 |
|                |                                                                              | Low efficiency in high waves                                                 |
|                |                                                                              | Require maintenance                                                           |
|                |                                                                              | Possibility of clogging with floating debris                                 |
|                |                                                                              | Cannot be used with inflammable oil products                                  |

Table 10: Advantages and disadvantages of adsorbents

| Adsorbents       | Advantages                                                                 | Disadvantages                                                                 |
|------------------|----------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Natural organics | Used with all kind of oil                                                  | Labour intensive                                                             |
|                  | Inexpensive                                                                | Work under selected weather conditions                                       |
|                  | Adsorbing capacity is 3-15                                                 | Need to be disposed off                                                       |
|                  | times of their weight in oil                                               | Adsorb water along with oil which lead to their sinkage                      |
|                  | Some amount of recovery of oil is possible                                 | Readily available                                                             |
| Natural inorganics | Used with all kind of oil                                                  | Labor intensive                                                              |
|                  | Inexpensive                                                                | Need to dispose with regulation                                              |
|                  | Adsorbing capacity is 4-20                                                 | Work under selected weather                                                   |
|                  | times of their weight in oil                                               | Potential health risk conditions                                              |
|                  | Readily available                                                           |                                                                              |
| Synthetic materials | Used with all kind of oil                                                  | Expensive                                                                    |
|                  | Simple                                                                     | Effective as final clean up step                                               |
|                  | No maintenance required                                                    | Labor intensive                                                              |
|                  | Have good hydrophobic and oleophilic properties                             | conditions                                                                    |
|                  | Can be reused after several times                                          | Nonbiodegradable                                                             |
|                  |                                                                              | Major problem with storage                                                    |

COMPARATIVE ANALYSIS OF OIL SPILL RESPONSE METHODS

The advantages and disadvantages of the physical, chemical, thermal and biological methods listed in Table 8-14 were used as the basis for the comparative analysis performed on these remediation methods for marine oil spill response. Ten evaluation criteria were used to evaluate these methods: cost, efficiency, time and impact on marine life, reliability, level of difficulty, oil recovery, weather, effect on physical/chemical characteristics of oil and the need for further treatment.

Table 15 shows the definitions and scores assigned to these criteria. The scores were assigned on the basis of the advantages and disadvantages of these method as they are related to criteria. The final results of comparative analysis are shown in Table 16. The analysis performed on the oil spill response methods showed that bioremediation had the highest score (73). Although in-situ burning scored a second position (59), it is not advisable for all locations of oil spill. Booms and skimmer scored third position (55), as they are always good with all kind of oil type but their efficiency very much depends on weather and sea conditions. Dispersant scored fourth position (54), as they are always used to enhance the bioremediation process.
Table 11: Advantages and disadvantages of physical remediation methods of marine oil spill

| Physical means of remediation | Advantages | Disadvantages |
|------------------------------|------------|---------------|
| Booms                        | All kind of oil | Expensive |
|                              | Recovery of oil is possible | Labour intensive |
|                              |                                                      | Complex |
|                              |                                                      | Contain oil and must be used with other technologies |
|                              |                                                      | Efficient in selected weather conditions |
| Skimmers                     | All kind of oil except inflammable | Expensive |
|                              | Recovery of oil is possible | Labour intensive |
|                              |                                                      | Complex |
|                              |                                                      | Collected oil and need further treatment |
|                              |                                                      | Efficient in selected weather conditions |
|                              |                                                      | Possibility of clogging with floating debris |
|                              |                                                      | Required maintenance |
|                              |                                                      | Oil should be recovered before emulsified |
| Adsorbents                   | All kind of oil | Moderate expensive |
|                              | Effective as final clean up | Labour intensive |
|                              | Step | Selected weather conditions |
|                              | Simple | Need to dispose with regulation |
|                              | No maintenance required | Biodegradability is a problem with a synthetic sorbents |
|                              | Synthetic sorbents made of polypropylene or polyurethane have good hydrophobic and oleophilic properties | Sinkage in water is a problem with natural adsorbents |

Table 12: Advantages and disadvantages of chemical remediation methods of marine oil spill

| Chemical treatment | Advantages | Disadvantages |
|--------------------|------------|---------------|
| Dispersants        | All weather conditions | No oil recovery |
|                    | Quick | Not effective on highly viscous, non-spreading and waxy oil |
|                    | Effective on wide range of oil | The localized and temporary increase in amount of oil in water concentration that could have an effect on the surrounding marine life |
|                    | Accelerates the degradation of the oil by natural processes | If dispersion is not achieved other response method effectiveness may reduce on less disperse oil |
|                    | Advance formulations have reduced the previous concern about toxicity | |
|                    | Less man power needed | |
|                    | Less expensive than mechanical methods | |
| Solidifiers        | All weather conditions | Lack of practical application |
|                    | Quick | Large amount required |
|                    | | Selected oil |
|                    | | No oil recovery |
|                    | | Not effective |

Table 13: Advantages and disadvantages of thermal remediation method of marine oil spill

| Advantages | Disadvantages |
|------------|---------------|
| Effective  | No oil recovery |
| Quick      | Fear of flashback and secondary fires |
| Requires minimal but some specialized equipment | Emit many petroleum related compound to air environment |
| Less manpower needed | Selected oil |
| Cost effective | Threaten for marine life, human and surrounding resources |
|              | Burn residue is more viscous than original product |
|              | Advisable to open water area or area covered with snow or ice |

Table 14: Advantages and disadvantages of bioremediation method of marine oil spill

| Advantages | Disadvantages |
|------------|---------------|
| All weather conditions | No oil recovery |
| Less manpower needed | Selected oils |
| Cost effective | Less survival capacity of microbes against oil contaminants |
| Mineralize oil to CO$_2$ and H$_2$O | Depends on the indigenous microorganisms present at the site |
| | Depends on available nutrient at the affected site |
Table 15: Evaluation criteria for marine oil spill remediation methods

| Criteria                              | Definition                              | Score |
|---------------------------------------|-----------------------------------------|-------|
| Efficiency                            | 95-99% removal                          | 20    |
| Time                                  | Removes contaminant within days          | 15    |
| Cost                                  | Relatively inexpensive                  | 15    |
| Impact on marine life                 | No health risks involved with method    | 10    |
| Level of difficulty                   | Easy to maintain and operate            | 10    |
| Weather                               | Favorable for application of method     | 10    |
| Reliability                           | The method works the majority of the time| 5     |
| Oil recovery                          | Chances of oil recovery                 | 5     |
| Effect on physical/chemical characteristics of oil | Do not change physical/chemical characteristics of oil | 5     |
| The need for further treatment        | No further treatment required            | 5     |

Table 16: Assessment of marine oil spill remediation methods

| Criteria                              | Physical methods | Chemical method | In-situ burning | Bioremediation |
|---------------------------------------|------------------|-----------------|-----------------|----------------|
|                                       | Booms            | Skimmers        | Adsorbents      | Dispersants    | Solidifiers    | burning        | Bioremediation |
| Efficiency                            | 10               | 10              | 10              | 13             | 7             | 17             | 18             |                |
| Time                                  | 10               | 10              | 8               | 8              | 8             | 7              | 13             | 7              |
| Cost                                  | 7                | 7               | 8               | 8              | 7             | 10             | 12             |                |
| Impact on marine life                 | 9                | 9               | 9               | 5              | 5             | 5              | 3              | 9              |
| Level of difficulty                   | 2                | 2               | 2               | 5              | 4             | 5              | 8              |                |
| Weather                               | 5                | 5               | 4               | 8              | 8             | 5              | 10             |                |
| Reliability                           | 2                | 2               | 2               | 3              | 2             | 3              | 4              |                |
| Oil recovery                          | 4                | 4               | 1               | 0              | 1             | 0              | 0              |                |
| Effect on physical/chemical characteristics of oil | 5                | 5               | 0               | 0              | 0             | 0              | 0              |                |
| The need for further treatment        | 1                | 1               | 1               | 4              | 0             | 3              | 5              |                |
| Total score                           | 55               | 55              | 45              | 54             | 42            | 59             | 73             |                |

Adsorbent with a moderate score (45) are good as final cleanup after mechanical recovery or in-situ burning. Solidifiers scored least (42) as they are practically least efficient and the more costly remediation method for oil spill.

Basically, the role of oil response method is to provide net environmental benefits. Each response method has its own advantages and disadvantages. However, the selection of oil spill response method depends on several factors including: type of oil, physical, biological and economical characteristics of the spill location, weather and sea conditions, amount of oil spilled and rate of spillage, depth of water column, time of the year and effectiveness of clean-up (EPA, 1999a). Based on the factors involved in the oil spill, different remediation techniques may be used every time. Generally, combination of mechanical, chemical and biological methods can deal efficiently with oil spill at much reduced cost.

**CONCLUSION**

The oil spill response method included booms, skimmers, dispersants, solidifiers, in-situ burning and bioremediation. The advantages and disadvantages of various oil spill response methods are summarized. Ten criteria were used for evaluation of several remediation methods: efficiency, time, cost, impact on marine life, reliability, level of difficulty, oil recovery, weather, effect on physical/chemical characteristics of oil and the need for further treatment. Based on the comparative analysis, oil recovery with mechanical methods and the application of dispersants followed by bioremediation is the most effective response for marine oil spill. The response primary objectives are to prevent the spill from moving onto shore, to reduce the impact on marine life and to speed the degradation of any uncovered oil. To maximize those objectives, the techniques used for remediation will depend on several factors including: type of oil, physical, biological and economical characteristics of the spill location, weather and sea conditions, amount spilled and rate of spillage, depth of water column, time of the year and effectiveness of cleanup method. In permissible weather condition, booms can be used to contain or divert the oil spill and that oil can be recovered using skimmers or simply burned off. Dispersants can be effective in breaking up light - or medium-density oil spills, although degree of mixing, degree of oil weathering and strength of the dispersant used are the most important factors for its performance. Adsorbents may be used for small-volume spills, or to “polish up” after other recovery methods or
in-situ burning. Bioremediation is a beneficial approach compared to the very expensive and labor intensive traditional processes. However, the uncontrollable variables in an oil spill (such as the composition of the oil, the indigenous microorganisms present at the site, the water characteristics such as temperature and the available nutrients at the affected site) may affect the results of the oil spill response methods.

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