

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 runoff, 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 regulations for individual countries that serve as prevention measures 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;

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Fingas *et al.*, 1995; Buist *et al.*, 1999; Lessard and Demarco, 2000; Holakoo, 2001). It becomes necessary to understand the quantity and characteristics of oil spill, age of oil, weather conditions, surrounding environment, ocean behavior and impact on marine life in order to select the best oil spill cleanup technique. Practically, all oil spill response methods have some environmental impacts, so selection of a cleanup method inherently necessitate some kind of tradeoff between the effects of the oil spill versus the side effects of the cleanup. In this study, some of the commonly used techniques for oil spill cleanup are discussed and a comparative analysis is performed on those techniques.

CHARACTERISTICS OF OIL SPILLS

Marine oil spills include crude oil, refined petroleum products (gasoline, diesel and other by-products), heavier fuels (bunker fuel) and any oily white refuse or waste oil (API, 2002). The severity of the impact of an oil spill depends on the quantity 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 ball 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) (Neiwpc, 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	Isobutane, 2, 2-dimethylbutane Neopentane, 3-ethylhexane
Cycloalkanes	Cyclohexane, n-propylcyclopentane, ethylcyclohexane
Straight chain alkenes	Cis-2-butene, 1-pentene, trans-2-heptane
Branched alkenes	2-methyl-1-butene, 4,4-dimethyl-cis-2-pentene
Cycloalkenes	Cyclopentene, 3-methylcyclopentene
Alkyl benzenes (includes BTEX compounds)	Benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene 1,2-dimethyl-3-ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4,5-tetramethyl benzene,
n-ropylbenzene	
Other aromatics	Indan, 1-methylindan, phenol
Polycyclic Aromatic Hydrocarbons (PAHs)	Naphthalene, acenaphthene, acenaphthylene, anthracene, benz [a] anthracene, benzo [a] pyrene, chrysene, coronene, dibenz (a,h) anthracene, fluoranthene, fluorene

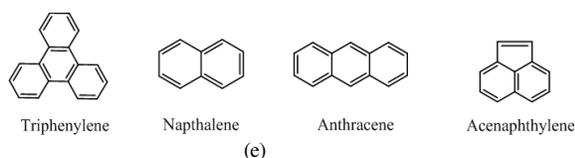
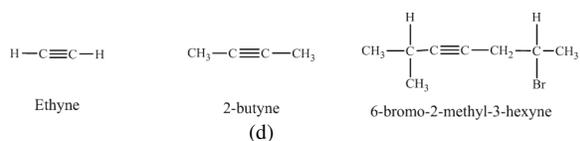
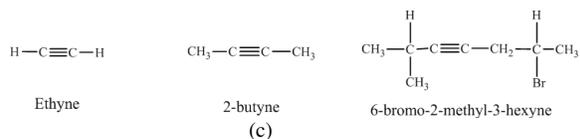
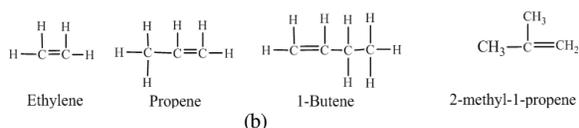
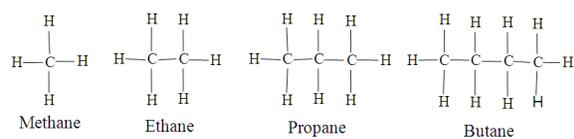


Fig. 1: IUPAC classification of hydrocarbons (Olah and Molnar, 2003) (a) Alkanes (b) Alkanes (c) Alkanes (d) Cyloalkanes (e) Aromatic hydrocarbons

Canadian prevention regulations: The Canada Oil and Gas Operations Act specifies that a development plan containing the scope, purpose, location, timing and nature of the proposed project for an oil pool or an oil field must

be approved before commencing the project construction. 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 revention 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: Booms 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).

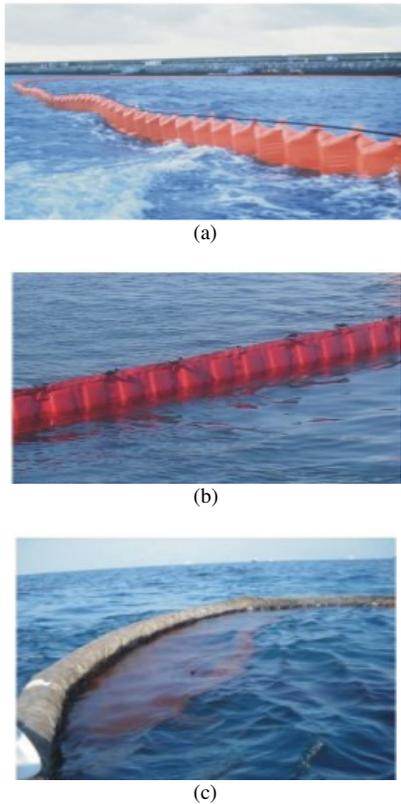


Fig. 2: Types of booms (OSS, 2010) (a) Fence boom (b) Curtain boom (c) Fire resistant boom

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 of 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.

Weir 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).

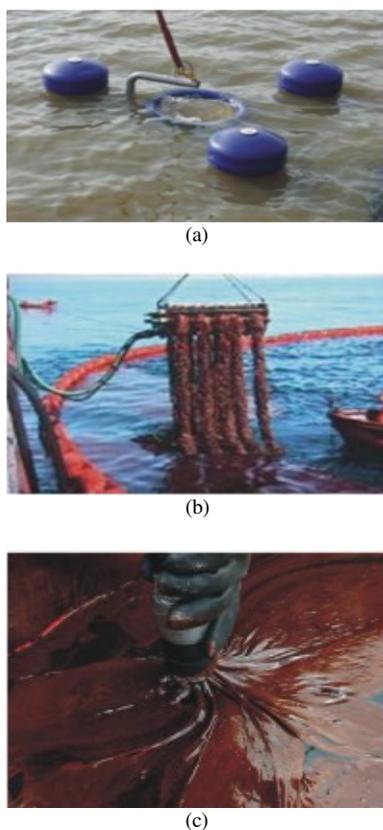


Fig. 3: Types of skimmers (USEPA, 1999b) (a) Weir skimmer (b) Oleophilic skimmer (c) Suction skimmer

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. Ghaly *et al.* (1999) reported a maximum adsorption of 6.7g 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 (4.5g 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, Tritom™, LTSA-35 MIL



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

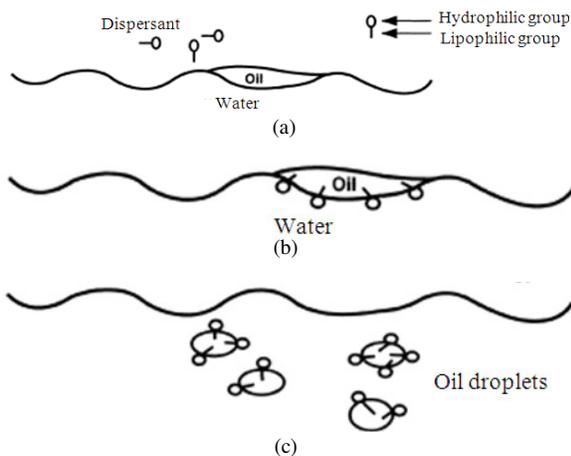


Fig. 5: Mechanism of dispersing oil (Lessard and Demarco, 2000) (Application of dispersant on oil) (b) Surfactant locates at interface (c) Oil slick disperse into the small droplets with minimal energy

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 dispersant/oil	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 ¹ to solidify	Toxicity ² (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

¹Values are the average of at least 3 measurements, average standard deviation is 6 ²Values are LC50 to Rainbow Trout in 96 h. this shows that all are insoluble and less than 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 (CO ₂)	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.*, 1979). 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	
<i>Arthrobacter spp.</i>	phenanthrene, methyl-tert-butyl ether, ethyl-tert-butyl ether and tert-amyl methyl ether
<i>Brevebacterium</i>	Asphaltenes, petroleum oil
<i>Brachybacterium</i>	
<i>Dietzia</i>	n-C12 to n-C38 alkane components
<i>Flavobacterium</i>	chlorophenols
<i>Janibacter</i>	Polycyclic hydrocarbon
<i>Mycobacterium</i>	Polycyclic hydrocarbon, pyrene, phenanthrene, diesel
<i>Nocardia spp.</i>	4-chlorobenzoate
<i>Pseudomonas spp.</i>	4-chlorobenzoate
<i>Rhodococcus</i>	Polychlorinated-biphenyl, hexadecane, trichloroethan, polycyclic hydrocarbon
Fungi	
<i>Aspergillus</i>	Pyrene, benzo(a)pyrene
<i>Candida</i>	Toluene
<i>Fusarium</i>	Methyl tert-butyl ether and tert-butyl alcohol
<i>Trichoderma</i>	phenanthrene
<i>Phanerochaete</i>	benzo(a)pyrene, phenanthrene and fluorene
<i>Mortierella</i>	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 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*, *corynbacterium*, *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 anitrogen and phosphorous 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 <i>Exxon Valdez</i> Disaster (1989) Prince William Sound, Alaska	Exxon mobil Corporation	41 million liters over 28,000 km ² \$31 million	Recreational fishing- loss of	Sea otters, harbor seals, bald eagles, seabirds harlequin ducks	Physical recovery methods (Booms and Skimmers)	US \$3 billion dollars	\$755.2 total lost due to ecosystem damage and depleted fish stock
			Commercial fishing-loss of \$300 million	Salmon fish	Dispersants (Corexit 7664, Corexit EC 9580, BP1100X)		
			Tourism-35% spending decreased		Bioremediation (Fertilizers: Inipol EAP 22 and Customblen)		
The <i>Prestige</i> oil spill (2002) Coast of Galicia of north-western Spain	Universe Maritime Ltd.	63700 tonnes Over 2,500 km ²	Commercial fisheriesand aquaculture-loss of €64.9 million	Sea birds, shark, marine mollusks, mussels, octopus, sardines, sole goose barnacle	Physical recovery methods (Booms and Skimmers)	US\$12billion dollars	Caused pollution in the area for ten years subsequent to the initial spill
			Tourism-loss of €133.8 million		Bioremediation (Fertilizer S200)		
Gulf of mexico oil spill (2010) Gulf of mexico	British Petroleum	780 million liters over 11,000 km ²	Recreational fishing-loss of \$138 million	Aquatic Invertebrates, fish, sea turtles, birds, beach mouse	Physical recovery methods (Booms and Skimmers)	Over US \$632 million by March 2011	Full assessment of the impact is still under investigation
			Commercial fishing-loss of \$18 million Tourism- loss of \$2.8 billion		<i>In-situ</i> burning		
					Dispersants (Corexit 9500, Corexit EC9527A)		

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

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 dolphins 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 in removal 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 Recovery of oil is possible High stability in waves	Expensive Labour intensive Complex Collected oil and need 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 Work well with debris or rough ice Less influenced by waves	Expensive Labour intensive Complex Collected oil and need further treatment Not able to deal with oil mixed with dispersants Possibility of clogging with floating debris Require maintenance Oil should be recovered before it is emulsified
Suction skimmers	Used with all kind of oil except inflammable Efficient in collecting oil residue Recovery of oil is possible	Expensive Labour intensive Complex Collected oil and need 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 Inexpensive Adsorbing capacity is 3-15 times of their weight in oil Some amount of recovery of oil is possible	Labour intensive Work under selected weather conditions Need to be disposed off Adsorb water along with oil which lead to their sinkage
Natural inorganics	Used with all kind of oil Inexpensive Adsorbing capacity is 4-20 times of their weight in oil Readily available	Readily available Labor intensive Need to dispose with regulation
Synthetic materials	Used with all kind of oil Simple No maintenance required Have good hydrophobic and oleophilic properties Can be reused after several times	Work under selected weather Potential health risk conditions Expensive Effective as final clean up step Labor intensive Used under selected weather conditions Need to be disposed off 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 Recovery of oil is possible	Expensive Labour intensive Complex Contain oil and must be used with other technologies Efficient in selected weather conditions
Skimmers	All kind of oil except Inflammable Recovery of oil is possible	Expensive 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 Effective as final clean up Step Simple No maintenance required Synthetic sorbents made of polypropylene or polyurethane have good hydrophobic and oleophilic properties	Moderate expensive Labor intensive Selected weather conditions Need to dispose with regulation Biodegradability is a problem with a synthetic sorbents 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 Quick Effective on wide range of oil Accelerates the degradation of the oil by natural processes Advance formulations have reduced the previous concern about toxicity Less man power needed Less expensive than mechanical methods	No oil recovery Not effective on highly viscous, non spreading and waxy oil The localized and temporary increase in amount of oil in water concentration that could have an effect on the surrounding marine life If dispersion is not achieved other response method effectiveness may reduce on less disperse oil
Solidifiers	All weather conditions Quick	Lack of practical application 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 Quick Requires minimal but some specialized equipment Less manpower needed Cost effective	No oil recovery Fear of flashback and secondary fires Emit many petroleum related compound to air environment Selected oil 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 Less manpower needed Cost effective Mineralize oil to CO ₂ and H ₂ O	No oil recovery Selected oils Less survival capacity of microbes against oil contaminants 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			
Efficiency	10	10	10	13	7		17	18
Time	10	10	8	8	8		13	7
Cost	7	7	8	8	7		10	12
Impact on marine life	9	9	9	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 compare 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.

REFERENCES

- Adebajo, M.O., R.L. Frost, J.T. Klopogge, O. Carmody and S. Kokot, 2003. Porous materials for oil spill cleanup: A review of synthesis and absorbing properties. *J. Porous Mater.*, 10: 159-170. DOI: 10.1023/A: 1027484117065.
- Alther, G.R., 2002. Removing oils from water with organo clays. *J. Am. Water Works Association*, 94: 115-121.
- Annunciado, T.R., T.H.D. Sydenstricker and S.C. Amico, 2005. Experimental investigation of various vegetable fibers as sorbent materials for oil spills. *Marine Pollution Bulletin*, 50: 1340-1346. DOI: 10.1016/j.marpolbul.2005.04.043.
- API, 2002. Arctic and Marine Oil spill Programme. American Petroleum Institute. At the request of the Marine Pollution Control Unit (mPCU) of the Coastguard Agency, UK Department of Transport, UK. pp: 100-110.
- ARPEL, 2006. ARPEL Environmental Guideline: A Guide to In-situ Burning of Oil Spills on Water, Shore and Land. ARPEL Emergency Response Planning Working Group. <http://www.cleancaribbean.org/userfiles/ARPEL%20Insitu%20Burning%20Guideline.pdf>.
- ASTDR, 1995. Chemical and physical information of oil. Toxic substance Portal. <http://www.atsdr.cdc.gov/toxprofiles/tp75-c3.pdf>.
- Atlas, R.M., 1995. Petroleum biodegradation and oil spill bioremediation. *Marine Pollution Bulletin*, 31: 178-182. DOI: 10.1016/0025-326X (95)00113-2.
- Atlas, R.M. and C.E. Cerniglia, 1995. Bioremediation of petroleum pollutants-diversity and environmental aspects of hydrocarbon biodegradation. *Bioscience*, 45: 332-338. <http://www.jstor.org/stable/1312494>.
- Atlas, R.M. and R. Bartha, 1973. Stimulated biodegradation of oil slicks using oleophilic fertilizers. *En. Sci. Technol.*, 7: 538-541. DOI: 10.1021/es60078a005.
- Banerjee, S.S., M.V. Joshi and R.V. Jayaram, 2006. Treatment of oil spill by sorption technique using fatty acid grafted sawdust. *Chemosphere*, 64: 1026-31. DOI: 10.1016/j.chemosphere.2006.01.065.
- Bragg, J.R., R.C. Prince, E.J. Harner and R.M. Atlas, 1994. Effectiveness of bioremediation for the Exxon Valdez oil spill. *Nature*, 368: 413-418. DOI: 10.1038/368413a0.
- Buist, I., J. McCourt, S. Potter, S. Ross and K. Trudel, 1999. In situ burning. *Pure Applied Chemistry*. 71: 43-65. <http://www.iupac.org/publications/pac/pdf/1999/pdf/7101x0043.pdf>.
- Capotorti, G., P. Digianvincenzo, P. Cesti, A. Bernardi and G. Guglielmetti, 2004. Pyrene and benzo (a) pyrene metabolism by an *Aspergillus terreus* strain isolated from a polycyclic aromatic hydrocarbons polluted soil. *Biodegradation*, 15: 79-85. DOI: 10.1023/B:BIOD.0000015612.10481.e6.
- Choi, H. and R.M. Cloud, 1992. Natural sorbents in oil spill cleanup. *Environ. Sci. Technol.*, 26: 772-776. DOI: 10.1021/es00028a016.
- Clayton, C., 2005. Chemical and physical properties of petroleum. *Petroleum Geology*, 10: 248-260.
- CWS, 2010. National policy on oiled birds and oiled species at risk. Canada Wildlife Services Environment Canada. <http://www.ec.gc.ca/eeue/default.asp?lang=en&n=A4DD63E4>.
- Dahl, W.A., R.R. Lessard and E.A. Cardello, 1996. Solidifiers for oil spill response. In: *The 1996 3rd International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Part 1 (of 2)*, New Orleans, LA, USA, pp: 803-810.
- Daling, P.S. and T. Strøm, 1999. Weathering of oils at sea: model/field data comparisons. *Spill Sci. Technol. Bulletin*, 5: 63-74. DOI: 10.1016/S1353-2561(98)00051-6.
- Davidson, W., K. Lee and A. Cogswell, 2008. *Oil Spill Response: A Global Perspective*. NATO Science for Peace and Securities Series-C: Environmental Security. Springer: Netherlands, pp: 24. ISBN-13: 978-1402085642.
- Davis, D.W. and R.J. Guidry, 1996. Oil spills and the state responsibilities, *Basin Research Institute Bulletin*, 6: 60-68. DOI: 10.1016/S1353-2561(99)00081-X.
- Davies, L., A. Lewis, T. Lunel and A. Crosbie, 1998. *Dispersion of emulsified oil at sea*. AEA Technology, Oxfordshire, UK. ISBN: 1 0-7058-1770-9.
- Delaune, R.D., C.W. Lindau and A. Jugsujinda, 1999. Effectiveness of "Nochar" solidifier polymer in removing oil from open water in coastal wetlands. *Spill Sci. Technol. Bulletin*, 5: 357-359.

- Deschamps, G., H. Caruel, M.E. Borredon, C. Bonnin and C. Vignoles, 2003. Oil removal from water by sorption on hydrophobic cotton fibers-Study of sorption properties and comparison with other cotton fiber-based sorbents. *En. Scie. Technol.*, 37: 1013-1015. DOI: 10.1021/es020061s.
- Diez, I., A. Secilla, A. Santolaria and J.M. Gorostiaga, 2009. Ecological monitoring of intertidal phytobenthic communities of the Basque Coast (N. Spain) following the Prestige oil spill. *En. Monitoring Assessment*, 159: 555-575. DOI: 10.1007/s10661-008-0651-5.
- Ding, Z., J.T. Klopogge, R.L. Frost, G.Q. Lu and H.Y. Zhu, 2001. Smectites and porous pillared clay catalysts. Part 2: A review of the catalytic and molecular sieve applications. *J. Porous Materials*, 8: 273-293. DOI: 10.1023/A: 1013113030912.
- DJC, 2010. Canada Oil and Gas Operations Act, Department of Justice, Retrieved on 13th March from <http://lois.justice.gc.ca/PDF/Statute/O/O-7.pdf>.
- Fingas, M., W. Duval, G. Stevenson and S. Galenzoski, 1979. The basics of oil spill cleanup: With particular reference to Southern Canada. Environmental Emergency Branch, Environmental Protection Service, Environment Canada, Minister of Supply and Services Canada, Hull, Quebec.
- Fingas, M.F., R. Stoodley and N. Laroche, 1990. Effectiveness testing of spill-treating agents. *Oil Chemistry Pollution*, 7: 337-348. DOI: 10.1016/S0269-8579 (05) 80048-6.
- Fingas, M.F., D.A. Kyle, N. Larouche, B. Fieldhouse, G. Sergy and G. Stoodley, 1995. Effectiveness Testing of Oil Spill-treating Agents. ASTM Special Technical Publication 1252, pp: 286-298.
- Fingas, M. and B. Fieldhouse, 2011. Review of Solidifiers. *Oil Spill Sci. Technol.*, 713-733. DOI: 10.1016/B978-1-85617-943-0.10014-0.
- Ghaly, R.A., J.B. Pyke, A.E. Ghaly and V.I. Ugursal, 1999. Remediation of diesel-oil-contaminated soil using peat. *Energy Sources*, 21: 785-799. DOI: 10.1080/00908319950014344.
- GPC, 2010. Curtain Booms. Global Spill Control. Retrieved on 7th March from <http://www.globalspill.com/uploads/downloads/page75oil-containment-boomscurtain-booms.pdf>.
- Hammoud, A.H., 2001. Enhanced oil spill recovery rate using the weir skimmer. Retrieved on 26th February, 2010 from <http://www.epa.gov/oem/docs/oil/fss/fss06/hammoud.pdf>.
- Hoch, M., 2010. New estimate puts gulf oil leak at 205 million gallons, PBS. Retrieved on March 9th, 2011 from <http://www.pbs.org/newshour/rundown/2010/08/new-estimate-puts-oil-leak-at-49-million-barrels.html>.
- Holakoo, L., 2001. On the capability of Rhamnolipids for oil spill control of surface water. Unpublished dissertation in partial fulfillment of the requirements for the degree of Master in applied Science, Concordia University, Montreal, Canada.
- Hussein, M., A.A. Amer, I. Ib. Sawsan, 2009. Oil spill sorption using carbonized pith bagasse. Application of carbonized pith bagasse as loose fiber. *Global NEST J.*, 11: 440-448. Retrieved on March 10th 2011 http://www.gnest.org/journal/Vol11_no4/440-448_539_Amer_11-4.pdf.
- ITOPF. 2010. Statistics. The International Tanker Owners Pollution Federation. Retrieved on March 10th, 2010 from <http://www.itopf.com/information-services/>
- Jackson, L.P., 2010. Statement by EPA Administrator Lisa P. Jackson from Press Conference on dispersant use in the Gulf of Mexico with US Coast Guard Rear Admiral Landry. Released on May 24th, 2010. Retrieved on March 10th, 2010 from <http://www.epa.gov/bpspill/dispersants/statement-dispersant-use-may24.pdf>.
- Jarre, W., M. Marx and R. Wurm, 1979. Polyurethanschaume mit hohem Olsorptionvermögen. *Die Angewandte Makromolekulare Chemie*, 78: 67-74. DOI: 10.1002/apmc.1979.050780104.
- Jensen, H., T.A. McClimans and B.O. Johannessen, 1995. Evaluation of weir skimmers without testing, Eighteenth AMOP Technical Seminar Proceedings, Edmonton, Alberta, Canada, pp: 689-704.
- Jimenez, N., M. Vinas, J. Sabate, S. Diez, J. M. Bayona and A.M. Solanas *et al.*, 2006. The Prestige oil spill. 2. Enhanced biodegradation of a heavy fuel oil under field conditions by the use of an oleophilic fertilizer. *En. Scie. Technol.*, 40: 2578-2585. PMID: 16683595.
- Karakasi, O.K. and A. Moutsatsou, 2010. Surface modification of high calcium fly ash for its application in oil spill cleanup. *Fuel*, 89: 3966-3970. ISSN: 0016-2361.
- Larson, H., 2010. Responding to oil spill disasters: The regulations that govern their response. Retrieved on 26th February, 2010 from http://www.wise-intern.org/journal/2010/HattieLarson_Presentation.pdf.
- Lee, J., 1997. TED Case studies: Exxon Valdez disaster. American University. Retrieved on March 9th, 2011 from <http://www1.american.edu/TED/exxon.htm>.
- Lessard, R.R. and G. Demarco, 2000. The significance of oil spill dispersants. *Spill Sci. Technol. Bulletin*, 6: 59-68. DOI: 10.1016/S1353-2561(99)00061-4.

- Lobon, C.M., C. Fernandez, J. Arrontes, J.M. Rico and J.L. Acuna *et al.*, 2008. Effects of the 'Prestige' oil spill on macroalgal assemblages: Large-scale comparison. *Marine Pollution Bulletin*, 56: 1192-1200. DOI: 10.1016/j.marpolbul.2008.02.009.
- Lucas, Z. and C. MacGregor, 2006. Characterization and source of oil contamination on the beaches and seabird corpses, Sable Island, Nova Scotia, 1996-2005. *Marine Pollution Bulletin*, 52: 778. PMID: 16403538.
- McMurry, J., 2004. *Organic Chemistry*. Thomson-Brooks and Cole, Belmont, CA. pp.1 1176. ISBN-13: 978-0534420055.
- Mullin, J.V. and M.A. Champ, 2003. Introduction/Overview to In Situ Burning of Oil Spills. *Spill Sci. Technol. Bulletin*, 8: 323-330. DOI: 10.1016/S1353-2561(03) 00076-8.
- NEIWPC, 2003. L.U.S.T. LINE-A report on federal and state programs to control leaking underground storage tanks. Bulletin 44, New England Interstate Water Pollution Control Commission. Retrieved on 22nd march from 2007. http://www.neiwpc.org/lustline/lustline_pdf/LustLine44cvr.pdf.
- Nomack, M. and C. Cleveland, 2010. Oil spill control technologies. In: *Encyclopedia of Earth*. <http://www.eoearth.org/articles/view/158385/?topic=50366>.
- Nordvik, A.B., J.L. Simmons, K.R. Bitting, A. Lewis and T. Strom-Kristiansen. 1996. Oil and water separation in marine oil spill clean-up operations. *Spill Sci. Technol. Bulletin*, 3: 107-122. DOI: 10.1016/S1353-2561(96)00021-7.
- NRC, 1989. *Using Oil Spill Dispersants on the Sea*. National Research Council, National Academy Press, Washington, DC. ISBN-13: 978-0-309-09045-2.
- Oil and Gas UK, 2011. Oil pollution emergency planning and reporting. Accessed on February 28th, 2011 from http://www.ukooaenvironmentallegislation.co.uk/Contents/Topic_Files/Offshore/OSCP.htm
- Olah, G.A. and A. Molnar, 2003. *Hydrocarbon Chemistry* (2nd edition). Wiley Interscience Publications. pp: 1-50. ISBN: 0471417823, 9780471417828.
- OSAT-2, 2011. Summary report for fate and effects of remnant oil in the beach environment. Operational Science Advisory Team, Gulf Coast Incident Management Team. Retrieved on March 17th, 2011 from <http://www.restorethegulf.gov/sites/default/files/u316/OSAT-2%20Report%20no%20ltr.pdf>.
- OSS, 2010. Oil spill solution. Retrieved on 26th February, 2010 from <http://www.oilspillsolutions.org/booms.htm>
- Payne, J.R. and C.R. Philips, 1985. Petroleum spills, in the marine environment-the chemistry and formation of water-in-oil emulsions and tar ball. Lewis, Chelsea, Michigan pp: 1-24.
- Potter, S. and J. Morrison, 2008. *World catalogue of oil spill response products* (9th Edn). S.L. Ross Environmental Research Ltd. Ottawa, Canada, pp:1-42.
- Restore Gulf, 2011. Oil spill cost and reimbursement fact sheet, [RestoreTheGulf.gov](http://www.restorethegulf.gov). Retrieved on March 17th, 2011 from <http://www.restorethegulf.gov/release/2011/03/11/oil-spill-cost-and-reimbursement-fact-sheet>.
- Siang, M.H.E., 1998. Evoikos oil spill-the Singapore experience. In: *Oil Spill Response '98*. IBC Asia Limited, Singapore.
- Sitting, M., 1974. *Oil Spill Prevention and Removal Handbook*. Noyes Data Corporation: Park Ridge, IL, USA. pp: 18.
- Sugai, S.F., J.E. Lindstrom and J.F. Braddock, 1997. Environmental influences on the microbial degradation of Exxon Valdez oil on the shorelines of Prince William Sound, Alaska. *En. Sci. Technol.*, 31: 1564-1572. DOI: 10.1021/es960883n.
- Swannell, R.P.J., K. Lee and M. McDonagh, 1996. Field evaluations of marine oil spill bioremediation. 60: 342-365. PMID: 8801437.
- Tangley, L., 2010. Bird habitats threatened by oil spill, National Wildlife Federation. Retrieved on March 9th, 2011 from <http://www.nwf.org/News-and-Magazines/National-Wildlife/Birds/Archives/2010/Oil-Spill-Birds.aspx>.
- TC, 2010. Environmental response systems: Managing Canada's marine oil spill preparedness and response regime-TP 14471 E. Transport Canada. Retrieved on 13th march from <http://www.tc.gc.ca/eng/marinesafety/tp-tp14471-menu-1024.html>.
- Teas, Ch., S. Kalligeros, F. Zanikos, S. Stournas and E. Lois *et al.*, 2001. Investigation of the effectiveness of absorbent materials in oil spills clean up. *Desalination*, 140: 259-264. DOI: 10.1016/S0011-9164(01)00375-7.
- UK Government, 1998. *The merchant shipping (Oil Pollution Preparedness, Response and Co-operation Convention) Regulations 1998*. Retrieved on February 28th, 2011 from http://www.ukooaenvironmentallegislation.co.uk/Contents/Topic_Files/Offshore/OSCP.htm.

- UK Government, 2001. The Control of Pollution (Oil Storage) (England) Regulations 2001. Retrieved on February 28th, 2011 from <http://www.legislation.gov.uk/ukxi/2001/2954/contents/made>.
- UK Government. 2005. The Offshore Petroleum Activities (Oil Pollution Prevention and Control) Regulations 2005. Retrieved on February 28th, 2011 from <http://www.legislation.gov.uk/ukxi/2005/2055/contents/made?view=plain>.
- US Senate. 2002. Federal Water Pollution Control Act. 33 U. S. C. 1251 et seq. Retrieved on February 28th, 2011 from <http://www.epa.gov/lawsregs/laws/cwa.html>.
- USEPA. 1999a. Behavior and effects of oil spills in aquatic environments: In Understanding oil spills and oil spill response. Environmental Protection Agency, USA. Retrieved on 27th February from http://www.epa.gov/osweroe1/docs/oil/edu/oilspill_book/chap1.pdf.
- USEPA, 1999b. Mechanical containment and recovery of oil following a spill Retrieved on 7th March from http://www.epa.gov/osweroe1/docs/oil/edu/oilspill_book/chap2.pdf.
- USEPA. 2010a. Spill Prevention, Control and Countermeasure (SPCC) Regulation, A facility owner/operator's guide to oil pollution prevention, 40 Code of Federal Regulation part 112. United States Environmental Protection Agency. Retrieved on February 28th, 2011 from <http://www.epa.gov/emergencies/guidance.htm#spcc>.
- USEPA. 2010b. EPA releases reports on dioxin emitted during Deepwater Horizon BP spill / reports find levels of dioxins created during controlled burns were below levels of concern. Release on December 11th, 2010. <http://yosemite.epa.gov/opa/admpress.nsf/d0cf6618525a9efb85257359003fb69d/6a2165dcf5f0bb5f852577d9005acf94!OpenDocument>.
- USEPA, 2011a. Sorbents. Emergency management. Retrieved on 7th March from <http://www.epa.gov/OEM/content/learning/sorbents.htm>.
- USEPA, 2011b. National contingency plan product schedule. Retrieved on 8th March from http://www.epa.gov/emergencies/content/ncp/product_schedule.htm.
- USEPA, 2011c. Questions and answers about the BP oil spill in the gulf coast. United States Environmental Protection Agency. <http://www.epa.gov/bpspill/qanda.html#dispersant>.
- USWFS, 2010. Deepwater Horizon Response consolidated fish and wildlife collection report (November 2, 2010). U. S. Fish and Wildlife Service and National Oceanic and Atmospheric Administration. <http://www.restorethegulf.gov/sites/default/files/documents/pdf/Consolidated%20Wildlife%20Table%20110210.pdf>.
- Venosa, A.D., J.R. Haines, W. Nisamanepong, R. Govind and S. Pradhan *et al.*, 1991. Screening of commercial inocula for efficacy in stimulating oil biodegradation in closed laboratory system. *J. Haz. Mat.*, 28: 131-144. DOI: 10.1016/0304-3894(91)87012-Q
- Vergetis, E., 2002. Oil pollution in Greek seas and spill confrontation means-methods, National Technical University of Athens, Greece.
- Ventikos, N.P., E. Vergetis, H.N. Psaraftis and G. Triantafyllou, 2004. A high-level synthesis of oil spill response equipment and countermeasures. *J. Haz. Mat.*, 107: 1-58. PMID: 15036642.
- Webb, C.C., 2005. Bioremediation of marine oil spill. <http://home.eng.iastate.edu/~tge/ce421-521/CaseyWebb.pdf>.
- Yang, S.Z., H.J. Jin, Z. Wei, R. He and X. Ji, *et al.*, 2009. Bioremediation of oil spills in cold environments: A review. *Pedosphere*. 19: 371-381. DOI: 10.1016/S1002-0160(09)60128-4.
- Zahed, M.A., H.A. Aziz, M.H. Isa and L. Mohajeri, 2010a. Effect of initial oil concentration and dispersant on crude oil biodegradation in contaminated seawater. *Bulletin En. Contamination Toxicol.*, 84: 438-442. DOI: 10.1007/s00128-010-9954-7.