



STUDY ON EFFECTIVE METHODS FOR OIL PRODUCTS CLEANING

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Abstract

The hydrocarbon compounds which are discharged in to the environment are affected by various physical, chemical and biological alterations. Oil spill are a global concern due to the environmental impacts. The main concern of the environmental experts is the pollution from the production and transfer of oil products in different ecosystems. Among the consequences of releases of various types of crude oil, it is possible to mention the adverse environmental effects, the death of marine organisms, the inappropriateness of seafood for human consumption and the reduction of the power of flying sea birds due to the impregnation of feathers into petroleum products. The cost of oil remediation depends on relatively large parameters such as the type of oil products that leads to pollution, the amount and severity of the contamination, the time of the accident, the location of the incident, the geographical, political, economical, physical and biological location of the accident. Therefore, in this paper reviews the latest methods for removing the hydrocarbon compounds from water, such as bioremediation technique, dispersants, sorption, skimmers and booms will be discussed.

Keywords : Oil Spill, Oil Products, Environmental effects, bioremediation, Dispersants, Sorption, Skimmers, Booms, sorbents.

Introduction

Production and refining of oil usually involves hydrocarbon emission, thus having negative impact on the environment and resulting in environmental disorder and ecosystem imbalance [1]. Oil and chemical spill accidents can be caused by human mistakes and carelessness, deliberate acts such as vandalism, war and illegal dumping, or by natural disasters such as hurricanes or earthquakes. Offshore and shoreline waters can be polluted by oil drilling operations, accidents involving oil tankers, runoffs from offshore oil explorations and productions, spills from tanker loading and unloading operations [2]. The hazards of oil spills to marine and freshwater environments have increased by the increase in production and transportation of crude oil all over the world. Oil spills have a worldwide concern due to its influence environmentally and economically. Hazardous chemicals are released from oil spills such as polycyclic aromatic hydrocarbons which have harmful effect to aquatic and human lives and may require too much time for healing [3]. Oil Spill Production and transportation of HC-hydrocarbons are always accompanied by the negative impact on the environment. Most large-scale disasters are typical for sea transportations of hydrocarbons. Volumes of oil pollution on a global scale are 20 million tons of oil per year. There is no an oil producing company without problems of oil pollution of environment, including water bodies. For example, the method of calculating the amount of damage caused to water bodies due to the violation of water legislation was approved in April 13, 2009. According to order of the Russian Ministry of Nature No 87; taxes for harm at oil pollution of water bodies by accidents are to 3.0 million rubles per ton of oil spill [4]. Most of the oil and petroleum products used in Canada and the United States are for transportation. According to trends in petroleum usage, this is not likely to decrease much in the future. Industry uses

oil and petroleum derivatives to manufacture such vital products as plastics, fertilizers, and chemical feed stocks, which will still be required in the future. In fact, the production and consumption of oil and petroleum products are increasing worldwide, and the threat of oil pollution is increasing accordingly. The movement of petroleum from the oil fields to the consumer involves as many as 10 to 15 transfers between many different modes of transportation including tankers, pipelines, railcars, and tank trucks. Oil is stored at transfer points and at terminals and refineries along the route. Accidents can happen during any of these transportation steps or storage times [5]. It is no exaggeration that oil fuels the world's economy, and it is used on a staggering scale. World production was some 80 Mbbl (11 Mt/day) by the end of 2000, and this is expected to increase by 1.9%/year in the next decade. Approximately 40% of the world's oil travels by water at some time between its production and final consumption, and again the volumes are staggering. For example, the US imported 350 000 t of oil per day from the Middle East alone in 1999. Unfortunately, despite the best efforts of the major part of the petroleum industry, a small amount is inevitably spilled. Fortunately this is only a tiny fraction of that transported, and there has been a general improvement in oil spill statistics in the last two decades [6]. Table 1, gives some information about major oil spills which were happened in the world by order of quantity. Crude oil spilled to land or marine environment is instantly subject to a verity of physical, chemical and biological changes. At sea, crude oil, which is usually lighter than water, will spread over the water surface area. Subsequently, oil film layer with about 1 mm thickness forms on the water surface. The rapidity of propagation of the oil on water surface is subject to the type of oil, water temperature, and weathering processes such as; atmospheric temperature, wind and flow Lighter components of the oil tend to

evaporate to the atmosphere. The degree of evaporation and the speed at which it occurs depend upon the volatility of the oil [7]. Releasing oil into the sea, not only harmful for aquatic life, but also threatens the lives of other drought-related food disturbances through food chains [8]. Figures 1 and 2, show the oil spill clean up efforts and the environmental impacts of oil products on birds in Exxon Valdez accident. Due to hazards of oil field effluents on environment, treatment is necessary before disposal. Treatment of these effluents may result in improved oil/water separation, improved water quality, oil recovery, water reuse, protection of downstream facilities and environmental permit compliance [9]. Oil spill in water bodies remains a serious concern to both local and international communities. Regulations have done much to prevent oil waste contamination during transport on the open seas. When crude oil spill in water surface does occur, the issue is not only the cleaning of the aquatic environment but also recovery of this precious commodity. Hence, any oil absorbing material used must also be able to release the oil [10]. There are several

separate phases to cleanup any types of oil products: prevention and minimization, containment, recovery or treatment, and temporary storage [11]. The adverse impacts to ecosystems and the long-term effects of environmental pollution by these and other releases call for an urgent need to develop a wide range of methods for oil clean up oil from oil impacted areas especially as the effectiveness of oil treatment varies with time, the type of oil and spill, the location and weather conditions [12].As previously mentioned, physical, chemical and biological methods are used to clean up oil spill. Adsorption, skimmers, boomers etc are used to physically remove oil products. In Situ burning, dispersion and solidifiers are used to chemically clean up [13]. Different techniques for oil spill clean up are summarized in Table 2.

So in this review, the latest methods for removing the Oil Products from water system are described. Then, the advantages and disadvantages of each technique are briefly mentioned.

Table 1 : Major oil spills in the world by order of quantity [14]

| Barrels | Spill Type | Location | Date |
|-----------------------|---------------------------------|-------------------------------------|---------------------|
| 9 000 000 | Lakeview Gusher | U.S Kern County, California | 5/14/1910-9/10/1911 |
| 4 100 000 – 4 300 000 | Deepwater horizon | U.S.Gulf of Mexico | 4/20-7/15.2010 |
| 2 000 000 – 6 000 000 | Gulf War oil spill | Iraq, Persian Gulf and Kuwait | 1/23/1991 |
| 3 329 000- 3 520 000 | Ixtoc I | Mexico, Gulf of Mexico | 6/3/1979-3/23/1980 |
| 2 105 000 | Atlantic Empress/Aegean Captain | Trinidad and Tobago | 7/19/1979 |
| 2 090 000 | Fergana Valley | Uzbekistan | 3/2/1992 |
| 1 907 000 | Nowruz Field Platform | Iran, Persian Gulf | 2/4/1983 |
| 1 635 000 | Amoco Cadiz | France, Brittany | 3/16/1983 |
| 1 056 000 | MT Haven | Italy, Mediterranean Sea Near Genoa | 4/11/1991 |
| 968 000 | Odyssey | Canada | 11/10/1988 |
| 257 000 – 750 000 | Exxon Valdez oil tanker | U.S. Prince Wiliam Sound, Alaska | 3/24/1989 |

Table 2 : Phases of oil spill cleanup [11]

| Activity | Examples |
|-----------------------------|---|
| Prevention and Minimization | Patches & plugs, good equipment design, Safe operating procedures, lightering |
| Containment | Oil booms, Chemical herder |
| Recovery or Treatment | Oil Skimmers, sorbents, chemical dispersants, neutralization |
| Temporary Storage | Barges, flexible bags, skimmer’s tanks |



Fig. 1 : Alaska, Prince Wiliam Sound, Knight Island. Exxon Valdez oil spill clean up efforts in the once pristine bays of Prince Wiliam Sound [15]



Fig. 2 : Environmental impacts of oil spills ,Exxon Valdez Oil Spill Trustee Council [16]

1. Dispersant

These are chemical compositions made from surfactants and other additives that help to reduce the interfacial surface tension between oil and water. For effectiveness, dispersants need to be sprayed uniformly with reasonable concentration. The following basic criteria are essential for effective dispersal of oil to take place chemically : (i) Dispersant must be deposited on the oil slick, (ii) Dispersant must diffuse to the oil/water interface or mix with the oil, (iii) It must have an optimum concentration that will initiate a maximum decrease in water-oil surface tension and (iv) It must be able to disperse the oil into droplets. The uses of dispersants are restricted or regulated because of their toxic nature [17]. In most cases of the oil spill accidents in the past, spilled oil was treated with oil dispersant for its effect. Quick treatment with oil dispersants can prevent spilled oil from spreading and reduce fishery damage to a minimum. However, the use of oil dispersants is strictly restricted nowadays in the world. With regard to the merits and demerits of oil dispersant, viewed from chemical and biological standpoints, it is better to leave it to specialists, arguments. It should be noted that the researches showed the oil spill dispersant is not so harmful to oceanic life as people argue in the world. It is true that in the case where oil dispersants are used in a massive oil spill, fish living in the vicinity of the surface of the water suddenly disappear from neighbouring waters and that a catch of mid-water fish also decrease. However, as far as oil dispersants of an emulsification and dispersion type which are being produced at present are concerned, it can be believed that their harmful effects will not extend over a long period of time [18].

As previously mentioned, the methods used to fight accidental spills of oil and oil products can be classified as mechanical, chemical, physicochemical and biological. From economic point of view, it is advisable to use the methods which allow collecting and utilizing the petroleum products. Sorbent materials have recently been found to be a successful, innovative way to clean oil spills [19]. In 2014, Idris *et al.* explained that sorbents are materials that have a high affinity for oil while being able to repel water. The researchers performed tests on empty palm fruit branches, which is typically disposed as waste. This tissue was found to serve as an economical and effective way to remove oil. This sorbent material is important to consider for large-scale operations as it is not only effective for cleanup but is also cost-effective [20]. Absorbents are attractive for some applications because of the possibility of collection and complete removal of the oil from the oil spill site. The addition of absorbents to oil spill areas facilitates a change from liquid to semi-solid phase and once this change is achieved, the removal of oil by sorbent structure then becomes much easier. Furthermore, these materials can, in some cases, be recycled [12]. In fact, Among all of the oil spill cleanup methods that show good results in removal of oil from the water surface, adsorption is considered to be one of the most efficient. Nowadays, about two hundred of various sorbents are produced. Sorbents can be divided into some basic groups: inorganic, natural organic and organo-mineral, and synthetic. Different types of sorbents are listed in Table 3.

Table 3 : Types of oil spill sorbents [21]

| Organic Vegetable | Organic Synthetic | Inorganic Mineral | Categories |
|---|--------------------------------|--|------------------|
| Cotton Fiber- Straw-Feathers- Sawdust-Wood Fiber | Polypropylene- Polyurethane | Glass-Wool- Sand- Graphite- Silica-Zeolites | Sorbent Types |

Oil spill cleanup sorbents, in particularly, shall satisfy hard requirements taking into account their ability to take up oil but not water and to become quickly saturated by oil, being the most effective in recovering oil. Moreover, it should have and retain buoyancy, remaining a float even when saturated with oil. When choosing sorbents for cleaning up spills, available oil recovery capacity of the sorbent and the oil sorbent material disposal method shall be considered as well [1].

2.1 Oil Sorbent Types

As previously mentioned, Oil sorbents material can be categorized in to three major classes: Inorganic mineral products, organic synthetic products and organic vegetable products [22].

2.1.1. Natural organic sorbents

Natural sorbents include organic and inorganic materials. Organic sorbents include straw, corn skin, peanut shell, fiber and peat which is made of rotten moss. Often sorbents structured into sheets, booms, or pads, which are reusable and easier to control in either open or confined spaces. The collection ability of these materials after application in an oil spill cleanup should be increased by such structures. The production of sheets or pads of cotton – containing non-wovens is of particular interest because of the easy availability, steady supply, and price compatibility of raw cotton. Low grade cotton fiber, which are generally unsuitable for apparel production, can be used in such an application [23]. Wood and lignocellulosic compounds have great potential for adsorbing oil pollution. Due to high physical sorption, the use of these materials will be effective in preventing the rapid spread of contamination. For example, in the French Canyon oil pollution accident, about 20,000 pieces of wood were spread over oil spills and then they were collected the coast. The cheap and availability, renewable, and biocompatible nature of these sorbents makes them more desirable [24]. The effectiveness of the sorbents in saturated aquatic environments would be enhanced if the density of the hydroxyl functional groups is decreased. The hydroxyl functionality of these fibers can be reduced by chemical modification such as acetylation, methylation, cyanoethylation, benzylation, acrylation, acylation, etc [25]. As already explained, natural products, such as cotton, kapok, rice straw, etc. are abundant, low-cost, biodegradable, non-toxic materials and therefore ideal for oil sorption in oil spill treatment. In fact, Cheaper and readily biodegradable plant biomass such as kapok fiber, cattail fiber, *Salvinia* sp., wood chip, rice husk, coconut husk and bagasse are used as inserts to remove oil from the storm water runoff of gas station effluent, with 70% greater oil removal capacity compared to synthetic polymer fiber sorbent, due to the presence of sample void spaces in their loose fiber structure and hydrophobicity [26]. Utilization of acetylated kapok fibers on the sorption of oil in water has been investigated by Wang *et al.*, in 2013. The results indicated that the acetylated kapok fibers exhibited a better oil sorption capacity than raw

fibers for diesel and soybean oil. Compared with high viscosity soybean oil, low viscosity diesel shows a better affinity to the surface of acetylated fibers [27]. In 2012, Kenes *et al.* studied the effectiveness of thermally treated rice husks for petroleum adsorption. The petroleum sorption capacity was examined for thermally treated rice husks, which mainly composed of amorphous SiO₂. Results showed that the petroleum sorption capacity of this material prepared at 700 °C was 15 g/g for heavy crude petroleum which means the oil sorption capacity of the rice husk increased after thermal treatment. In fact, the oil sorption depends on the adsorbent material and the adsorbate type. Also the results from experimental data showed the surface area of the rice husk increased with increasing heating temperature [28]. In another study, Wang *et al.* used hollow carbon fibers derived from natural cotton to remove oil spill by. Maximum oil sorption tests indicated that Carbonized cotton fibers showed the highest oil adsorption capacity and could absorb up to 32–77 times its own weight in pure oils and organic solvents, suggesting an increase of 27–126% compared with the capacity of cotton fibers. Also, repeatability, selectivity, and floating-ability tests suggested that CCFs-400 showed much better performance than cotton fibers in pure oil medium or water–oil mixtures [29].

2.1.2 Mineral sorbents

2.1.2.1. Silica Aerogels

Aerogels are the world's lowest-density solid materials composed of up to 99.98% air by volume but also highly porous and extremely rigid, capable of bearing weight many times their own. Aerogels are a diverse class of amazing materials with advanced properties. Transparent superinsulating silica aerogels exhibit the lowest thermal conductivity of any solid known. Ultrastrong, bendable x-aerogels are the lowest density structural materials. Normally aerogels are brittle and fracture under too much force. Overcoming the characteristic stiffness of the aerogels could open up a whole new range of uses such as oil absorption applications [30]. They are nanoporous materials with open foam-type structures which allow for penetration of varying sizes of compounds into the solid. The combination of the solgel and supercritical drying techniques used for the synthesis of these materials impart into them unique properties such as large surface areas (up to 1000 m²/g and greater), high porosity, low density and low thermal conductivity [12].

2.1.2.2. Perlite

Perlite is a glassy volcanic rock that expands to about 20 times its original volume upon heating within its softening temperature range of 760 to 1100 °C. The uses of expanded perlite are many and varied and are based primarily upon its physical and chemical properties. As most perlitites have a high silica content, usually greater than 70%, they are chemically inert in many environments, hence they are excellent filter aids and fillers in various processes. Furthermore, perlite is also used as a catalyst in chemical reaction. The main consumption of perlite is in construction related fields [31].

2.1.2.3. Zeolite

Zeolites are naturally occurring silicate minerals, which can also be synthesized at commercial level. Probably clinoptilolite is the most abundant of more than 40 natural zeolite species [32]. The use of natural zeolites for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence. Application of natural zeolites for water and wastewater treatment has been realised and is still a promising technique in environmental cleaning processes. In the past decades, utilization of natural zeolites has been focussed on ammonium and heavy metal removal due to the nature of ion exchange and some review papers have been appeared. Apart from the presence of cations in water, anions and organic compounds are widely presented in wastewater [33].

2.1.3 Organic Synthetic products

Among synthetic products, polypropylene and polyurethane foam are the most widely used sorbents in oil spill cleanup because of their highly oleophilic and hydrophobic properties. A disadvantage of these materials is that they degrade very slowly as compared with mineral or vegetable products [34].

3. Skimmers

A skimmer is a device for recovering spilled oil from the water's surface. Skimmers may be self-propelled, used from shore, or operated from vessels. The efficiency of skimmers is highly dependent upon conditions at sea. In moderately rough or choppy water, skimmers tend to recover more water than oil. Different types of skimmers offer advantages and drawbacks depending on the type of oil being recovered, the sea conditions during cleanup efforts, and the presence of ice or debris in the water [35].

4. Booms

It is important to quickly corral off the oil released into the body of water to minimize its spread and to facilitate cleanup. This is achieved through a quick and skillful deployment of containment booms [36]. The success of booming operations can be limited by the rapid spread of floating oil and the effects of currents, tides, wind and waves. Effective boom design and a well-planned and coordinated response can reduce these problems, Although in some circumstances the use of any boom might be inappropriate. Booms are floating barriers designed to perform one or more of the following functions:

4.1. Oil containment and concentration: Surrounding floating oil to prevent its spread over the water surface and increase its thickness to facilitate recovery;

4.2. deflection : diverting the oil to a suitable collection point on the shoreline for subsequent removal, for example by vacume trucks, pumps, or other recovery methods;

4.3. Protection: diverting the oil away from economically important or biologically sensitive sites such as harbor entrances, power station cooling-water intakes, mariculture facilities or nature reserves [37].



Fig. 3 : Mechanical skimmers working inside boom [38]

5. Bioremediation

This involves the use of microbes, plants or fungi to clean up an oil contaminated environment. Scientists believe that naturally occurring microorganisms in the marine environment have the ability to degrade oil, but limited availability of nutrients such as nitrogen and phosphorous hamper this ability [36]. Because of the difficulty of achieving sufficient oil removal by physical washing and collection, especially for oil that had moved into the subsurface, bioremediation became a prime candidate for continuing treatment of the shoreline. Bioremediation had been independently identified as a potential emerging technology within weeks of the spill. Both the EPA and Exxon quickly began laboratory tests, which were soon followed by field trials to determine whether fertilizer addition would enhance the rates of oil biodegradation. Field tests showed that fertilizer addition enhanced rates of biodegradation by the indigenous hydrocarbon-degrading microorganisms [39]. In 1995, Atlas investigate the petroleum biodegradation and oil spill bioremediation. The results showed in the case of the *Exxon Valdez* spill, the largest and most thoroughly studied application of bioremediation, the application of fertilizer (slow release or oleophilic) increased rates of biodegradation 3-5 times. Because of the patchiness of oil, an internally conserved compound, hopane, was critical for demonstrating the efficacy of bioremediation. Multiple regression models showed that the effectiveness of bioremediation depended upon the amount of nitrogen delivered, the concentration of oil, and time [40]. Dashti *et al* researched the effect of Olive-pomace harbors bacteria on hydrocarbon biodegradation, nitrogen fixation and mercury resistance as promising material for waste –oil-bioremediation. They figure out that the Olive-pomace is useful as a sorbent for spilled oil and its biodegradation and could be applied in oil-remediation, not only as a physical sorbent, but also for bioaugmentation purposes as a biological source of hydrocarbonoclastic bacteria [41]. In another study, oil removal from water with yellow horn shell residues treated by ionic liquid has been investigated by Jili *et al.*, in 2013. The maximum sorption capacities of Il-treated shell residues (0.39–0.61 g/g) were about 1.5-fold to those of untreated shell residues (0.32–0.42 g/g), respectively. It was found that the Il-treated shell residues could be reused for several times. The results indicated that Il-treated yellow horn shell residues could be developed as an ideal biosorbent for oil removal from water [42].

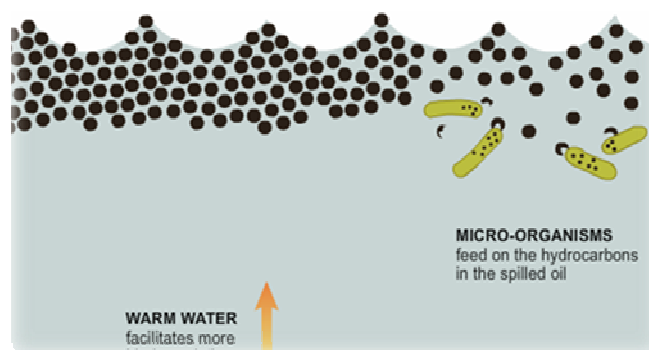


Fig. 4 : Biodegradation using microorganisms [43]

5.1. Ecological evaluation of bioremediation

It worth to mention that effective bioremediation of crude oil polluted environment will require a consortium of microbial communities. An ecological balance of the key microbes required in all aspects of bioremediation of crude oil polluted ecosystem, including cometabolising bacteria, is very important [44].

5.2. Biosurfactant extraction

To effectively degrade hydrocarbons of crude oil, emulsification with a surfactant is of importance due to their low water solubility, especially polyaromatic components in solid and liquid discharges of petroleum. Some strains, such as *P. putida*, and *B. subtilis*, can produce rhamnolipid biosurfactant, which can dramatically enhance aqueous dispersion via emulsification, and stimulate the biodegradation of organic compounds. The emulsification plays an important role in the degradation of organic compounds, especially for polyaromatic hydrocarbons, such as naphthalene and n-paraffin fractions, and such emulsification usually can be observed in 24-48 hrs after inoculation with some effective microbial strains [14].

Bioremediation has generally received a positive response from the public. Nevertheless, there are still concerns about potentially adverse effects associated with the application of bioremediation agents on contaminated marine environments. Among these are the possibility that the addition of fertilizers or the generation of metabolic byproducts from oil degradation will cause eutrophication, leading to algal blooms and oxygen depletion. In addition, components of the fertilizer formulations and/or oil degrading bacterial strains could induce a toxic response in humans and the marine biota before products are used in the field, they should be tested to ensure that they have a low toxicity to the environment and that they are efficacious [45].

Conclusions

In this study, the environmental effects of oil spill and the available techniques for controlling were investigated. From this review, it is clear that oil spills are harmful to the environment. In this paper, we reviewed effective methods for oil products cleaning. As previously mentioned the main concern of the environmental experts is the pollution from the production and transfer of oil spill in different ecosystems. The effects of oil spills can have wide ranging impacts that are often dicribed by the media as long lasting environmental disasters. Such conceptions are understandable as they are often fuelled by distressing images of oiled birds and other wildlife. Therefore,

considering the negative consequences of the spread of oil pollution in to the environment, the most important solution after the application of different technical methods, obtaining the necessary knowledge to collect, remove and quickly oil spill cleanup.

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