Remediation processes for petroleum oil polluted soil

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Oil spill either marine or terrestrial is a real concern to human health and environmental safety. The adverse impacts on economy, environment, human health and society have been documented in case of both offshore and onshore oil spills. Oil spillage on soil greatly impacts surrounding environments, which highlights urgent need for effective removal of petroleum hydrocarbon pollutants from polluted soil. Existing conventional physico-chemical methods of crude oil polluted soil remediation suffer from severe constrains, such as, low efficiency, high operational cost and large amount of sludge generation. Over the last three decades, considerable work has been done with the goal of applying microorganisms as bioremediation agents to treat oil polluted soils. In recent years, the focus of the research has been on a combination of methods used for remediation of petroleum oil polluted soil. The present paper provides selective overview of past and present scenario of using various remediation processes for removal of petroleum hydrocarbon pollutants from crude oil polluted soil. Updated information on integration of various remediation methods, viz., physical-chemical, physical-biological and biological-chemical is also discussed.

Keywords: Bioremediation, crude oil, hydrocarbon pollutants, oil spill, remediation process

Introduction

Crude oil is an important natural resource, which greatly improves the living quality of mankind. However, frequent oil-spill accidents have happened during petroleum oil exploration and transportation processes. This brings catastrophic effects to human health and marine ecosystem. Exxon Valdez oil spill, Alaska (1989) spilled approx 11 million gallons crude oil into the sea and damaged around 1300 miles of shoreline. Only 10% of spilled oil was recovered despite clean-up efforts by various technologies. Another typical example of devastating oil spill is the Deepwater Horizon (DWH) blowout in Gulf of Mexico (2010), which is one of the largest accidental ocean spillage in the history, which released 210 million gallons of crude oil into the ocean. Deepwater Horizon oil spill resulted in severe damage to coastal wetlands, marine ecosystem, fishing industry, tourism etc. Apart from marine oil spill incidences, industrial oily waste water is released into environment through petroleum industry crude oil exploration, transport and storage activities, which causes terrestrial oil spill. Oil spills either marine or terrestrial threaten public health and terrestrial as well as marine ecosystem. Remediation of spilled crude oil, which pollutes shoreline, soil and water, is a challenging task due to toxicity and persistency of petroleum hydrocarbons in environment.

Most clean-up efforts for crude oil spilled on water, soil and shoreline need mechanical and tedious methods as they are quick and simple solution to remove petroleum oil pollutants. Application of high pressure washing to displace petroleum oil destroys the microbial populations and chemical sorbents as well as dispersants may be harsh and pose negative impacts to the environment. Mechanical methods are labour intensive, time consuming and can remove oil pollutants up to a certain extent, leaving behind a large amount of petroleum oil adsorbed in soil. These primary response actions are not able to achieve complete clean-up of oil spills under a short/limited time period. There is an urgent need to find efficient, affordable and more environment-friendly methods for cleanup of petroleum oil polluted soil, especially in the developing countries like India.

The remediation processes for crude oil polluted soil can be classified into: (a) chemical, (b) thermal, (c) physical and (d) biological. Various processes available for remediation of petroleum oil polluted soil, which ranges from applied methods (solvent extraction & bioremediation) to emerging methods (electrokinesis remediation & sonication). Following sections will discuss about remediation processes for petroleum oil polluted soil in detail with
emphasis on combination of different remediation technologies.

**Oil Spill—A Global Concern**

Oil spill is generally described as a release of liquid petroleum hydrocarbons into the environment either soil or marine areas or other water bodies due to human activities or natural disasters\(^1,10\). If oil is released in ocean or coastal water it is called marine oil spill and in terrestrial oil spill, oil is released on land\(^5\). The massive oil spill of 20\(^{th}\) April, 2010 in the east Mississippi Canyon area (N 28.73667, W 88.38694) in the northern Gulf of Mexico (NGOM) took place 66 km off the coast of Louisiana (LA). It was due to an explosion on the Deepwater Horizon (DWH) drilling rig, which led to a catastrophic oil and gas blowout at the British Petroleum operated Macondo Prospect (MC252)\(^1,2\). Some other major oil spills disasters are the Exxon Valdez in Alaska, Gulf War in Kuwait, the Erika in France, the Prestige in Spain and the Deepwater Horizon in Gulf of Mexico\(^1,19\). Table 1 summarizes few oil spills incidences with their year of occurrence, fuel type and amount of oil spilled.

**Effects of Petroleum Hydrocarbon Pollutants—Environmental, Public Health and Social**

Petroleum hydrocarbon pollutants are carcinogenic, mutagenic, immunotoxic and neurotoxic. They cause acute or chronic and short or long-term threats to environment and biological forms\(^4,10,19,20\). Spilled oil affects agriculture by decreasing soil fertility and cause poor growth of plants\(^1\). Crude oil and its by products when come in contact with water spread form a thin layer on water surface, which prevents gas exchange between air and water thereby blocks sunlight to reach to phytoplankton and disturbs food chain\(^1,2\). Structural changes due to presence of petroleum pollutants are reported in phytoplankton\(^2\). Sea birds, sea turtles, corals, marine mammals and fishes are badly affected by oil spill disasters\(^2,12\). Endocrine system of humans is disturbed by petroleum hydrocarbon pollutants\(^20\). Crude oil compounds are absorbed by human skin and quickly spread in the body if ingested or inhaled\(^2\). Absorption of these pollutants depends on physical and chemical properties of crude oil compounds\(^1\). For example, benzene is reported to be the most toxic hydrocarbon and may cause depression of pluripotent primitive blood cells; edema, hemorrhage, bone marrow damage and fibrosis, which interfere with blood cell production; leukemia and liver cancer. These pollutants also cause embryo toxicity\(^2\).

Damage to environment, cost for clean-up and research, socio-economic losses etc. cumulatively account for economic cost of oil spill, generally this cost can be estimated by oil spill modeling\(^2,12\). Historical data throw a light on oil spill clean-up cost.

<table>
<thead>
<tr>
<th>Oil spill</th>
<th>Year of oil spill</th>
<th>Fuel type</th>
<th>Location of oil spill</th>
<th>Amount of oil spilled (million gallons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amoco Cadiz</td>
<td>16(^{th}) March, 1978</td>
<td>Light Iranian and Arabian crude oil and bunker fuel</td>
<td>Brittany coast, up to Channel Islands; Portsall, France</td>
<td>68.7</td>
</tr>
<tr>
<td>Ixtoc 1 oil well</td>
<td>3(^{rd}) June, 1979</td>
<td>Crude oil</td>
<td>Bay of Campeche, Gulf of Mexico, Campeche, Mexico</td>
<td>140</td>
</tr>
<tr>
<td>Exxon Valdez</td>
<td>24(^{th}) March, 1989</td>
<td>Crude Oil</td>
<td>Prince William Sound, Alaska, USA</td>
<td>11</td>
</tr>
<tr>
<td>Nowruz oilfield</td>
<td>10(^{th}) February, 1983</td>
<td>Crude Oil</td>
<td>Nowruz Field Platform, Persian Gulf, Iran</td>
<td>80</td>
</tr>
<tr>
<td>Castillo de Bellver oil spill</td>
<td>6(^{th}) August, 1983</td>
<td>Light crude oil</td>
<td>Table Bay; Saldanha Bay, South Africa</td>
<td>78.5</td>
</tr>
<tr>
<td>Odyssey oil spill</td>
<td>10(^{th}) November, 1988</td>
<td>North Sea crude oil</td>
<td>North Atlantic, off the coast of Nova Scotia, Canada</td>
<td>43</td>
</tr>
<tr>
<td>Gulf War</td>
<td>23(^{rd}) January, 1991</td>
<td>Crude oil</td>
<td>Persian Gulf, Kuwait</td>
<td>240-336</td>
</tr>
<tr>
<td>M/T Haven Tanker oil spill</td>
<td>11(^{th}) April, 1991</td>
<td>Crude oil</td>
<td>Mediterranean Sea; Genoa, Italy</td>
<td>45</td>
</tr>
<tr>
<td>ABT Summer</td>
<td>28(^{th}) May, 1991</td>
<td>Iranian crude oil</td>
<td>Off coast of Angola, Africa</td>
<td>80</td>
</tr>
<tr>
<td>Deepwater Horizon</td>
<td>20(^{th}) April, 2010</td>
<td>Crude Oil</td>
<td>Mexican Gulf, Mexico</td>
<td>210</td>
</tr>
</tbody>
</table>
Important cost driving factors are oil type, shoreline proximity, location, clean-up processes and spill size\(^2\). Usually shoreline length polluted and spill size is positively correlated with cleaning cost, and vice versa is for the distance from shoreline and spill size\(^12\). The social consequences of oil spills usually are found at micro, macro and community levels\(^21\). Main impacts are residential and economic viability in the community\(^1,12,21\). After the Deepwater Horizon oil spill, 20% of Gulf Coast residents are reported a drop in income, and 25% thought that they might have to migrate at some other place from the Gulf\(^2,12\).

**Petroleum Hydrocarbon Pollutants—Remediation Processes**

**Chemical Process**

Various oxidants have been studied for remediation of crude oil polluted soil through chemical oxidation reactions. Some of these oxidants are Fenton's reagent, hydrogen peroxide, persulfate, ozone and peroxymonosulfate\(^15,22-27\). While applying these chemical oxidants to remediate soil polluted with diesel and fuel oil magnetite, Fe\(^{2+}\), zero-valent iron, goethite, hematite, manganese oxide and cobalt are reported to work as a catalyst\(^15,22,25,26,27,28\). In this process, the pollutant removal efficiency was noted 35-90%, which depends on type of chemical oxidant and the catalyst used\(^15,24,25,28\). Usman et al.\(^15\) have performed studies to check efficiency of magnetite mixed with Fe\(^{2+}\) to activate both persulfate and hydrogen peroxide on crude oil polluted soil at neutral pH. They noted that application of magnetite provided high efficiency of crude oil remediation (80%) for both oxidants. If soluble Fe\(^{2+}\) used alone, low remediation efficiencies (10-15%) under the same experimental conditions were obtained. They concluded that magnetite could be used to activate both persulfate and hydrogen peroxide oxidants for crude oil polluted soil remediation (neutral soil pH), hence soil natural properties are not hampered by application of this remediation process\(^15\). Chemical oxidation method is useful for remediating petroleum oil polluted soil as it is non-selective and not affected by toxicity of the pollutant. This minimizes pollutants dispersion and helps to remediate crude oil pollutant\(^15,25\). This method is also having advantage of simplicity and operation as it gives fast results with low operational costs\(^24\). Excessive dosage of chemical oxidants causes adverse impact on environment. Therefore, limited additions of chemical oxidant should be applied to protect environment\(^25,25\).

Electrokinetic remediation processes are also a type of chemical process for petroleum hydrocarbon pollutants clean-up. This is an in situ process employing low levels of direct electric current between appropriately distributed electrodes, viz., anodes and cathodes\(^14\). These electrodes are embedded at each side of crude oil polluted soil mass and form an electric field across the area. As a result, voltage is formed, which causes fluid medium to flow preferentially towards cathode, while dragging pollutant together with bulk flow\(^20,30\). These processes are also used to explore bacterial diversity in crude oil polluted site\(^18,29\). Various mechanisms of these processes are electroosmosis, electromigration and electrophoresis\(^30\). This process is having advantage of less time consumption and having lower operating cost\(^18\). The major drawback is that electrolysis process creates thermal hot spots in the soil around the electrodes, which alters soil pH after an extended period of operational time. This hampers environmental quality\(^14\).

**Thermal Processes**

Thermal remediation of crude oil polluted soil employs heat to remove pollutants. These processes are mainly of three types: (a) incineration\(^31\) (b) microwave frequency heating\(^17,32\) and (c) thermal desorption\(^33,34\). In incineration process, crude oil polluted soil is burnt from 300-1000°C in an incinerator to remove pollutants. It is one of the easiest method to remove pollutants from soil, but on the other side it causes environment pollution, especially air pollution\(^33\). Microwave frequency heating processes convert microwave energy into thermal energy, which remove pollutants through heating and volatilization. However, many pollutants and soil particles are resistant to microwaves, which cannot absorb microwave energy directly to heat up pollutants. Hence microwave energy is converted to thermal energy by mixing microwave absorbers to crude oil polluted soil\(^32\).

Temperature is manipulated in case of thermal desorption processes to increase vapour pressure of petroleum hydrocarbon pollutants, which causes volatilization and subsequent desorption of these pollutants from soil\(^33,34\). From diesel polluted soil, 99.5% diesel was removed in a laboratory experiment. In this experiment desorber was indirectly heated using two electrical resistor elements at 300-400°C\(^34\). Thermal processes are very effective in cleaning up petroleum oil pollutants when high heat is applied. Incineration method is usually applied in major oil spill sites, hence large volumes of polluted sites can be
treated by incineration. Thermal processes are quick, reliable and effective in removal of hazardous materials up to 99%\textsuperscript{31}. On the other hand, they cause environmental pollution to large extent. Sometimes they may convert one pollutant to another form instead removing it from environment\textsuperscript{17,21}.

**Physical Processes**

Physical remediation processes used for petroleum hydrocarbon pollutants removal from soil are ultrasonication\textsuperscript{35-37} and flotation\textsuperscript{16,38-39}. Crude oil removal from polluted soil using ultrasonication is usually performed by: (a) formation and collapse of cavitation bubbles, and (b) generation of shock waves from collapse of cavitation bubbles\textsuperscript{36}. Because of sudden increase in pressure during implosive collapse of bubbles and also bubble formation, at nucleation sites, localised hot spots in liquid are formed\textsuperscript{37}. High temperature enhances breakage of bonds and desorbs petroleum oil pollutants from soil particles\textsuperscript{40}. It has been reported that fine soil particles producing high viscosity slurries impede ultrasound cavitation, which decreases net removal of spilled crude oil\textsuperscript{35}. The advantages and disadvantages of this processes are discussed earlier\textsuperscript{36,41}.

Flotation process mainly depends on: (a) collision between petroleum hydrocarbon pollutants and bubbles, (b) attachment of crude oil pollutants and bubble, (c) flotation of bubble-pollutant because of difference in buoyancy, and (d) detachment of pollutant from bubble-pollutant\textsuperscript{16,39,42}. This process is simple having low operational cost and high crude oil pollutant removal efficiency. It can separate very small or light weight particles with low settling velocities. The major drawback with this process is high downstream cost for treatment of wastewater as it requires large amounts of water for the process to complete\textsuperscript{16,38}.

**Biological Processes**

Bioremediation came to be known in the late 1980s, because of the famous Exxon Valdez oil spill, as a process for clean-up of petroleum hydrocarbon polluted shorelines or soil by use of organisms\textsuperscript{3,12}. It is as a method of accelerated biodegradation process of spilled crude oil. If bioremediation can be achieved by using microorganisms, \textit{viz.}, bacteria, fungi and algae, it is called microbial degradation or biodegradation\textsuperscript{4,9,19}. If plants are used for bioremediation then it is called phytoremediation. Phytoremediation works on various mechanisms, such as, hydraulic control, phytovolatilization, phytostabilization, phytodegradation, rhizoremediation and phytotransformation\textsuperscript{45}. Different plant species, \textit{viz}., \textit{Mirabilis jalapa}, \textit{Medicago sativa}, \textit{Phragmites australis}, \textit{Pinus densiflora}, \textit{Thuja orientalis}, \textit{Bassia scoparia} and \textit{Jatropha curcas} have been reported for phyto remediation of petroleum hydrocarbon pollutants\textsuperscript{44-48}.

Microbial degradation is mainly divided in two parts: (a) biostimulation and (b) bioaugmentation\textsuperscript{4,49}. For biostimulation, nutrients (fertilizers & biosurfactants) and oxygen required for growth of microorganisms are supplied externally. If required, environmental growth factors, such as, temperature and pH, are also need to be controlled externally\textsuperscript{43,49,50}. Alternatively, some microorganisms have an ability to synthesis surfactants, which enhance biodegradation rate by solubilizing hydrophobic crude oil pollutants\textsuperscript{43,50}. Bioaugmentation can be defined as enhancing microbial performance through addition of genetically engineered/modified bacteria with specific metabolic activities, which have ability to increase biodegradation rates\textsuperscript{4,49}. It has been reported that there is no single strain of bacteria, which has metabolic capacity to degrade all petroleum hydrocarbon components. Hence cocktail of microorganisms is preferred to achieve efficient biodegradation\textsuperscript{7,49}. Natural attenuation also take place in case of oil spills in which native hydrocarbon degrading microorganisms play an important role\textsuperscript{13,43}. Bioremediation of spilled oil is affected by various factors, \textit{viz}., environmental and nutritional conditions, pollutant and soil characteristics, and microorganisms\textsuperscript{5,43,49,51}. \textit{Ex situ} bioaugmentation study was performed using indigenous \textit{Pseudomonas aeruginosa} NCIM 5514. The organism showed 60.63\% crude oil (3\%, v/v) degradation in 60 d and considered as a potential bioremediation agent for biodegradation of petroleum hydrocarbon polluted sites as well as management of oil spills\textsuperscript{52}. Pros and cons of above discussed bioremediation processes are reported earlier\textsuperscript{5,8,43,49,51}.

**Integrated Remediation Approaches**

Several research groups in both India and abroad have worked on integration of remediation technologies for clean-up of polluted soil by crude oil, diesel, fuel oil \textit{etc}\textsuperscript{53-58}. Some of them are discussed in this section.

**Integrated Physical-Chemical Approach**

Solvent extraction method is widely used for soil remediation, in which petroleum hydrocarbon pollutants are removed from polluted soil using a
single or mixture of solvents. This process mainly uses (a) water or other organic solvent and (b) chemical surfactant, viz., sodium dodecyl sulphate (SDS) and alkyl polyglucosides (APG) for remediation of polluted soil. Soil vapour extraction (SVE) is an in situ soil remediation process that removes crude oil pollutants from unsaturated zone of soil using either horizontal or vertical screened wells. Extracted vapour is drawn towards extraction wells for the next step of treatment with activated carbon. This process along with chemicals also use a part of mechanical processes, such, as magnetic/mechanical agitation, mechanical shaking and incubation etc., hence it is known as integration of physical and chemical processes for remediation of petroleum oil polluted soil.

Effect of ultrasonication time coupled with Triton X-100 micellar solution to remove heavy oil from polluted soil was studied earlier. Clean soil was contaminated with crude oil (soil:oil ratio of 9:1, %w/w) and was mixed with Triton X-100 solution then stirred at 70°C, 180 rpm, 30 min. Ultrasonication was carried out at a frequency of 28 kHz and power density of 80 W/L. Increase in ultrasonication time from 6 min to 30 min showed increase in efficiency of solvent extraction from 66.4% to 88.7%. They concluded that increase in crude oil removal efficiency was attributed to increase in number of shock waves from ultrasonication, which decreases interfacial forces between the soil particles and pollutants. Due to which Triton-X easily penetrated into the soil particles' surface, enhancing remediation of polluted soil.

**Integrated Physical-Biological Approach**

Efficiency and sustainability of integrated solvent extraction and biodegradation for remediation of petroleum hydrocarbon polluted soil was studied by Wu et al. The polluted soil was mixed with mixture of hexane and pentane (4:1, %v/v) for 20 min in a mechanical shaker. Then organic solvent mixed soil was bioremediated using microcosms bioaugmented with Bacillus subtilis FQ06 and rhamnolipid for 132 d. Approx 90% pollutants were removed after 15 min of solvent extraction process. Subsequent bioremediation further reduced petroleum hydrocarbon pollutants up to 97% after 132 d. The authors concluded that integration of remediation processes is beneficial for remediation polluted soil.

**Integrated Biological-Chemical Approach**

Integrated chemical oxidation and bioremediation processes for petroleum hydrocarbons polluted soil has been studied in the last decade. Research on bioremediation followed by chemical oxidation process for remediation of crude oil polluted soil has been performed. Bioremediation was carried out as bio-stimulation process by adding nutrients and peanut hull as a bulking agent for up to 8 wk. Modified Fenton oxidation was then conducted by adding of H2O2 directly into bioremediated soil. The crude oil pollutant removal during bioremediation stage showed 38.6% removal followed by an increase to 88.9% with addition of H2O2. Better efficiency of biological and chemical methods had been proved when they are used in combination for removal of petroleum hydrocarbon pollutants.

**Conclusion**

Petroleum hydrocarbon pollutants enter in the environment by accidental or deliberate oil spills. Major causes of oil spills are transportation, petroleum industry exploration activities and leakage from storage or waste disposal sites. Deepwater Horizon and Exxon Valdez are classical examples of the worst oil spills in the history. Oil spills are environmental disasters that lead to negative and short/long-term impacts on the environment. To minimize oil spill impacts, preparedness and response are pre-requisites for any oil spill, which generally includes monitoring, prevention, reduction, response and remediation of crude oil pollution. There is a need to develop advanced materials and technologies for clean-up of crude oil pollutants from petroleum hydrocarbon polluted water, soil and shoreline. Successful remediation strategy for crude oil polluted soil should be tailored in such a manner that due consideration be given to environment and human health. Bioremediation is a newly accepted technology that is gaining a worldwide interest for clean-up of petroleum hydrocarbon polluted sites. However, integration of various processes gives better results than individual process used for remediation of crude oil polluted sites.

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