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Remediation of Polluted Wastewater Effluents: Hydrocarbon Removal

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ABSTRACT

The onset of the industrial revolution has led to a surge in the quantity of hazardous compounds that are released into the environment. These hazardous pollutants consist of a variety of hydrocarbons and other organic compounds that pose serious risks to humans, animals and the environment. The presence of hydrocarbons in wastewater effluents is due to a variety of sources, which include oil spillage, pesticides, urban storm water discharges and automobile oil. The removal of hydrocarbons from wastewater before discharge into receiving water bodies from wastewater effluents entails a variety of processes, with the most common processes being phytoremediation, bioremediation and chemical remediation. Phytoremediation is a cost effective method of reducing risk to human and ecosystem health posed by contaminated water. It entails the use of plants for the removal of contaminants and could involve mechanisms such as phytodegradation, rhizodegradation, rhizofiltration, phytoextraction, phytovolatilization, hydraulic control and phytostabilization. On the other hand, bioremediation is the use of microorganisms to breakdown or degrade pollutants in a contaminated site. The technology is low cost and has a generally high public acceptance. It consists of biostimulation (addition of nutrients to indigenous microorganisms) and bioaugmentation (addition of hydrocarbon degrading microorganisms). In the case of chemical remediation, it involves the use of chemicals for the treatment of contaminated sites. Substances, such as dispersants and solidifiers are used in chemical remediation. This study was aimed at reviewing the sources, impacts and remediation processes for hydrocarbon polluted wastewater effluents. This review was able to describe the sources and impacts of hydrocarbon polluted wastewater effluents and the various methods of treatment.

Key words: Hydrocarbon, remediation, pollutants, wastewater

INTRODUCTION

Hydrocarbons are heterogeneous group of organic substances that are composed of hydrogen and carbon. They are made up of aliphatic compounds, which contain chains of carbon atoms strung together and aromatic compounds, which contain one or more benzene rings bonded together. Hydrocarbons are abundant in modern societies, with some of their uses including fuels, gasoline, paints and solvents (Reeves, 2000; Mbhele, 2007).

The release of petroleum hydrocarbons and their derivatives, either accidentally or deliberately to the environment is known to pose problems of increasing magnitude throughout the world (Orji *et al.*, 2013). Hydrocarbon contamination in the environment is a very serious problem whether it comes from petroleum, pesticides or other toxic organic matter. The pollution caused by petroleum is of great concern because petroleum hydrocarbons are toxic to all forms of life (Abha and Singh, 2012). The toxicity from hydrocarbon ingestion can affect several body organs, such as the lungs, liver and kidney. Also, hydrocarbon contaminated water is reported to be carcinogenic and mutagenic, when present at high concentration (Mbhele, 2007). A variety of hydrocarbon pollutants in receiving water bodies are known to cause disruptions of the natural equilibrium between living species and their natural environment (Abioye, 2011). To avoid the adverse effects of untreated hydrocarbon polluted wastewater effluents to the environment and the health of humans and animals, there is the need for the treatment before discharge into receiving water bodies.

The remediation of hydrocarbon polluted wastewater can be achieved by three methods, which are phytoremediation, bioremediation and chemical remediation. Phytoremediation entails the use of plants to reduce the volume, mobility and toxicity of contaminants in soil and water. This could be achieved through a variety of processes, which are rhizodegradation, phytodegradation, rhizofiltration, phytostabilization, phytoextraction, phytovolatilization and hydraulic control. Although the mechanism of action of the different processes is known to differ, each is indicated to have effect on the volume, mobility or toxicity of the intended contaminants (USEPA, 2000a).

Bioremediation, which involves the use of microorganisms for contaminant removal is reported as one of the most effective and inexpensive technologies for hydrocarbon clean-up (Das and Mukherjee, 2007). It can occur on its own through natural attenuation or can be spurred on through the addition of fertilizers to increase the bioavailability within the medium (Sharma, 2012). The process of bioremediation can be implemented in two ways, bioaugmentation and biostimulation. With respect to hydrocarbon removal, bioaugmentation is the addition of hydrocarbon degrading organisms to the environment while biostimulation is the addition of nutrients to the affected site, which enhances the degradation process of the existing hydrocarbon degraders (Abioye, 2011).

Chemical remediation is the use of chemicals to remove hydrocarbons from contaminated sites. The major processes for chemical remediation are through the use of dispersants, solidifiers and oxidants (Dave and Ghaly, 2011). The aim of this study was to review the sources and impacts of hydrocarbon polluted wastewater effluents. Also discussed in the study were the various methods for hydrocarbon remediation in wastewater effluents.

SOURCES AND IMPACTS OF HYDROCARBON POLLUTED WASTEWATER EFFLUENTS

Hydrocarbon pollution in wastewater can come from a number of sources, such as petroleum, pesticides or other toxic organic matters that are discharged as effluents into water bodies (Abha and Singh, 2012). The presence of hydrocarbons in receiving water bodies is known to be carcinogenic, mutagenic and neurotoxic to living organisms, including plants and animals (Das and Chandran, 2011). The major sources of hydrocarbon contaminants in wastewater effluents are oil spillage, automobile oils, pesticides, contaminated lands and urban storm water discharges.

One of the main sources of hydrocarbon in wastewater is through oil spills. Oil spills are known to occur either accidentally through wrecks of tankers and equipment faults or deliberately through discharges, such as flushing tankers with sea water (Abha and Singh, 2012). Oil spills can also be caused by nature and human activities, when large amount of oil is spilled from oil seeps from ocean floors, as well as leaks that occur when petroleum products and other forms of oil are used on lands and later washed off into water bodies (Latimer *et al.*, 1990). Another source of oil spill in water is leaking pipelines and underground oil storage tanks (Husaini *et al.*, 2008).

In addition, the emergence of various kinds of automobile or vehicles has brought about an increase in the use of automobile oil, which is a source of hydrocarbon pollution in wastewater. When automobile oil leaks or escapes from the car or drops on the ground, it could be washed through runoffs from rain into the water bodies, thereby causing pollution (USEPA, 1996; Husaini *et al.*, 2008).

Another source of hydrocarbon pollution in receiving water bodies is pesticides. Pesticides include herbicides, fungicides and insecticides. When pesticides are applied to agricultural fields, only a little amount of them is said to reach their target while a significant proportion remain in the soil. During rainfall, the amount left in the soil is washed off into receiving water bodies (Ward *et al.*, 1993). Of all pesticides, herbicides are indicated to be the most dangerous since they are applied directly on the soil to kill weed, leaving them more prone to be washed away by rain into water bodies.

Also, contaminated land, which is lands that had former industrial activity or land where some kind of industrial activity has been carried out, is another source of hydrocarbon pollution in water. These lands could be contaminated by hydrocarbons and other organic chemicals, which can be washed away by rainfall into the water bodies thereby causing pollution (FWR, 2008).

Furthermore, urban storm water discharges are indicated to be major sources of hydrocarbons in water. In urban communities, roads and car parks, which are often polluted with oil and gasoline from vehicles are large runoff producing. During rainfall, these pollutants are washed into drains and into receiving water bodies where they cause contamination (Van Metre *et al.*, 2000; FWR, 2008).

Hydrocarbon polluted wastewater has its impacts on the environments, plants, animals and humans. Hydrocarbon polluted wastewater has various impacts to the environment, which include reduction in crop yield, shortage of oxygen and effects on marine plants. When a farmland is irrigated hydrocarbon contaminated wastewater it leads to improper growth of crops, which could bring about reduction in crop yield and available food for households (Osuji and Nwoye, 2007; Ordinioha and Birisibe, 2013). The presence of oil in water can also reduce soil fertility to an extent that most of the essential nutrients are no longer available for crop utilization, which could lead to reduction in crop yield. A reduction in crop yield could also lead to a decrease in a farmer's income (Emmanuel *et al.*, 2006; Abii and Nwosu, 2009).

Another environmental impact of hydrocarbon pollution is the shortage of oxygen. The majority of economic trees, which are main sources of oxygen in the environment, are known to depend on rainfall and sometimes water from water bodies for growth. In the presence of oil spill, the resulting oil which is denser than water reduces and in some cases prevents root penetration due to the hydrocarbons that fill the soil pores thereby expelling water and air. This in turn deprives the roots of the much needed water and air (Henry and Heinke, 2005). This resultant effect of this is a distortion in the growth or death of such plants, thereby causing shortage of oxygen for human consumption (Edema *et al.*, 2009). The presence of hydrocarbon in water prevents enough light from penetrating the water and gaseous exchange from taking place for utilization by marine

plants. When this occurs, the plants are unable to photosynthesize, thus leading to their death and a resultant effect on the food chain. In addition, plants may absorb hydrocarbon pollutants from water and pass them up to the food chain to consumer animals and humans (Gibson and Parales, 2000).

With respect to effects on human, the highly toxic hydrocarbons such as the polycyclic ones are indicated to pose serious threats to the human body. When ingested, they damage organs and systems, such as the respiratory system, nervous system, immune system, circulatory system, reproductive system, kidney, liver etc (Ordinioha and Birisibe, 2013). The extent of damage is dependent on the level of exposure and the susceptibility of the individual (Abha and Singh, 2012). Other impacts of hydrocarbon polluted effluents to humans include the risk of cancer, hormonal problems that can disrupt reproduction and developmental processes (Urum *et al.*, 2004; Mbhele, 2007; Aguilera *et al.*, 2010).

The discharge of polluted hydrocarbon wastewater into receiving water bodies poses threat to animals through inhalation, ingestion and absorption. Sea birds, which spend most of their time close to water bodies, are the most vulnerable to the effect of hydrocarbon pollution in water (Alonso-Alvarez *et al.*, 2007). The presence of oil in water could destroy the protective layer of the feathers in sea birds, thereby leading to abnormal reduction in temperature (Nwilo and Badejo, 2005). In addition, birds that are scavengers, such as vultures and ravens could also be at risk when they feed on carcasses of contaminated fish and other preys (Piatt *et al.*, 1990). In the case of fish, in hydrocarbon polluted waters, during respiration they absorb hydrocarbons that are dissolved in the water through their gills and store it in their liver, stomach and gall bladder, thus making them unfit for human consumption (USFWS, 2004).

REMEDICATION OF HYDROCARBON POLLUTED WASTEWATER

The environmental and health risks posed by hydrocarbon polluted wastewater effluents has led to efforts, both nationally and internationally to remediate such sites. In general the remediation of hydrocarbon contaminated sites can be performed by three methods; phytoremediation, chemical remediation and bioremediation (Dave and Ghaly, 2011; Abha and Singh, 2012).

Phytoremediation: Phytoremediation refers to the use of plants for the degradation, extraction, reduction, removal, containment or immobilization of contaminants from soil, sludge, groundwater, surface water and wastewater (Peer *et al.*, 2006; Martin *et al.*, 2004). The process takes advantage of the ability of plants to take up, accumulate and degrade constituents that are present in polluted environments (Mbhele, 2007; FRTR, 2012). It encompasses a number of different mechanisms that can lead to contaminant degradation, accumulation, dissipation and immobilization (Pivetz, 2001; Kamath *et al.*, 2007). A summary of the different phytoremediation applications with typical examples of plants that are used in each of the applications is shown in Table 1.

The degradation processes can either be rhizodegradation or phytodegradation (phytotransformation). During degradation, the contaminants are either altered or destroyed (Moutsatsou *et al.*, 2006; Yan, 2012). Rhizodegradation is the enhancement of naturally-occurring biodegradation in soil through the influence of plant roots and ideally will lead to destruction or detoxification of an organic contaminant (Pivetz, 2001). It is the degradation of an organic contaminant in soil through microbial activity enhanced by the presence of the root zone or rhizosphere (Martin *et al.*, 2004). It is believed to be carried out by bacteria or other microorganisms whose numbers typically increase in the rhizosphere (Etim, 2012).

Table 1: Typical plants used in various phytoremediation applications

Application	Media	Contaminants	Typical plants
Phytotransformation	Soil, ground water, landfill leachate, land application of wastewater	Herbicides, aromatics, chlorinated aliphatics, nutrients, ammunition wastes	Phreatophyte trees (poplar, willow, cottonwood, aspen, Grasses (rye, bermuda, sorghum, fescue, Legumes (clover, alfalfa, cowpeas)
Rhizosphere bioremediation	Soil, sediments, land application of waste water	Organic contaminants (pesticides, aromatics and polynuclear aromatic hydrocarbons)	Phenolics releasers (mulberry, apple, osage orange) Grasses with fibrous roots (rye, fescue, bermuda) for contaminats 0-3 ft deep Phreatophyte trees for 0-10 ft Aquatic plants for sediments
Phytostabilization	Soil, sediments	Metals (Pb, Cd, Zn, As, Cu, Cr, Se, U), hydrophobic organics) PAHs, PCNBs, dioxins furans, pentachlorophenol, DDT, deldrin)	Phreatophyte trees to transpire large amounts of water for hydraulic control Grasses with fibrous roots to stabilize soil erosion Dense root systems are needed to sorb/bind contaminants
Phytoextraction	Soil, brown fields, sediments	Metals (Pb, Cd, Zn, Ni, Cu) with EDTA addition for Pb Selenium (volatilization)	Sunflowers Indian mustard Rape seed plants Barley, Hops Crucifers Serpentine plants Nettles, Dandelions
Rhizofiltration	Groundwater, water and wastewater in lagoons or created wetlands	Metals (Pb, Cd, Zn, Ni, Cu), radionuclides (137Cs, 90Sr, U), hydrophobic organics	Aquatic plants: Emmergents (bulrush, cattail, coontail, pondweed, arrowroot, duckweed); submergents (algae, stonewort, parrot, feather, Eurasian water, milfoil, Hydrilla

Source: Schnoor (1997)

The increased microbial populations and activity in the rhizosphere can result in increased contaminant biodegradation. The degradation of the exudates can stimulate co-metabolism of contaminants in the rhizosphere. Rhizodegradation is said to occur primarily in the soil, although in the root zone of aquatic plants, stimulation of microbial activity could possibly occur (Pivetz, 2001).

Lin and Mendelssohn (1998) indicate that the salt marsh grasses *Spartina alterniflora* and *S. patens* could potentially increase subsurface aerobic biodegradation of spilled oil by transporting oxygen to their roots. Some advantages of rhizodegradation include destruction of the contaminant in situ, the possible complete mineralization of organic contaminants and that translocation of the compound to the plant or atmosphere is less likely than with other phytoremediation technologies since degradation occurs at the source of the contamination. Harvesting of the vegetation is not necessary as in rhizofiltration since there is contaminant degradation within the soil, rather than contaminant accumulation within the plant (Pivetz, 2001).

Phytodegradation, also known as phytotransformation, is the uptake of organic and nutrient contaminants from soil and groundwater and the subsequent transformation by plants (Schnoor, 1997). It is applicable to both soil and water and involves the degradation of contaminants through plant metabolism (Moutsatsou *et al.*, 2006). Phytodegradation is the uptake, metabolizing and degradation of contaminants within the plant, or the degradation of contaminants in the soil, sediments, sludge, ground water, or surface water by enzymes produced

and released by the plant. It is not dependent on microorganisms associated with the rhizosphere (Pivetz, 2001). Unlike microbes which metabolize organic contaminants to carbon dioxide and water, phytodegradation relies on plant enzymes to metabolize or mineralize chemicals completely into carbon dioxide and water (ITRC, 2009).

The accumulation processes are processes that remove contaminants by containment. They include phytoextraction and rhizofiltration (Mbhele, 2007; Yan, 2012). Phytoextraction, which is also known as phytoaccumulation refers to the uptake and translocation of metal contaminants in the soil by plant roots into the above ground portions of the plants. Phytoextraction is primarily used for the treatment of contaminated soils (USEPA, 2000b). It is the use of metal-accumulating plants that translocate and concentrate metals from the soil in roots and above ground shoots or leaves (Schnoor, 1997). On the other hand, rhizofiltration is the removal by plant roots of contaminants in surface water, waste water or extracted ground water through adsorption or precipitation onto the roots or absorption into the roots (Pivetz, 2001). The root environment or root exudates may produce biogeochemical conditions that result in precipitation of contaminants onto the roots or into the water body. The contaminant may remain on the root, within the root or be taken up and translocated into other portions of the plant depending on the contaminant, its concentration and the plant species (Schnoor, 1997; Mbhele, 2007).

Rhizofiltration and phytoextraction are similar in that they each result in accumulation of the contaminant in or on the plant. In rhizofiltration, the accumulation can occur in the roots or in the portion of the plant above water, whereas for effective phytoextraction the accumulation occurs aboveground, not in the roots. In addition, rhizofiltration differs from phytoextraction in that the contaminant is initially in water, rather than in soil (Pivetz, 2001). In rhizofiltration the plants to be used for cleanup are raised in greenhouses with their roots in water rather than in soil. To acclimatize the plants, once a large root system has been developed, contaminated water is collected from a waste site and brought to the plants where it is substituted for their water source. The plants are then planted in the contaminated area where the roots take up the water and the contaminants along with it. As the roots become saturated with contaminants, they are harvested (Etim, 2012). In rhizofiltration, either aquatic or terrestrial plants can be used. Given a support platform to enable growth on water, terrestrial plants offer the advantage of greater biomass and longer, faster-growing root systems than aquatic plants (Dushenkov *et al.*, 1995). The use of seedlings has been suggested in place of mature plants due to the fact that seedlings can take up metals but do not require light or nutrients for germination and growth for up to two weeks. Rhizofiltration can be conducted *in situ* to remediate contaminated surface water bodies or *ex situ*, in which an engineered system of tanks can be used to hold the introduced contaminated water and the plants. Either of these systems will require an understanding of the contaminant speciation and interactions of all contaminants and nutrients. Monitoring and possible modification of the water pH or of the flow rate and contaminant concentration of influent water may be necessary (Terry and Banuelos, 2000). Sunflower, Indian mustard, tobacco, rye, spinach and corn have been studied to have the ability to remove metals from the water with sunflower having the greatest ability. In one study, after only one hour of treatment, sunflowers reduced lead concentrations significantly (Raskin and Ensley, 2000).

The dissipation processes are those that remove organic or inorganic contaminants into the atmosphere. An example of a dissipation process is phytovolatilization (Jussila *et al.*, 2006). Phytovolatilization involves the uptake and release of contaminants into the atmosphere and usually happens during transpiration (USEPA, 2010). Phytovolatilization is the use of plants to

take up contaminants from the soil, transforming them into volatile forms and transpiring them into the atmosphere (USEPA, 2000b). Once taken up by plants, the contaminants are modified or broken down into volatile forms and thus diffuse from the plants to the atmosphere through open stomata on leaves together with a small amount of radial diffusion through stem tissues and bark (Kamath *et al.*, 2007; ITRC, 2009). Studies have shown that trees, especially poplars (*Populus* sp.) and willows (*Salix* sp.), can successfully dissipate or attenuate fuel contaminants such as benzene toluene-ethyl benzene-xylene and methyl tertiary-butyl ether in contaminated groundwater and soils, because their half-life in aerobic environment is relatively short compared to saturated anaerobic conditions (Cook *et al.*, 2010; Kamath *et al.*, 2007). The disadvantage of this method is that the contaminant released into the atmosphere is likely to be recycled by precipitation and then re-deposited back into lakes and oceans (USEPA, 2000b).

In immobilization processes, the organic or inorganic contaminant is contained. It consists of phytohydraulics and phytostabilisation (Kamath *et al.*, 2007; ITRC, 2009). Phytohydraulics, which is also known as hydraulic control, is the ability of plants to capture and evaporate water off the plant and thus prevent the migration of contaminants into groundwater (ITRC, 2009). It is the use of plants to influence the movement of groundwater and soil water, through the uptake and consumption of large volumes of water (Pivetz, 2001). In Phytohydraulics, deep-rooted, high-transpiring, water-loving phreatophytes are particularly useful. Trees in the Salicaceae family, such as cottonwood, hybrid poplars and willows are often used (Kamath *et al.*, 2007; ITRC, 2009). In this mechanism, water as well as contaminants from soils and aquifers is drawn upwards and either oxidized into harmless or volatile forms in aerobic soil or taken up and modified into volatile forms in plants, preventing further dispersion and migration (Cook *et al.*, 2010; Kamath *et al.*, 2007). The rate of contaminant removal is highly associated with transpiration rate, contaminant concentration and uptake efficiency in soil water (Yan, 2012). Factors that affect the potential uptake of organic chemicals into plants through the transpiration stream include hydrophobicity, polarity, sorption properties and solubility (ITRC, 2009).

In the case of phytostabilization, which is also referred to as in-place activation, it entails the use of certain plant species to immobilize contaminants in the soil and ground water through absorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone of plants (Etim, 2012). It involves the use of plants to reduce the mobility of the contaminants and prevents migration to the soil, water and air (Moutsatsou *et al.*, 2006; ITRC, 2009). Grasses, sedges, forage plants and reeds with high transpiration rates are widely used in phytostabilization (Peer *et al.*, 2006). Phytostabilization takes advantage of the changes that the presence of the plant induces in soil chemistry and environment. These changes in soil chemistry may induce adsorption of contaminant onto the plant roots or soil or cause metals precipitation onto the plant root (Etim, 2012).

Bioremediation: Bioremediation is known as the use of natural microorganisms in the correction of a contaminated environment (Sharma, 2012). The process uses naturally occurring microorganisms such as fungi, yeast and bacteria for the breakdown or degradation of hazardous substance into less toxic or non-toxic substances (Mbhele, 2007). It is also a process whereby microorganisms degrade and metabolize chemical substances and restore environment quality (Dave and Ghaly, 2011). The major microorganisms that have been implicated in hydrocarbon remediation are shown in Table 2.

Table 2: Hydrocarbon degrading microorganisms

Bacteria	Yeast and fungi
<i>Achromobacter</i>	<i>Aspergillus</i>
<i>Acinetobacter</i>	<i>Candida</i>
<i>Alcaligenes</i>	<i>Cladosporium</i>
<i>Arthrobacter</i>	<i>Penicillium</i>
<i>Bacillus</i>	<i>Rhodotorula</i>
<i>Brevibacterium</i>	<i>Sporobolomyces</i>
<i>Corynebacterium</i>	<i>Trichoderma</i>
<i>Flavobacterium</i>	<i>Fusarium</i>
<i>Nocardia</i>	<i>Trichoderma</i>
<i>Pseudomonas</i>	
<i>Vibrio</i>	

Source: Zhu *et al.* (2001), Webb (2005) and Kamath *et al.* (2007)

The aim of bioremediation is to accelerate the natural attenuation process through which microorganisms assimilate organic molecules to all biomass and produce by-products such as carbon dioxide, water and heat (Atlas and Cerniglia, 1995). This technique utilizes the natural biological activity of microorganisms or enzymes to transform the toxic petroleum components into less toxic or harmless metabolites (Abha and Singh, 2012). Bioremediation is indicated to be the preferred alternative in the long-term restoration of petroleum hydrocarbon polluted systems. It is said to have an added advantage of cost efficiency and environmental friendliness (Okoh and Trejo-Hernandez, 2006).

Bioremediation is reported to entail two processes, bioaugmentation and biostimulation.

Bioaugmentation is the addition of microorganisms that have the ability of degrading the toxic hydrocarbons in order to achieve a reduction of the pollutants (Sharma, 2012). It is also the inoculation of contaminated water with hydrocarbon degrading microorganisms (Dave and Ghaly, 2011). This may sometimes involve addition of genetically engineered microorganisms suited for biodegradation of the hydrocarbon contaminants into the contaminated water (Gentry *et al.*, 2004). It is argued that since most environments naturally contain hydrocarbon degrading microorganisms, bioaugmentation is not used very often. Because the addition of these non-indigenous microorganisms will often cause competition with existing beneficial microbes, it is argued that bioaugmentation is not as effective for use in oil spill remediation sites (Swannell *et al.*, 1996).

Biostimulation is the addition of nutrients needed by indigenous hydrocarbon degrading microorganisms in order to achieve maximum degradation of toxic compounds present (Sharma, 2012). During oil spillage, the increase in carbon stimulates the growth of already present oil degrading microorganisms. Because the microorganisms are limited in the amount of growth and remediation that occur due to the amount of available nitrogen and phosphorus, the addition of supplemental nutrients in the proper concentrations, enhances the hydrocarbon degrading of microorganisms. This is because the microorganisms are capable of achieving their maximum growth rate and hence the maximum rate of pollutant uptake (Boufadel *et al.*, 2006; Zahed *et al.*, 2010). To achieve maximum biostimulation, the important factor is obtaining the ideal concentration of nutrients needed for maximum growth of the microorganisms and keeping concentration for the microorganisms as long as possible (Lee *et al.*, 2007).

A major advantage of bioremediation over other remediation processes is the low cost involved and the savings in the time put forth by workers to clean a contaminated site. Also bioremediation

allows for savings in that it continues to clean the contaminated site without the constant need of workers. This saves a great deal of money which would be spent on labour hours (Zhu *et al.*, 2001). The process is also indicated to be environmentally friendly. This is because no foreign or toxic chemicals are added to the site, hence does not allow for any disruptions to the natural habitat (Dave and Ghaly, 2011). It allows for the natural organisms to degrade the toxic hydrocarbons into simple compounds which pose no threat to the environment and this also eliminates the need to remove and transport the toxic compounds to another site. Despite the advantages, some of the drawbacks of bioremediation remediation are that it is slow and depending on where the pollution occurs, it may be difficult to provide the proper nutrient concentration to the oil degrading microorganisms (Swannell *et al.*, 1996; Dave and Ghaly, 2011).

Chemical remediation: Chemical remediation process entails the use of chemicals. A number of chemicals are used for the treatment of contaminants. These chemicals have the capacity to change the physical and chemical properties of the contaminant especially oil (Vergetis, 2012). The chemicals are grouped into three categories, dispersants, solidifiers and chemical oxidants (Watts *et al.*, 1990; Dave and Ghaly, 2011; Abha and Singh, 2012).

Because most dispersants consists of surfactants, they have the ability to breakdown the slick of oil into smaller droplets and transfer it into the water where it undergoes rapid dilution and can be easily degraded (Lessard and Demarco, 2000). Chemical dispersants are used to allow for rapid treatment and slow down the formation of oil water emulsions that will make the oil less likely to stick to surface and accelerate the rate of natural biodegradation by increasing the surface area of the oil droplets (Nomack and Cleveland, 2010). They are usually used to render oil spills harmless for aquatic life and other living organisms. This is achieved through reduction of the oil slicks to droplets that can be degraded by naturally occurring bacteria (Lessard and DeMarco, 2000; Abha and Singh, 2012). Some examples of chemical dispersants are Slickgone NS, Neon 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, 2011).

In the case of solidifiers, they are dry granular materials that react with oil and change its liquid state into solid rubber like state that can be easily removed by physical means. They can be applied in various forms, which include dry particulate and semi-solid materials, such as pucks, balls, sponge etc. They are applicable in moderately rough seas, since the water provides the mixing energy which enhances solidification. A major drawback to the use of solidifiers is they are difficult to recover after solidification. Also, because they are relatively less efficient, large amount is always required for clean-up (Fingas *et al.*, 1995; Nomack and Cleveland, 2010).

For chemical oxidation, it is a technique that is used that utilizes chemical agents that are capable of oxidizing organic contaminants (Watts *et al.*, 1990). In some cases, chemical oxidation is accomplished by introducing the agents into the soil or water at a contaminated site using injection and the mixing apparatus. The effectiveness of the process is reported to be dependent on the quantity of oxidant that is used, the geological conditions, the residence time of the oxidant and the effective contact between the oxidant and the contaminant (Karpenko *et al.*, 2008). Some of the advantages of chemical remediation are that it is quick and can be applied in all weather conditions. Details of the other advantages and disadvantages are shown in Table 3.

Table 3: Advantages and disadvantages of chemical remediation

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

Source: Dave and Ghaly (2011)

CONCLUSION

The remediation of hydrocarbon polluted wastewater effluents is vital to safeguard public health and prevent its negative impacts on environment and the health of humans and animals. The three main processes for hydrocarbon remediation in polluted waters are phytoremediation, bioremediation and chemical remediation.

Phytoremediation which is the use of plants to remove contaminants from a contaminated site is a method used for remediating a polluted site. However, not all its mechanisms could be used for remediating hydrocarbon polluted wastewater but those that can be used such as rhizofiltration which is the use of plants roots for absorption of contaminants and phytodegradation involving the degradation of contaminants through plant metabolism are less cost effective and also environmentally friendly.

Bioremediation is also a method used for remediating polluted sites; it entails the use of microorganisms. With regards to the two methods of bioremediation, bioaugmentation and biostimulation, biostimulation is the more effective methodology to use. Depending on the concentration of the already present natural nutrients at the site, biostimulation can have an intense effect on the growth rate of the hydrocarbon degrading microorganisms which allows for an inexpensive cleanup method at a much more accelerated rate than natural biodegradation alone. Chemical remediation is the use of chemicals such as dispersants and solidifiers and it is also a method used for remediating a polluted site. Each of the remediation processes is indicated to have their merits and drawbacks.

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