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Review

Sustained nutrient delivery system: A new perspective in bioremediation

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Crude oil induced pollution on soil environment is an increasing trend due to incessant accidental release of this component into the environment. Bioremediation which is considered the most effective clean-up tool is faced with the challenge of sustained nutrient delivery to enhance and sustain the activities of oleophilic microbes. Slow release fertilizer (SRF) is a purposely designed system that releases nutrients in synchrony with sequential needs of organisms hence they provide optimized nutrient use efficiency. This approach aids in mitigating challenges associated with the conventional fertilizer application such as eutrophication, soil hardening, increased fertilizer loss rate and other environmental devastation. Superabsorbent polymers are hydrophilic gels as they exhibit the ability of swelling and retaining water which supports its use in SRF production. Most SAP used in practice are synthetic and semi-synthetic polymers with high production cost and environmentally unfriendly properties. Natural based polymers such as guar gum, cellulose, chitosan, and starch are abundantly available from plant and other sources but most of these biopolymers have other application which may lead to scarcity for other uses. In most part of the world, enormous quantity of waste is generated which invariably causes pollution. World agro and industrial waste materials with little or no value is therefore recommended to be applied as SAP for SRF formulation. This review therefore provides insight on the potential use of controlled release fertilizer system as a useful tool in ensuring sustained nutrient delivery during bioremediation and also suggest more eco-safe and cost-effective approaches of SRF formulation.

Key words: Hydrocarbons, encapsulation, degradation, organic fertilizer.

INTRODUCTION

One of the major environmental problems today is hydrocarbon contamination resulting from oil and gas exploration and exploitation activities. As the demand for liquid petroleum increases, the release of this essential energy source into the environment becomes inevitable and has caused devastating consequences to marine/

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coastal waters, shorelines and land as well (Macaulay and Rees, 2014). Hydrocarbon components have been known to belong to the family of carcinogens and neurotoxic organic pollutants which constitutes a major health challenge globally (Das and Chadran, 2011). Soil pollution causes an extensive damage of local systems since accumulation of pollutants in animal and plant tissues may cause death or mutations. Due to the threat posed by large oil spills to the environment, it is imperative to identify clean-up techniques that are cost effective, swift, eco-friendly and sustainable that will optimize and facilitate biorestoration of highly petroleum hydrocarbon inundated terrestrial ecosystems for agricultural use or for ecological balance. A range of cleaning techniques has been successfully developed to limit the environmental impact caused by oil pollution (Okpokwasili, 2006). However, there is evidence that some of these techniques can be detrimental to the recovery of certain sensitive habitats like the soil and water (Ollivier and Magot, 2005). Emphasis has thus been steered towards techniques which assist nature's recycling capabilities to remove hydrocarbon pollutants (Stroud et al., 2007; Yakimov et al., 2007). Bioremediation is such a technique and in the context of oil spills is aimed at stimulating the biodegradation rate of oil. This is achieved by supplying indigenous hydrocarbon-degrading microbial community with electron acceptors and nutrients that are limiting (Swannell et al., 1996; Kigigha and Odayibo, 2014).

The depuration of petroleum hydrocarbon polluted ecosystems is mandatory in promoting sustainable development and the process of bioremediation forms an integral part of the numerous remediation techniques for the detoxification of polluted terrestrial environments. Bioremediation, defined as the ability of microorganisms to detoxify or remove pollutants owing to their diverse metabolic capabilities, is an evolving method for the removal and degradation of many environmental pollutants including the products of petroleum industry (Macaulay and Rees, 2014). One of the bioremediation methods of enhancing the natural propensity of indigenous hydrocarbon utilizing organisms (oil-loving or oil-eating) that has been explored by researchers is a process known as biostimulation which employs organic and inorganic nutrients to stimulate the propagation of oleophilic microbes to increase their innate ability to degrade complex chemical compounds. Many authors have considered biostimulation a more efficient approach compared to other oil spill control techniques (Agamuthu et al., 2013; Adams et al., 2015). However, researchers have also enumerated the challenges associated with this approach especially application of inorganic fertilizers in detoxifying chemical pollutants such as losses from volatilization, leaching, gaseous emissions, run-offs to nearby open systems and water eutrophication. Also, in the treatment of oil contaminated soils, inorganic nutrients have been found to cause soil hardening (that is, hardening of soil layers, disallowing the free movement of nutrients, water and oxygen within the soil) and decline in soil fertility (Alkindi and Abed, 2016). On the other hand, organic fertilizers (manures) has proven to be highly efficient and improves soil fertility, however, it may be challenging to produce organic nutrients in commercial quantities (Macaulay and Rees, 2014).

To mitigate the shortcomings of nutrient application and maximize the degradative potentials of indigenous hydrocarbon utilizing microbes, it is of paramount importance to develop systems that are sustainable in the supply of nutrients and similarly prevent challenges associated with the use of conventional nutrient application system outlined above. This review is intended to identify challenges associated with biostimulation, provide emerging strategies to curtail the excessive use of nutrients and also provide useful information on how to optimize the inherent catabolic potentials of oleophilic microbes in a petroleum hydrocarbon compromised terrestrial environment while taking into consideration environmental safety and also suggest more cost effective ways of formulating controlled release fertilizer.

ENVIRONMENTAL CONSEQUENCES OF PETROLEUM HYDROCARBON IN SOIL

An appraisal on the impact of petroleum hydrocarbons is inevitable due to the frequent spillage on agricultural soils, and the consequent fouling effect on all forms of life, rendering the soil (especially the biological active surface layer) toxic and unproductive. Oil reduces soil's fertility such that most of the essential nutrients are no longer available for plant growth, crop utilization and microbial activity (Abii and Nwosu, 2009). The severity of toxicity by oil spillage on crop performance is exemplified in loss of vegetation in mangrove swamp. UNEP (2011) reported that oil pollution in many intertidal creeks has left mangroves denuded of leaves and stems, leaving roots coated in a bitumen-like substance sometimes 1 cm or more thick. Apparently, any crop in areas directly impacted by oil spills will be damaged, and root crops, such as cassava, will become unusable. When farming recommences, plants generally show signs of stress and yields are reportedly lower than in non-impacted areas. A similar investigation was conducted by Kadafa (2012a) to assess the environmental impact of oil exploration and exploitation in the Niger Delta region of Nigeria, the findings present an alarming environmental impact on all forms of the ecological structure and recommended an urgent polyphasic approach in the biorestoration of the environment to avoid total loss of agricultural heritage and aquatic life in the region. Osuji and Nwoye (2007) assessed the impact of petroleum hydrocarbons on soil fertility in Owaza using physicochemical conditions of the soil and microbial index to ascertain the degree of impact.

Table 1. Factors that influence microbial degradation of petroleum hydrocarbon in soil.

Physical factors	Optimal conditions
Temperature	Affects the chemistry of the pollutants as well as physiology and diversity of pollutants. Optimal at 30 - 40°C in soil
Nutrient	Stimulates the growth of indigenous oleophilic microbes in the environment. C:N:P ratio - 100:10:1
pH	Soil pH affects availability of nutrients and it's important in the survival of microbes within a certain pH range. Optimal at pH 7. Acceptable range: 6 - 8
Moisture	Soil microorganisms require moisture for cell growth and function. Optimal moisture content for petroleum hydrocarbon degradation ranges between 45 and 85% of the water holding capacity.
Oxygen	Major degradation pathways for petroleum hydrocarbons involves oxygenates and molecular oxygen since most degradation process is aerobic

Evidence of severe hydrocarbon contamination, low acidity (pH 4.9-5.1), low electrical conductivity as well as high temperature and moisture provided assertion on reduced metabolic activities on the affected site. However, the results obtained indicated a low soil fertility which in turn implied low agricultural productivity and reduced source of livelihood in the affected area.

In terms of organisms, they vary greatly in their sensitivity to petroleum hydrocarbons. Effects tend to reflect the amount of toxic hydrocarbon in the environment and the different susceptibility of organisms, populations, ecosystem and doses are directly proportional to the amount released. The type of petroleum hydrocarbon released into the environment must be considered and the susceptibility of the organisms due to environmental processes acting on the released petroleum hydrocarbon. The chemical and physical properties of the petroleum hydrocarbon components determine the bioavailability to organism.

The bioavailability and persistence of specific hydrocarbons, the ability of an organism to accumulate and metabolize hydrocarbons, fate of the metabolized products, metabolites of the hydrocarbon interphase with the normal metabolic process may alter the survival and proliferation of organisms in the environment (Kadafa, 2012b). As a result, oil spill causes a decline in the microbial diversity and dynamics due to the toxic effect it has on the organisms. The diversity and the number of organisms at a given site may help to characterize the site with respect to the toxicity of the hydrocarbons to the microbiota, age of the spill and concentration of the pollutant. In addition, microbial isolates from soils that are historically exposed to hydrocarbon pollution exhibit a higher potential of biodegradation than others with no history of such exposure.

In a crude petroleum-polluted soil, the biodiversity and microbial prevalence of certain microbe(s) may indicate how well the soil is supporting the growth of that microbe(s). Fresh spills and/or high levels of pollutants often kill or inhibit large sectors of the soil microbial population, whereas soils with lower levels of aged pollution show greater numbers and diversity of microrganisms microorganisms (Saadoun et al., 2008).

MICROBIAL STRUCTURE OF PETROLEUM HYDROCARBON IMPACTED SOIL

Contamination of soil by petroleum hydrocarbons stimulates indigenous microbial populations which are capable of utilizing the petroleum hydrocarbons as their carbon and energy source thereby degrading the contaminants. The ability to metabolize hydrocarbons is displayed by different types of bacteria (Bogan et al., 2003; Malooktian et al., 2009; Abdusalam and Omole, 2009; Onuoha et al., 2011; Chikere and Ekwuabu, 2014a) and fungi (Chailan et al., 2004; Singh, 2006; Ibiene et al., 2011; Leitao et al., 2012). Different bacterial and fungal genera have been characterized from hydrocarbon polluted soils in different geographical and ecological contexts (Van Hamme et al., 2003; Malia et al., 2006; Refaat, 2010). There are innumerable amount of literature on the subject of hydrocarbon degradation by microorganisms and it is now a generally accepted fact that no single species will completely degrade any complex class of hydrocarbons (Gargouri et al., 2013; Zafra et al., 2016). Although, it is widely accepted that bacteria and fungi are primary mediators in hydrocarbon degradation, bacteria have been shown to be more versatile than fungi and therefore may play a greater role during biodegradation of hydrocarbons. Apparently, fungi play a central role in biodegradation or decomposition and are producers of an array of extracellular enzymes. In particular, filamentous fungi have been implicated in the biodegradation of a wide range of aromatic hydrocarbons and thus could contribute significantly to bioremediation efforts (Ferrari et al., 2011). Dissipation of petroleum hydrocarbons from the environment by microbial action is largely engineered by terrestrial and meteorological conditions such as pH, nutrients, temperature and other abiotic factors (Table 1).

BIODEGRADATION OF PETROLEUM HYDROCARBONS IN SOIL

Biodegradation of petroleum hydrocarbons is a complex process that depends on the nature and on the amount of the hydrocarbon present. Petroleum hydrocarbons are divided into four broad categories: saturates (branched, unbranched and cyclic alkanes), aromatics-ringed hydrocarbon molecules such as monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAHs), resins (polar oil-surface structures dissolved in saturates and aromatics) and asphaltenes (dark-brown amorphous solids colloidally dispersed in saturates and aromatics). In the structural arrangement of the four main hydrocarbon components of crude oil, saturates make up the outermost layer of the oil whilst asphaltenes constitutes the innermost portion of the oil due to their greater molar masses (Macaulay and Rees, 2014). Hydrocarbons differ in their susceptibility to microbial attack. The susceptibility of hydrocarbons to microbial degradation can be generally ranked as follows: Linear alkanes > branched alkanes > small aromatics > cyclic alkanes (Das and Chandran, 2011). Some compounds such as high molecular weight polycyclic aromatic hydrocarbons, asphaltenes and resins are highly recalcitrant in the environment and thus demands the urgent attention of research frontiers in designing novel remedial techniques for the removal of these carcinogenic, neurotoxic and priority pollutants from the environment.

Microbial degradation is the major and ultimate natural mechanism by which one can clean up the petroleum hydrocarbon pollutants from the environment (Liang et al., 2011; Zafra et al., 2016) and this is as a result of the enzyme systems microorganisms have that can degrade and utilize different hydrocarbons as source of carbon and energy to satisfy cell growth and energy (Das and Chandran, 2011). Onuoha et al. (2011) reported that Nigeria soil may harbour hydrocarbon degraders that have been exposed to hydrocarbons as a result of the increased multifarious activities of the oil industry especially in the Niger Delta region. Chikere and Ekwuabu (2014b) confirmed this report by conducting an investigation in Bodo community, Ogoniland, Nigeria to characterize the active culturable indigenous hydrocarbon utilizing microbial population. A significant population of hydrocarbon utilizing bacteria and fungi corresponding to the long-term impact of crude oil in the study area was observed. Hydrocarbon degrading microbes have an inherent capacity to assimilate hydrocarbons and/or its products (Atlas and Bartha, 1992) and this process is therefore regarded as a complex biological oxidation process involving mostly aerobic organisms which may be enhanced by supplementation with fixed nitrogen, phosphate and other rate-limiting nutrients.

NUTRIENT ENHANCED BIOREMEMDIATION: BIOSTIMULATION

soil (e.g., adding key nutrients, increasing oxygen transport or adding surfactants) and/or enhancing the numbers and activity of hydrocarbon- degrading microorganisms, this approach is known as biostimulation (Tyagi et al., 2011; Agarry et al., 2013). Numerous laboratory studies have demonstrated the efficiency of biostimulation (Swannell et al., 1996; Head et al., 2006) for enhancing the biodegradation rate of hydrocarbons in soils and other ecosystems. Spilled petroleum hydrocarbons represent an essential carbon source for the indigenous microorganisms, whereas, in most environments, the presence of nitrogen and phosphorus is limited. Thus, biostimulation accelerates the decontamination rate as the addition of one or more rate-limiting nutrients to the system improves the degradation potential of the inhabiting microbial population (Nikolopoulou and Kalogerakis, 2008; Tyagi et al., 2011). Addition of nutrients to optimize the degradation rate of petroleum hydrocarbon has been extensively studied and documented (Sarkar et al., 2005; Joshi and Pandey, 2011; Tyga et al., 2011; Agarry et al., 2013).

The source of nutrient (usually nitrogen and phosphorus) could be organic or inorganic. Inorganic nutrient sources such as NPK, K_2HPO_4, NO_3-N, have been described to be successful in the clean-up of crude oil both on land and water by stimulating the growth of remediating microbes (Kingston, 2002; Evans et al., 2004; Xia et al., 2007). However the use of a nutrient source as a biostimulant in addressing crude oil pollution challenge should be considered to be eco-friendly and cost effective. Ogbo and Okhuoya (2008) reported the treatment of oil-contaminated soils using direct application of inorganic fertilizers to cause soil hardening (that is, hardening of soil layers, disallowing the free movement of nutrients, oxygen and water within the soil) and reduction in soil fertility.

Inorganic fertilizers have the tendency to be released rapidly into the environment (probably due to their availability in the free state), and therefore, have a higher potential to cause eutrophication and leaching and also have been found to be a more expensive nutrient application system than organic nutrients as a result of re-application of fertilizers due to leaching, run offs and emission of nitrogen gas. Therefore, some scientists have considered using organic nutrients as a result of their cost effectiveness, slow release rate and consequently, lower potential to cause eutrophication and other environmental damages. It has been established by research frontiers that organic fertilizers (manures) are highly efficient in facilitating biodegradation, improving soil fertility and ecologically-safe since the release of nutrients is slower and the source is organic (Akiakwo et al., 2005; Joshi and Pandey, 2011). Nduka et al. (2012) and Agbor et al. (2012) investigated the potential of organic fertilizers as an ecologically-safe source of nutrient since the release of nutrient is slower, although may be too slow to accelerate biodegradation. Agarry et al. (2013) during a environments contaminated with crude oil within the first 21 days showed higher crude oil degradation in the organic waste treatment when compared with NPK treatment. This study amongst others documented elsewhere upholds the efficiency of organic nutrients Natural biodegradation processes of the indigenous microbial biomass may be accelerated by manipulating (manures) as supplements for optimizing land oil spill clean-up and has proven to be more productive as it will not only provide nutrients to microbes for hydrocarbon reduction, but will enrich the soil as well to support agricultural activities and restore biodiversity.

However, with all the benefits and advantages associated with the use of organic nutrients, it may be challenging to produce organic fertilizers in large quantities which may explain why the use of inorganic fertilizers has persisted. Although eutrophication is not common on land, the problem of soil hardening, loss of soil fertility, volatilization and leaching caused by excessive application of inorganic nutrients could also be managed effectively using the slow release nutrient application strategy. As an alternative Macaulay and Rees (2014) suggested that the combination of both organic and slow release inorganic nutrients can be applied using a nutrient-rotation strategy. The rotation strategy will help mitigate the effect of the toxicity and high cost of inorganic nutrient usage as well as augment the low commercial production of organic nutrients. The report also captured that the regulatory system will maintain the prolonged nutrient supply at optimum levels as well as prevents the possible under-supply of nutrients to the inhabiting microbes (Campos et al., 2014; Campos et al., 2015).

MECHANISM AND APPLICATION OF SLOW RELEASE FERTILIZER (SRF)

The goals of SRF use are that nutrients should not be limiting for microbial metabolism and function, there should be improved nutrient uptake efficiency and nutrient-leaching potential reduced (Morgan et al., 2009). It is very essential to be accustomed with mechanism of slow release nutrient system and the direct measure of the effectiveness of the process. Generally, the concept is difficult to conceive as it depends on numerous factors such as the nature/type of coating material, agronomic conditions and much more. Different mechanisms are cited in literature and these are still under development. However, Shaviv (2005) proposed a release mechanism for coated fertilizers called the multi-stage diffusion model. According to this model, after applying the coated fertilizer, irrigation water penetrates the coating to condense on the solid fertilizer core followed by partial nutrient dissolution. Subsequently, as osmotic pressure builds within the containment, the granule consequently swells and causes two processes. In the first, when osmotic pressure surpasses threshold membrane resistance, the coating bursts and the entire core are spontaneously released. This is referred to as the "failure mechanism" or " catastrophic release". In the second, if the membrane withstands the developing pressure, core fertilizer is thought to be released slowly via diffusion for which the driving force may be a concentration or pressure gradient, or combination thereof called the "diffusion mechanism" (Figure 1). The failure mechanism is generally observed in frail coatings (e.g. sulfur or modified sulphur). The controlled release of nutrients also depends on ambient temperature and moisture with the release rate increasing at higher temperatures with greater moisture content (Azeem et al., 2014). The coated fertilizer release mechanism is basically a nutrient transfer from the fertilizer–polymer interface to the polymer–soil interface, driven by water. The governing parameters for the release mechanism are: (i) diffusion/swelling; (ii) degradation of the polymer coating, and (iii) fracture or dissolution. A similar release mechanism was presented by Liang et al. (2007) and Wu and Liu (2008).

SUPERABSORBENT COATING MATERIALS FOR PREPARING SRF

Superabsorbent polymers (SAPs) also referred to as hydrogels or hydrophilic gels are systems of polymer chains fused together sometimes as colloidal gels in which water is the dispersing medium. SAPs exhibit the ability of swelling in water and retaining a significant fraction (<20%) of water within their structure, without dissolving in water (Zohuriaan-Mehr and Kabiri, 2008). SAPs have recently caught the attention of research circles due to its interesting properties that favour SRF production. These SAPs are 3-dimensional hydrophilic groups that are able to absorb and retain fluids and to release the fluids under certain conditions (Mas'ud et al., 2013). A polymer is characterised as a superabsorbent if its ability to absorb water is 100 times its original weight (Zhang et al., 2007).

SAPs are classified into groups based on the presence and absence of electrical charges, type of monomeric unit used in the chemical structure and original source. Currently, most of the SAP used in practice is mainly petroleum-based synthetic polymers such as polysulfone (PSF), cellulose acetate (CA) and polyacrylonitrile (PAN), which have high production cost and poor environmentally friendly characteristics and thus the development of natural polymer based superabsorbents has become subject of great interest due to their commercial and environmental advantages (Ray and Bousmina, 2005; Wang and Wang, 2010). Presently, many natural polysaccharides such as guar gum, cellulose, chitosan, starch, alginate and their derivatives have been adopted to prepare new types of superabsorbents (Wang and Wang, 2010). However, starch has recently caught the attention of researchers because it occurs naturally as a polysaccharide biopolymer that is abundantly

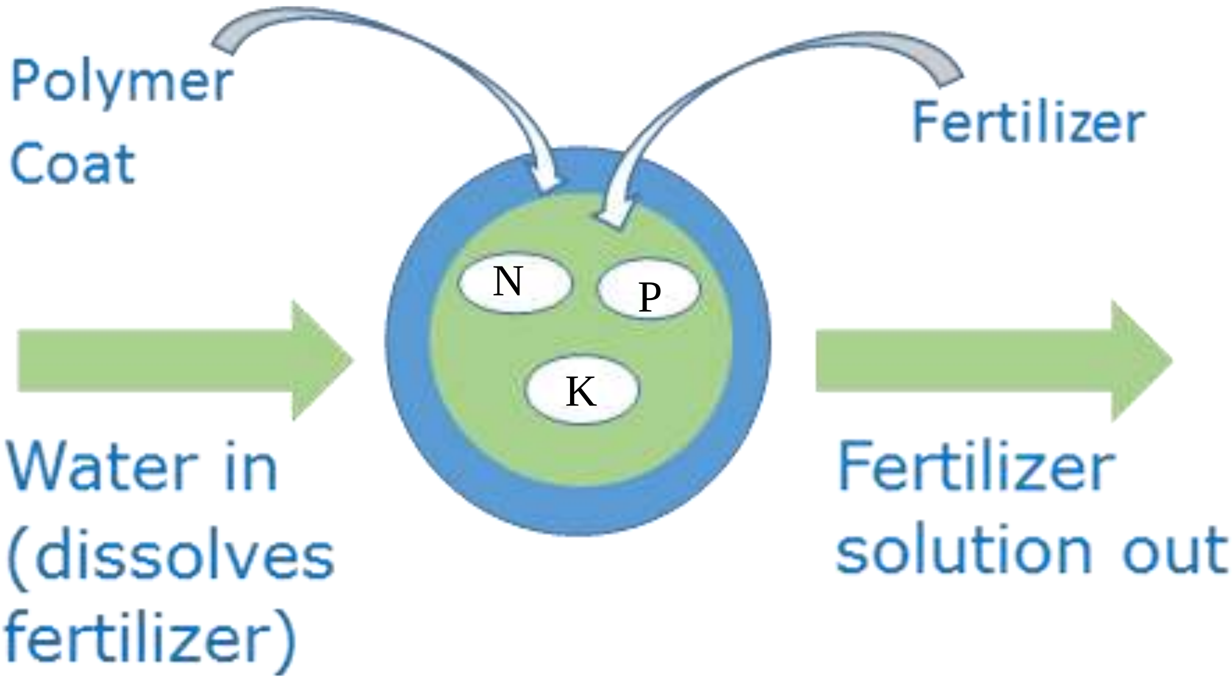

Figure 1. Schematic diagram of how polymer coated fertilizer works.

available from many renewable plant sources. Due to its low cost, biodegradability and abundance, several non-food applications of starch have been investigated (Akaranta and Agiri, 2010) with starch based controlled release coating material as one of the numerous areas (Jiang et al., 2013; Teli and Waghmare, 2010; Mas'ud et al., 2013). Other biopolymers such as cellulose, alginate, wheat gluten and rubber have been explored for their suitability in enhancing the efficiency of fertilizer release (Fernadez-Perez et al., 2008; Dubey et al., 2011; Ni et al., 2011; Li and Wang, 2012; Wang et al., 2012). The advantages of these biopolymers over petroleum-based polymers are their sustainability, biodegradation properties and base components that are non-toxic (Nnadi and Brave, 2011). In addition, they should undergo testing for degradation to evaluate if they can form any toxic substance that could affect the ecosystem. Liu et al. (2011) formulated a superabsorbent material based on wheat straw and attapulgite. Wheat straw was used as skeletal material in co-polymerization on which acrylic acid monomer can be grafted to form superabsorbent composite. The product possessed a core/shell structure. Its core was urea in attapulgite and alginate matrix and the shell was chemically modified wheat straw-g-poly(acrylic acid)/attapulgite superabsorbent composite. The results of the experiment showed the product had a preferable slow release property, efficiently improved the water holding capacity of soil, economical, non-toxic in soil and eco-friendly. Prior to the above stated experiment, Liu et al. (2009) prepared a superabsorbent polymer material from ethylcellulose (EC) and poly(acrylic acid-co-acrylamide). The biodegradation screening of EC coating in soil was assessed by differential scanning calorimetry (DSC) measurements which showed that the class transition temperature (T_g) of EC coating decreased with the time prolonged, an indication of the biodegradability of EC coating in soil. Although further studies are required to reduce cost of the product and improve its performance.

Due to higher costs and process complexity along with issues of environmental pollution caused by polymers, research circle shifted towards developing low cost, easily fabricable and environmentally friendly materials (Niu and Li, 2012). Many materials have been reported to be used as coatings, such as poly-sulfone (Jarosiewicz and Tomaszewska, 2003), polyvinyl chloride (Hanafi et al., 2000), polystyrene (Liang and Liu, 2006). However, after the release of fertilizers, remaining coating materials in the soil are very difficult to degrade and can accumulate over time to become a new type of pollution. Therefore, environmentally safe and biodegradable coating materials are expected to be used (Liu et al., 2009). Nandi and Brave (2011), Hu et al. (2009) and Liu et al. (2011) demonstrated the production of slow release coating materials with biodegradability potentials. Although, more research should be directed towards developing natural based polymer coating materials with properties suitable for withstanding environmental variations and efficiently deliver nutrients over a period of time synchronized with the requirements of oleophilic microbes in a crude oil compromised ecosystem.

Sustained nutrient delivery is key in achieving a

Table 2. Types of SAP used in SRF formulation.

Types of SAP	Author(s)
Starch phosphate-graft-acrylamide/attapulgite	Wang et al., 2006
Poly(acrylic acid)/diatomite and chitosan	Wu et al., 2008
Starch polyvinyl alcohol (PVA)	Han et al., 2009
Ethylcellulose-g-poly(acrylic-acid-co-acrylamide)	Liu et al., 2009
Amaranthus starch and a mixture of acrylamide, acrylic acid and KPS	Teli and Waghmare, 2010
Poly(N-isopropyl acrylamide)-co-polyurethane	Mattews, 2010
Carboxylmethylcllulose and starch	Nnadi and Brave, 2011
Wheat straw-g-poly(acrylic acid)/attapulgite	Liu et al., 2013
Phosphate rock grafted on sulfonated corn starch poly(acrylic acid)	Jiang et al., 2013
Modified cassava waste pulp grafted on acrylamide, ammonium per sulphate and N'N-methylene bisacrylamide	Mas'ud et al., 2013

successful bioremediation process.

SRF FORMULATIONS

Slow/controlled release fertilizer (SRF) is a purposely designed manure that releases active fertilizing nutrients in a controlled, delayed manner in synchrony with the sequential needs of organisms for nutrients, thus, they provide enhanced nutrient use efficiency along with enhanced growth (Shaviv, 2005; Subbarao et al., 2013; Sempeho et al., 2014). Inorganic fertilizer combined with superabsorbent polymers to obtain slow-release fertilizers with water retention properties has been extensively studied (Hu et al., 2009; Liu et al., 2009; Jiang et al., 2013; Azeem et al., 2014). An ideal controlled release fertilizer is coated with a natural or semi-natural, environmentally friendly macromolecule material that retards fertilizers releases to such a slow pace that a single application to the soil can meet nutrient requirements for the metabolic activities of microbes. Slow/controlled-release fertilizers are also called coated or encapsulated fertilizers because the release is controlled by a polymer coating that contains a water-soluble fertilizer. Due to cracks or uneven thickness of the coating, these materials produced irregular results. Today's coatings are made of natural, synthetic and semi-synthetic materials allowing for better control of nutrient release (Table 2). Following the issue with sulphur, polymeric materials were widely used to coat fertilizers since sulphur were easily disrupted by microorganisms whereas polymer coatings were not. In polymer coating fertilizer, the core is covered by a single or multiple layers of polymers. The method of preparing polymer coated fertilizers depends largely on the nature of the coating material. According to Adhikaria et al. (2014), the simplest method of coating involves dissolving the polymer in an organic solvent or water which is then sprayed onto the fertilizer using a coating drum or a fluidized bed or spray dryer. The nutrient release from polymer coating is affected by diffusion as a function of coating thickness and soil temperature. However, polymer spray coating involves organic solvents that not only inflict additional costs of the lean solvent and solvent recovery, but also cause hazardous gaseous emissions (Azeem et al., 2014). Hence the use of aqueous polymeric solutions was used to counter these issues. Liu et al. (2009) prepared a double-coated slow-release and water retention NPK fertilizer by crosslinked poly (acrylic acid)/diatomite-containing urea (PAADU) (the outer coating) chitosan (CTS) (the inner coating), and water-soluble granular fertilizer NPK (the core). The product as reported not only has slow-release property but also could absorb a large amount of water and preserve the soil moisture at the same time. In addition, the outer coating (PAADU) could protect the inner coating (CTS) from mechanical damage. Wu et al. (2012) on the contrary reported that thicker coating layers may damage soil quality if they are not degraded in parallel with nutrient release. With this in mind, urea coating with polyurethane although costly but its thinner coating layer was said to reduce coating cost by coating greater quantities of urea granules with less material although the biodegradability of polyurethane in the environment was not ascertained.

PROSPECTS OF SLOW-RELEASE FERTILIZER IN BIOREMEDIATION

Slow/controlled release fertilizer (SRF) is a purposely designed manure that releases active fertilizing nutrients in a controlled or delayed manner in synchrony with the sequential needs of organisms for nutrients, thus, they provide enhanced nutrient use efficiency along with enhanced growth (Shaviv, 2005). Crude oil pollution elicits toxic effects on the environment as well as drastic reduction of essential nutrients required for microbial activities. To this end the sustained availability of nutrients will provide maximum microbial functions in the environment. The rate-limiting step in bioremediation majorly is the sustained availability of nutrients to drive the process and also maintain a balanced and healthy environment. Conventional nutrient application system has posed numerous environmental and public health challenges from eutrophication, soil hardening and destruction of soil structure when applied overtime. This approach limits the biodegradation efficiency of the native microbes. However, slow release fertilizer is promising in enhancing a sustained availability of these nutrients for a more efficient and rapid mineralization of petroleum hydrocarbons. Slow release fertilizer has been used in bioremediation of sediments, shorelines and marine systems but limited research have been directed towards this system in bioremediation of terrestrial environment.

According to Atlas (1995), the *Exxon Valdez* spill formed the basis for a major study on bioremediation through fertilizer application and the largest application of this emerging technology.

Three types of nutrient supplementation were considered: Water soluble (23: 2 N: P garden fertilizer formulation), slow-release (isobutylenediurea and Customblen), and oleophilic (Inipol EAP22). Each fertilizer was tested in laboratory simulations and in field demonstration plots. The application of the oleophilic fertilizer to field test plots produced very dramatic results, stimulating biodegradation so that the surfaces of the oil-blackened rocks on the shoreline turned white and appeared to be free of surface oil within 10 days after treatment. The striking visual results strongly supported the idea that oil degradation in Prince William Sound was nutrient limited and that fertilizer application was a useful bioremediation strategy. A range of nutrient regimens comprising soluble nutrients (SN) only, Inipol EAP-22 only (Ip), Osmocote (Os) only and combinations of SN + Os, Ip +Os and IP + SN were used by Xu and Obbard (2003) to treat oil-contaminated beach sediments.

Their results showed that sediments amended with the controlled release fertilizer Os, maintained nutrient levels at a concentration that was beneficial for the bioremediation of the oil-contaminated soils more than that observed in Ip- and SN-treated sediments. Xu et al. (2005) in a related study observed that addition of 0.8% of slow release fertilizer, osmocote consisting of 18, 4.8 and 8.3% NPK (w/w) to oil polluted sediments was sufficient to maximize metabolic activity of the microbial biomass and biodegradation of straight-chain alkanes (C10 - C33); and application of 1.5% rate resulted in optimal biodegradation of recalcitrant branched-chain alkanes such as pristine and phytane.

The success of slow release fertilizer in enhanced bioremediation of crude oil polluted shorelines, sediments and open systems have been extensively documented but there's paucity of information on the possible use of controlled release fertilizer in the treatment of crude oil polluted soil, however, research frontiers have devised numerous SRF formulations to alleviate and optimize nutrient availability in the soil which is a rate-limiting factor for microbial proliferation and plant growth. Cartmill et al. (2014) conducted an experiment to determine the effect of the application of controlled release fertilizer on *Lolium multiforum Lam.* survival and potential biodegradation of petroleum hydrocarbons in sandy soil. Petroleum induced-toxicity resulted in reduced plant growth, photosynthesis, and nutrient status at the initial phase of the experiment. Consequently, plant adaptation, growth, photosynthesis and chlorophyll content were enhanced by the application of SRF in contaminated soil. Petroleum degradation was enhanced in the rhizosphere by the application of SRF especially when plants were exposed to intermediate and high petroleum contamination and concluded that SRF allowed plants to overcome the growth impairment induced by the presence of petroleum hydrocarbons in soil. The application of this system in soil bioremediation is promising in ensuring petroleum hydrocarbon reduction and total environmental recovery.

CONCLUSION

The continuous application of inorganic fertilizers directly into our environments exerts short and long term effects to our terrestrial and aquatic ecosystems. The use of slow/controlled release fertilizer singly or in combination with other organic nutrients in bioremediation is promising. This approach which has not received much attention in environmental sustainability and reclamation provides a platform for a safe and swift bioremediation practice. Challenges associated with biostimulation of petroleum polluted soil have been extensively reviewed. The current techniques in-use to mitigate the environmental challenges of fertilizer nutrient delivery is limited by: Biodegradable coating material, cost of SRF formulation, availability of organic fertilizers in commercial quantities and control of environmental changes for optimal utilization of nutrients by oleophilic microbes. These limitations have been addressed with the possible use of environmental-friendly, cost effective natural based superabsorbent polymer material as coating for SRF production and the adoption of nutrient-rotation strategy which is a combination of both organic fertilizers (manures) and inorganic nutrients (slow release) to help reduce toxicity and optimize nutrient use efficiency. The application of these strategies in bioremediation is relatively new but has been implicated in agriculture, horticulture and floriculture and shown very promising result. However, it may be necessary to employ an integrated biostimulation technique (slow release fertilizer, organic-inorganic nutrient rotation system and landfarming) in order to create an aggressive synergistic approach which presents an optimal environment for oleophilic microbes and soil enrichment. Nutrient enhancement of crude oil inundated soil and stimulation of indigenous oleophilic microbes by fertilizer application has been extensively studied and accepted by researchers to be highly effective in oil spill clean-up. Despite these positive benefits, there are economic and environmental challenges associated with this practice. This review has therefore outlined the economic and environmental damages caused by the current nutrient application system and also provided potential remedial approaches to combat this menace. Lack of data regarding the release kinetics of SRF in various types of soil, changes in temperature, ambient moisture, bioactivity of the soil, wetting and drying cycles of the soil which makes the release rate of the fertilizers unpredictable, is a challenge that requires further research to improve oil spill management globally.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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