Carbon Nanotubes—A Novel Approach to Oil Spill Cleanup

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1 Introduction

Oil spill cleanup techniques that have been used for containing the spill or to reduce the immediate effects of an oil spill include bioremediation, in situ burning of oil on water, mechanical equipment like skimmers and booms, spraying of chemical dispersants and oil sorbents (Majed et al. 2012). But these techniques are not very effective. The industry requires a more novel technique in order to combat oil spills. Some oil spill cleanup techniques along with their limitations and impact on the environment are discussed below.

1.1 In Situ Burning

This is one of the techniques which have been used a lot. This method involves burning of oil on the site where oil spill has occurred. Oil spill should not spread to a greater area. For the in situ burn to be a success, layer of oil on the sea surface should be at least 2–3 mm thick in order to counter the cooling effect of sea winds and to sustain fuel source (Majed et al. 2012). Oil spill if spread to a greater area will need to be contained against a barrier. Ignition is incorporated using variety of devices like diesel-soaked rag to more advance equipments like helitorch. Helitorch is kind of a flame-thrower which is suspended beneath a chopper. A huge amount of smoke is generated as the oil is burned which results in contamination of land, water table and environment. The viscous residue has the ability to sink and get accumulated which

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would adversely affect the marine life-forms. Carbon monoxide and sulfur dioxide are frequently formed as toxic compounds when oil is burnt on the sea surface.

1.2 Booms

Booms are temporary floating mechanical barriers used to contain marine spills and assist in recovery. Booms are available in various shapes and sizes as per the coverage area. A boom includes a containment partition that floats on and extends above the water surface to prevent water from splashing over, and a “skirt” or “curtain” that sinks into the water which prevents water escape from below.[1] Booms may be deployed in various configurations, depending on winds and other environmental conditions. Booms also facilitate the containment for in situ burning. However, oil drainage is still a problem for spills over greater area.

1.3 Thickeners

Thickeners are often referred to as herding agents. They are deployed to increase the viscosity and increase the surface tension between oil and water. This leads to a better containment and eases the oil recovery as the spilled oil will not spread in larger area after the deployment of thickeners. However, thickeners are expensive as well as toxic. The affected oil with thickeners will sink soon. Hence, the problem may be increased while containing the oil spill.

1.4 Dispersants

Dispersants are chemically active agents that assist to break up an oil droplet on the sea floor into further smaller droplets by lowering the surface tension between oil and water. But the chemical constituents of the dispersants pose a threat to the natural habitat because of their toxicity. Dispersants are sprayed on the area of spill by specially equipped boats or planes (guidelines on implementing spill impact mitigation process (SIMA) 2017). Dispersants can lead to contamination of water table. However, in the present scenario, the use of dispersants has been minimized.

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[1] http://www.oilspillprevention.org/oil-spill-cleanup/oil-spill-cleanup-toolkit/booms.

1.5 Skimmers

Skimmers represent a variety of mechanical equipment that facilitate oil removal. An important aspect to be noted is that only lighter oils can be separated effectively.[2] Some skimmer technologies involve suction to recover spilled oil, while weir skimmers work on the principle of gravity to gather skimmed oil into underwater storage tanks. Skimmers are generally effective when used in calm water, and suction skimmers are prone to clogging by floating debris (guidelines on implementing spill impact mitigation process (SIMA) 2017). However, skimmers leave much of the recovered oil mixed with water, thus making this process expensive and economically impractical.

1.6 Bioremediation

It is a technique that involves biological agents that attracts microorganism which speeds up the process of biodegradation at the contamination site. This process is usually deployed in areas near shoreline. Nitrogen and phosphorus-based fertilizers are dropped in the contaminated area in order to enhance the growth of microorganisms (Wadhwani 2017). Bioremediation is not effective when sunken oil is involved. This method cannot be used in areas with low temperature and insufficient oxygen.

1.7 Sorbents

Sorbents are used for sorption and are the most popular technique that have been applied for the treatment of oil spills. Principle of adsorption is involved in the process. A variety of sorbent materials have been tested in order to determine the best one. Sorbents must be oleophilic and hydrophobic in order to combat oil spills (Wadhwani 2017).

1.8 Natural Organic Sorbent

These type of sorbent materials are abundant either in nature or as a by-product of an industrial process. These materials include straw, moss, etc., and are environmentally friendly as they do not harm the environment and the habitat. The limitation posed by use of such materials is the cost involved in recovering the oil-soaked sorbent after removing the oil and later re-using it again (Majed et al. 2012). Organic sorbents can

[2] http://www.oilspillprevention.org/oil-spill-cleanup/ocean-oil-spill-cleanup-toolkit/skimmers.

adsorb around 3–15 times their weight in oil. Many sorbents loose particles and are difficult to collect. These problems are countered by the use of floatation devices.

1.9 Inorganic Sorbents

These sorbents are very fine grained, highly dense, natural or processed. They are used to sink the oil floating on the surface. These sorbents contaminate the sea beds and are harmful to the flora and fauna. Due to low retention capacity, they release large amount of adsorbed oil while sinking. They are not economically viable. Examples of inorganic sorbents are fly ash, zeolites, silica, activated carbon and graphite.

1.10 Synthetic Sorbents

This category of sorbent is the most efficient and effective in recovery of oil. Polyurethane and polypropylene are the most widely used polymers in sorbents. They are known for their significant oleophilic and hydrophobic property along with their high adsorption capacity. Some synthetic sorbents include cross-linked polymers and materials like rubber. Most of these sorbents can adsorb up to 70 times their own weight. However, these substances fail to adsorb the chocolate mousse which is formed when the spilled oil is pitched and rolled on waves. If these sorbents are not recovered, ecological problems may arise.

2 Carbon Nanotubes—Structure and Properties

Carbon nanotubes are one of the best examples of the nanoscale materials that are derived from the bottom-up approach in chemical synthesis. The CNTs are a prime example of the advancements that the modern science and technology has undergone (Wang et al. 2013). The carbon nanotubes are tubular form of carbon which is composed of hexagonal lattice of carbon atoms. These tubes have a hollow core with diameter in the range of 1–50 nm and thickness much less than that of a human hair. These nanostructures exhibit some very unique and effective properties which makes them an ideal material to be used in the fields of electronics, optics, material sciences, nanosciences, etc.

The CNTs are allotropes of carbon and their structure can be easily understood as a one carbon atom thick sheet of graphene which is rolled at certain specific and discrete angles to form long and seamless tubes (McNeish 2008). The angle at which the sheet is rolled is known as the chiral angle. CNTs possess several interesting properties such as an extremely high aspect ratio which is nearly 1,000,000:1, ultra low density, extreme mechanical stiffness, tensile strength as well as elasticity. The value of Young's modulus of elasticity −1700 gigapascals is about eight times that of steel. The tensile strength of a CNT can range up to 100 gigapascals (approx. 15,000,000 psi). The density of carbon nanotubes varies around 1.3–1.4 g/cm^3 which is far less than the value of density for steel that ranges up to 7.8 g/cm^3 (Gui et al. 2013) (Fig. 1).

This strength of the carbon nanotubes is a result of the sp_2 hybridization found in between the carbon atoms, wherein each carbon atom is bounded to the nearby atoms via one double and two single covalent bonds. Hence, they are stronger than diamond which involves sp_3 hybridization among the interlinked carbon atoms.

2.1 *Structure of CNT*

Based on the structure, carbon nanotubes are broadly classified into two categories—single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT).

A single-walled nanotube consists of a one carbon atom thick sheet of graphene which is rolled into a seamless cylinder with a diameter of nearly 1 nm (McNeish 2008). The structure of SWCNTs may be arm chair, zigzag and chiral depending upon the angle at which the graphene sheet is rolled (Fig. 2).

Multi-walled carbon nanotubes comprise several coaxial cylinders, each of which is made of a single graphene sheet surrounding a hollow core. The outer diameter of MWCNTs is in the range of 2–100 nm, while the inner diameter varies between 1 and 3 nm, and their length is one to several micrometers (Lee and Parpura 2010).

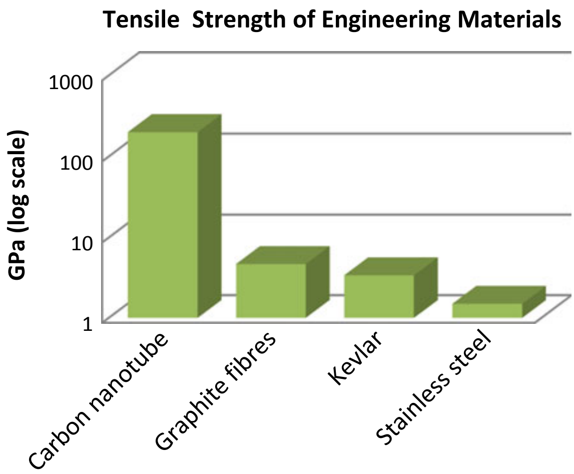

Fig. 1 Comparative study of tensile strength of engineering materials. Source: https://worldofnanoscience.weebly.com/nanotube--carbon-fiber-overview.html

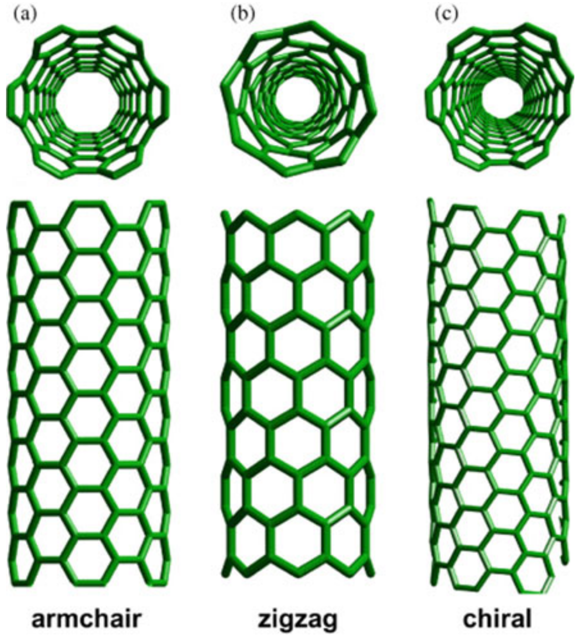

Fig. 2 Different types of CNT based on their structure. Source: Karthik et al. [2014]

2.2 Carbon Nanotube Sponge—An Ideal Material for Oil Spill Cleanup

CNT sponge is a three-dimensional framework of the carbon nanotubes. In contrast to the parallel arrangement of the individual nanotubes, a CNT sponge comprises an interconnected, cross-linked network of the nanotubes. This interconnected framework makes the material strong in three dimensions rather than the parallel arrangement of nanotubes whose strength is restricted only in the axial direction of tubes (Gui et al. 2011). The cross-linking is achieved by adding boron atoms during the synthesis.

Introduction of a foreign atom inside the hexagonal carbon lattice which is composed of a network of thin tubes, leads to disruption in the arrangement of the network since the foreign atoms do not wish to be a part of the same (Deng et al. 2013). Boron, being next to carbon in the periodic table, has one less electron in its valence shell. So, due to the addition of boron atoms, the curvature of the material changes, thus initiating a different type of growth. This encourages the formation of "elbow" junctions that enable the nanotubes to grow into a three-dimensional network (Varshney 2014). The individual threads are tangled together into a complex network, and thus a macroscale, spongy block of nanotubes is obtained which is thick and large enough to be used as a sorbent material in an oil spill cleanup (Wu et al. 2014).

The main highlight of this sponge is that it exhibits excellent hydrophobic and oleophilic properties. Owing to the superhydrophobicity, it floats on water and adsorbs only oil from an oil–water interface. It possesses high sorption capacity as much as 93.2 gm of oil adsorbed by 1 gm of the sponge. A CNT sponge provides an enormously large specific surface area whose experimental value is found out to be 253 m^2/gm, thus enhancing its sorption capacity and making it an ideal material for adsorbing oil (Gui et al. 2011).

An additional feature of CNT sponge is that they are robust, highly flexible and can withstand a series of compressive forces, without their properties getting affected (Kharisov et al. 2014). The above properties prove to be extremely useful for recovering the oil and also add to the reusability of the material. The adsorbed oil can be removed just by mechanically squeezing the sponge. This resistance to cyclic strains is achieved due to the inter-connecting cross-linkage in between the atoms. Incineration of the material causes absolutely no change in the internal network and structure. Upon the adsorption of oil, if the sponge is put to fire, only the adsorbed oil burns and the CNT sponge is recovered unaltered. The reusability of the sponge is further enhanced owing to this exclusive property (Golnabi 2012).

Along with the above-mentioned properties, it also shows salubrious magnetic properties which are produced due to the metal catalyst used during the synthesis process (Liu et al. 2007). Thus, the movement of the sponge on the sea floor can be controlled by the use of appropriate magnets and the sponge can be recovered back after the cleanup process. This gives it an additional advantage over other sorbent materials which cannot be recovered again after their use, are left behind after the cleanup and cause environmental degradation.

3 Experiment

The MWCNT proves to be the best sorbent material that can be used in oil spill cleanup due to its excellent selective adsorption capacity and its reusability (Wu et al. 2014). For the experiment petrol, kerosene and diesel were used. The CNT was gratefully provided to us by the UPES R&D Center.

To investigate the sorption capacity and its variation with the number of reuses, simple experiments were performed. 0.2 gm of CNT was put in an injection syringe (used in medical practices) for the oil absorption process.

The removal of oil from the CNT was realized using two different techniques.

1. Extruding the oil by pushing the piston of the syringe against the CNT to remove the oil.
2. Incinerating the CNT to burn the oil.

The steps for the experiment were as follows:

1. 0.2 gm was loaded in a 5 ml syringe.
2. The piston was pushed to extrude air from the sponge.
3. The oil was then sucked into the syringe by drawing the piston upwards, which was then taken out.

4. The extra oil was allowed to drip out by hanging the syringe for over 2 h.
5. The oil loaded CNT sponge was then weighed to determine the amount of adsorbed oil.

4 Results and Discussion

The adsorption capacity and reuse performance of the CNT were checked for all three oil samples (petrol, kerosene and diesel). The observations have been plotted in the following graphs (Fig. 3).

The results in the following graphs clearly show that the adsorption capabilities of the CNT tend to decrease in both the methods and then later acquire a near constant value. The adsorption capacity of the incinerated CNT is found to be higher than that of the extruded CNT.

For the extruded CNT, the adsorption capacity decreases with the no. of reuses but later reaches a stable value. The decrease is due to the deformation of the nanotube and hence decreases in its pore gap. Moreover, the value of the adsorption capacity is more for heavy oils, which are denser and have longer carbon chain (Liu et al. 2015). The decreased tube radius and increased viscosity (in heavier oils) of the oil assist adsorption. This makes them suitable for adsorbing crudes.

In case of the incinerated CNT, although the initial adsorption capacity is higher, but its repeated use induces a cooking process within the nanotube which decreases the internal gap and available adsorption sites. The extent of coking is more for heavier oils, i.e., oils having longer carbon chains (Liu et al. 2015). This makes the incinerated CNT less effective in the case of crudes.

Thus, it would be much more effective and efficient to utilize the extrusive reusability of CNT sponges in oil spill cleanup processes rather than incineration, wherein the oil is lost to combustion.

4.1 Deployment Strategy

The natural sorbent materials used for oil spill cleanup do not possess selective adsorbtivity, and thus adsorb water too. The synthetic adsorbents like polyurethane have good amount of oleophilicity but that is very low as compared to the MWCNT sponge. The CNT sponge has superhydrophobicity which makes it an excellent material to be used effectively in areas with very thin oil spill layer.

The CNT sponge can be conveniently used to adsorb the oil by physical contact of the sponge with the oil spill surface. This helps to restrict the spill radius and the same method can also be employed at places where the small quantity of oil floats far away from the spill (Gui et al. 2013).

The technique used to extract the soaked oil from the CNT sponge includes a conveyer belt system that is mounted on the deck of a container ship. The sponge

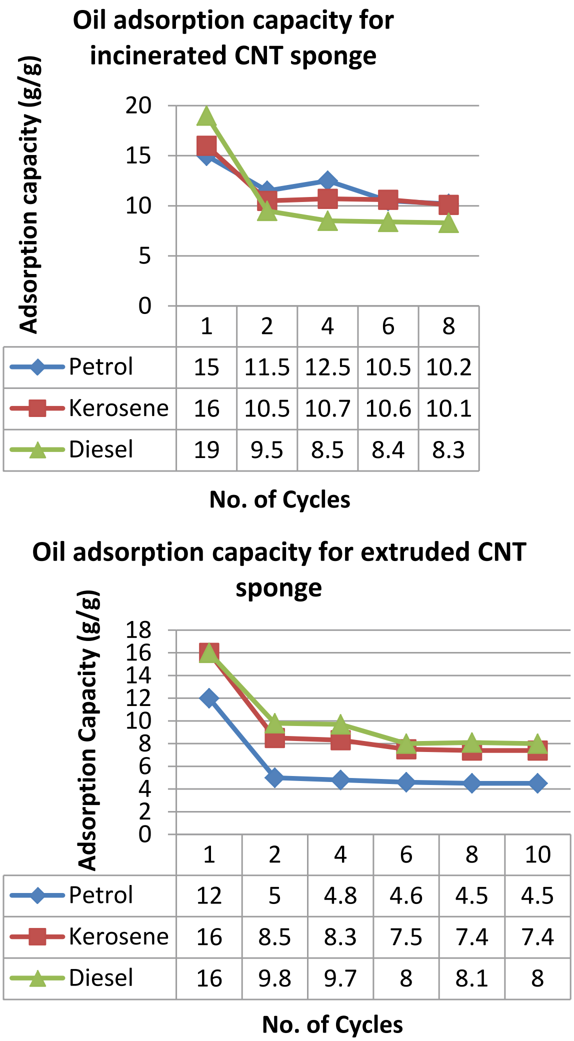

Fig. 3 Comparative study of the performance of the CNT sponge on extrusion and incineration to recover the oil

is attached to the outer, coarse surface of the conveyer belt, which is then squeezed by a roller press to extract the oil. This system efficiently utilizes the reusability of CNT sponge for continuous and efficient recovery of oil (Fig. 4).

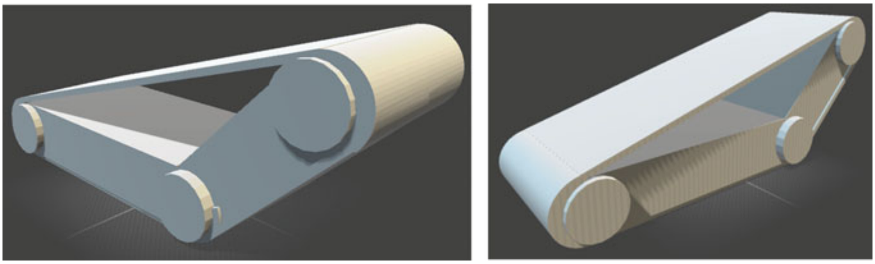

Fig. 4 Illustration of the conveyer belt system

5 Conclusion

The commercial viability of any technology in an oil spill cleanup largely depends upon the production cost, oil adsorption capacity, environmental friendliness, reusability as well as disposability.

The use of CNT sponge is extremely efficient and eco-friendly. The sponge can be reused a number of times and can also be recovered back after the cleanup (Gui et al. 2011). Moreover, the CNT sponge surpasses aerogels in the recovery of oil due to its less production cost. The average cost for the production of 1 kg CNT sponge varies around 6–10$, whereas it takes 2870$ in the synthesis of aerogels by supercritical drying.

Thus, it is evident from the above factors that the CNT sponge shows enormous potential to come out as an innovative solution for the oil spill cleanups.

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