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# Oil spill cleanup: A review

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### Abstract

Oil is a vital source of energy in the modern industrial world. It has to be transported from the production source to many locations throughout the world via oceans and inland transport. Oil spillage over the water bodies happens during transit due to accidents or deliberate action during wartime, causing environmental degradation. Fiber based sorbents have been found to be the finest material for cleaning up oil spills. The material and structure of the sorbents, as well as the physical properties of the oil, impact the sorbents' oil sorption and retention behaviour. This review paper studies the various oil spill cleanage methods with a special emphasis on oil sorption technique using fibers as biosorbent material. In addition to the available sorbents viz cotton, wool, milkweed floss, kenaf, kapok, sugarcane bagasse etc, the use of bamboo fibre has been suggested as a supreme sorbent.

Keywords: Clean up; Oil spill; Fiber; Sorbent; Sorption

### 1. Introduction

Oil is the utmost need of today's world and major source of energy for modern industrial world as it is used to oil the wheels, fuel automobiles, provide energy source in industrial plants, make plastics and non-flammable clothes, to regulate the temperature in home, manufacture fertilizers for the growth of food and in paint manufacturing [1]. The increasing demand for energy by emerging economies has led to enhancement of oil production up to 86.91% million barrels per day[1]as one third contribution of global primary energy supply is fulfilled by oil.[2]Oil is a mix bag of many compounds predominantly sulphur, nitrogen, metals and hydrocarbons.[3] Among of these compounds, hydrocarbons are further subdivided into different parts viz saturated hydrocarbons, unsaturated hydrocarbons, aromatic hydrocarbons out of which polyaromatic hydrocarbons demonstrates the long term or short term harmful effects on living beings [4].

Crude oil and natural gas are formed from the decomposition of organic matters like large trees, ferns and other leafy plants. Organic materials assimilated into sedimentary rocks, remains of marine and other organisms are responsible for the formation of oil. The whole process of oil formation needs millions of years and specific geological conditions [2]. Further, physiochemical behaviour and chemical composition of crude oil is very sensitive to the source from where it is extracted, time of extraction and refining processes. Crude oil extracted from same source at different time behaves differently [3]. Therefore, the assessment of toxicity of complex mixture of crude oil is challenging because many other things like additive, synergistic and antagonistic factors are also involved [4]. Components of crude oil possess different properties such as specific gravity, volatility, flammability, viscosity, on the basis of which can be categorized into five groups as in the Table 1.

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Oil groups	Specific gravity	Nature	Toxicity
Gasoline Products	Specific Gravity G <0.80; API Gravity >45	Volatile, Low Viscosity, Highly Flammable, Non-Sticky	Terribly toxic to animals and plants
Light Crude Oils	Specific Gravity is 0.80-0.85; API Gravity 35-45	Moderately Volatile, Low to Moderate Viscosity, Form Thin Slicks	More bioavailable than lighter oils, so these are more likely to affect animals in water and sediments
Medium Crude Oils and Intermediate Products	Specific Gravity of 0.85-0.95; API Gravity 17.5-35		More bioavailable than lighter oils, so these are more likely to affect animals in water and sediments
Heavy Crude Oils and Residual Products	Specific Gravity of 0.95-1.00; API Gravity Of 10-17.5	Very Viscous, Less Volatile, Form Stable Emulsions	Low acute toxicity to biota, so it can cause long-term effects via coating
Sinking Oils	Specific Gravity of >1.00; API Gravity <10	Form Stable Emulsions	Low acute toxicity to biota, so it can cause long-term effects via coating

Table 1 Characterization of various oil groups

API = (141.5/specific gravity) - 131.5. API gravity is inversely related to specific gravity; API gravity= American Petroleum Institute gravity.

# 2. Oil spills and environment

Oil spills are recently emerging environmental catastrophe which needs mitigation measures and awareness to eradicate its long-term impacts on environment and ecosystem. Now, oil production and transportation activities from production phase to consumption phase have increased the vulnerability of coastal lines and marine environment to oil spill menace. The unrestrained exposure of crude oil to environment is designated as oil spill. There are many factors which are responsible for this including human error, corrosion of pipelines and storage tanks, mishandling during loading and discharging operation, fire or explosion during drilling operation [5]. Several sources which cause spillage of crude oil are enlisted in below Table 2 [6].

**Table 2** Sources of spillage of crude oil in aquatic environment [6].

Sr.No.	Sources of spillage of crude oil	Quantities (k.tones)
1	Transportation accidents	390
2	Tanker operations	710
3	Fuel combustion	300
4	Erosion	300
5	Municipal, industrial and surface run-off	1400

In marine life, oil spill may affect the many organisms by direct toxicity [7]. Therefore, oil spills have become a global issue to be deal with as this affects sea life, harm the beauty of polluted sites along with excessive growth of green algae [8]. In recent days, threat to lives of sea fauna and environmental damages are increased by the discharge of petroleum pollutants and their derivatives in environment while its exploration, production, transportation, storage and utilization [9]. The adverse effect of oil spills on marine life can be evidenced from the oil spill accident in the Gulf of Mexico: Lyxtoc I spill in 1979-1980 and The Deep-Water Horizon in 2010 [10]. Also, World Health Organisation has drawn the attention of many states about the adverse effects of oil spillage on both living and non-living components of environment either directly or indirectly. This includes the gastro-intestine dermatological and neurological effects [11]. Major oil spills which have been encountered till now are enlisted below in Table 3.

 Table 3 Various oils spill around world

Spill name	Region	Country	Amount (Barrels)	Date	Environmental effect	Clean-up Method Used	Cause of Spillage
SS Frank H. Buck / SS Prestige Coolidge	San Francisco Bay, California	USA	74951.5	March 1937	22,000 birds died	Unknown	Collision of two company tankers Frank H. Buck and liner President Coolidge
Santa Barbara Spill	USA	80,000- 100,000		January 1969	Coastal damage, marine life polluted	Dispersant Sorbents, Booms	Underwater pipe rupture
West Falmouth oil spill	West Falmouth	USA	4762	September 1969	All kinds of marine invertebrates and fish were affected	Booms, Detergents and Emulsifiers	Barge Florida went aground and hit the rocks
Texanita Collision/ Oswego- Guardian oil spill	Near Stilbaai	South Africa	84500	August 1972	Thirty three causalities	Unknown	Collision of two tankers Oswego- guardian and Texanita because of blurred vision in intense fog
Amoco cadlizoil spill	Offshore of Brittany,	France	1,604,500	March 1978	Death of 20,000 birds, dead molluscs, sea urchins and other benthic species	Dispersant Skimmers, Labour	Tanker Amoco Cadliz ran aground off the coast of Brittany following a steering gear failure
Ixtoc I spill	Bay of Campeche, Gulf of Mexico	USA	30,000- 10,000 (barrels per day)	June 1979	Population of fish either died off or moved on, crabs and other beaches in fauna were reduced greatly, female population of Kemp's Rid were reduced	Skimmers, Booms, lowering a cap over the well, plugging the leak with mud, use of dispersant	Wellhead blowout and explosion
Exxon Valdez Oil Spill	Prince William Sound, Alaska	USA	260,000- 900,000	March 1989	Immediate death of 250,000 birds, sea otters, sea birds and	Burning, Mechanical cleanup, dispersant, Hot	Ship gone off course from main ship land

					harbour seals were affected	Washing , and High Pressure Washing	and struck Bligh Reef
Braer spill	Off Shetland, Scotland	υк	718250	January 1993	1500 oiled birds collected, mortality was 5000	Chemical dispersants	Tanker Braer runs aground in hurricane force wind and breaks up into three parts.
Sea Empress spill	South west coast, Wales	UK	608400	February 1996	4600 oiled birds were collected and mortality was 10,000- 15,000	Dispersants, Booms, Mechanical methods, Sorbents	Single hull oil tanker hit rocks
Tanker Nakhodka oil spill	Sea of Japan off the Oki Islands of Shimane Prefecture	Japan	50700- 50800	January 1997	Immediate death of most benthic animals	Skimmers, Coastal Booms, Dispersant	breakage of tanker in two parts
Erikaoil spill	Off the coast of Brittany	France	30,000	December 1999	74,000oiledbirdswererecorded,Outofwhich42,000weredead.	Skimmers, Booms and other Equipment Like Scrapers, Buckets, Spades	Tanker ERIKA, broke in two in a severe storm
Prestige oil spill	Offshore of Spain and Portugal	Spain/ France	532350	November 2002	15,610Oiledbirdswerecollectedandmortalitywas115,000-230,000	Booms, Manual Cleaning, Detergents	Tanker PRESTIGE suffered hull damage
MT Hebei Spirit Oil Spill	Off the west coast of the Republic of Korea	Korea	2197000	December 2007	30 beaches have been affected, no migratory birds arrival.	Booms, Dispersants, Mechanical methods, Skimmers and Sorbents	Collision of a barge carrying a crane with oil tanker MT Hebei Spirit
Deepwater Horizon oil spill	Gulf of Mexico	USA	4.9 million	April 2010	Loss of Birds, marine mammals, habitat and human uses	In-situ burning, dispersant, Booms, Sorbents and Skimmers	Accidental Oil Well Eruption
Mumbai oil spill/ MV MSC Chitra& MV Khalija	Arabian sea, Mumbai	India	6760	August 2010	mangrove turn black due to the oil slick, snakes and fishes were filled with oil, marine life was contaminated	Oil skimmers, Booms, Chemical Dispersants, Bioremediation	Two cargo ships MV MSC Chitra and MV Khalija collided

Guarapiche river oil spill	Venezuela, Maturin, Monagas	South America	60,000- 80,000	February 2012	Water services were cut- off, killed the flora and fauna in 21,000 square kilometres in river basin.	Absorbents,	Pipeline Rupture
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## 3. Weathering process

From the very starting point, when oil comes in contact of sea water, complex behaviour of oil transformation is seen as oil in marine environment rapidly loses its original properties and disintegration into hydrocarbons takes place [12]. Weathering process transforms the organic components into inorganic components which results into depletion of dissolved oxygen [13]. Moreover, spreading of spilled crude oil on sea surface forms a thin layer referred to as oil slick. Further, degradation of this oil slick occurs due to action of several natural processes [14]. The main stages of oil weathering process on sea floor are spreading, evaporation, dispersion, emulsification, dissolution, oxidation, sedimentation, microbial degradation and aggregation. Weathering of oil spill varies by the effect of temperature of ocean, sunlight of spill site, behaviour of sea and amount of microbes. Furthermore, properties and composition of oil also affects the progression, duration and results of these transformations. During oil weathering process, the modified behaviour of oil slick makes it more lasting to marine waters and favours its lifespan in marine biology [14]. Oil spills are threat to marine life in various forms viz toxicity in fishes includes lymphocytosis, epidermal hyperplasia, and haemorrhagic septicaemia, toxicity in mammals possesses an anticoagulant potency [15], enhanced poisonousness by UV radiations (referred to as photoenhanced toxicity). This, photoenhanced toxicity actually occur through activation of some chemical residues that accumulate in aquatic organisms [16]. Figure1 shows the transformation of oil by weathering process which involves the following processes:

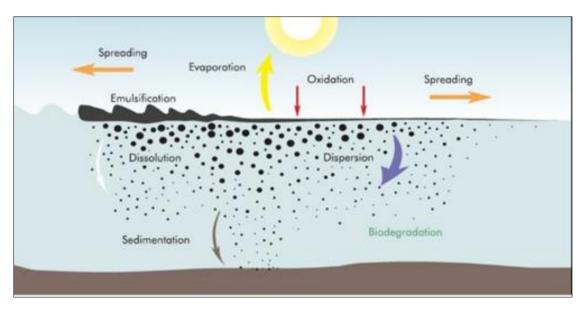


Figure 1 Weathering process of oil: Complex behaviour of oil in marine water [14].

### 3.1. Spreading

As soon as oil is spilled, it starts to spread on the sea floor. Speed of oil spreading greatly depends upon the temperature of sea water and composition of oil (viscosity of oil). At high temperature, viscosity of oil is low and speed of spreading is more. Conversely at low temperature, viscosity of oil rises as they are inversely related, hence, display low speed of spreading [17].

### 3.2. Evaporation

Evaporation is the process in which light and highly volatile components of oil vaporises by the action of sunlight. The rate and speed, at which it occurs, depend on the basic nature of oil. It can be described by considering examples of kerosene and gasoline, both of which are light in nature and evaporate speedily in comparison of heavy oil [17].

#### 3.3. Dispersion

Waves of the sea surface defragment the oil slick in to oil droplets of varying sizes. Small droplets have fewer tendencies to recombine and remain suspended on sea floor. On the other side large sized oil droplets become part of upper-level sea water column and thus, reform the slick. Speed of oil dispersion depends largely on nature of oil (low viscosity and light nature) and state of sea viz winds speed and surface tension. Dispersion is more in the direction of wind and high speed of wind accelerates the dispersion promptness [12, 18].

### 3.4. Emulsification

Emulsification is the process in which oil-in-water emulsion is formed by the suspended sea water droplets in oil which ultimately increases its persistence on sea floor and delays the other weathering processes [17]. Emulsification depends upon the oil composition and surface tension of sea water as these forces decrease the dispersion of oil. Hence surface-active agents and emulsifiers can be used to abolish oil spill [12].

### 3.5. Oxidation

Chemical transformations of oil on sea floor are generally of oxidative nature. They carry out photochemical reactions by means of the ultraviolet waves of solar spectrum. These photo oxidation reactions result into the polymerisation of complex oil composition which ultimately increases the viscosity of oil hence solid oil aggregates [12].

Degradation of crude oil is never complete and some complex residues are resulted as leftovers of degradation which usually appear as black tar containing high proportions of Asphaltic compounds [19,20]. Asphalt is a black, viscous, sticky material that contain bitumens as chief component. Bitumens occur naturally or manufacture during oil processing. They are effective for the construction of roads, roofing, coatings, adhesive and batteries because of their waterproofing and binding properties. Also asphalts are perfect absorbers, that is why they are black in colour [20].

# 4. Clean-up methods for oil spill

Components of oil sludge constitute serious ecology and environmental concerns such as coastal damage, marine life pollution (like effect on flora and fauna), human health, economy, and policy. Therefore, to eradicate the adverse effects related to oil spillage, oil spill response methods have been continually grown and are progressively on going like chemical dispersants (physical method), combustion (chemical method), booms and skimmers (natural method), bioremediation (biological method), solidifiers (chemical method) and sorbents (natural method). Now, the selection of clean-up method employed to confiscate oil spillage chiefly depends upon the risk of oil spillage, size of oil spill, risk vulnerability of neighbouring habitat, weathering pattern, composition of oil and sea conditions such as temperature, gravitation forces, surface tension of water. Various clean-up methods employed are enlisted below:

#### 4.1. Chemical dispersants

Chemical dispersants fall in a category of physical response method of cleanup. Chemical dispersants enhance the natural degradation of oil and help to remove the oil from sea surface by the mechanism of break-down of oil into tiny droplets. When dispersants are added to the oil-in-water emulsion, it helps to separate the particles by reducing the interfacial tension between oil and sea water and further transfer them to the water column. In this way, oil spill cleanup takes place and helps to eradicate their impact on coastlines and natural habitat to a considerable extent [21]. The statistics study of ITOPF's database has shown that dispersants are used as the mitigation measures for 258 marine incidents from 1995 to 2005 [22]. The main or concentrated types of dispersants are Slickgone NS, Neos AB3000, Corexit 9500, Corexit 8667, Corexit 9600, Finasol OSR 52, Nokomis 3-AA, Nokomis 3-F4, Saf-Ron Gold, ZI-400, Finasol OSR 52, Ardrox 6120 and Tergo R-40 [23]. Now, the effectiveness and use of dispersants as cleanup method depends upon physical and chemical properties of oil, composition of dispersants, effect of dispersed oil on marine habitat, geological conditions and ratio of dispersant to oil. Therefore, their use is restricted in some European states especially in Baltic Sea (because of geological conditions and low water exchange) and countries where use of dispersants is allowed, have not been practised for decades. On the other hand, in UK, dispersants are used as preferred solution of oil spill because of favourable weather conditions. Moreover, different countries have different policies regarding the use of dispersants such as in France, use of dispersants is permissible at shallower depths; in USA, they can be in depths greater than 10 m. Further, use of dispersants is less effective for heavy oil as well as is very much dependent on geological conditions and oil slick thickness [22]. Mechanism of work plan of dispersants as given below in steps in Figure 2.

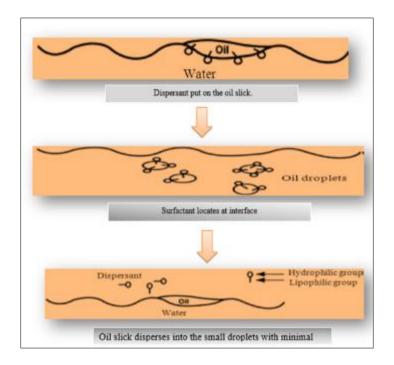


Figure 2 Mechanism of work plan of dispersants as given below in steps:[24]

# 4.2. Combustion

Combustion is a type of chemical method of oil spill cleanup. Combustion is also known as in-situ burning. Combustion is basically a burning of oil on water. In-situ burning is done only if the oil layer thickness is at least several millimetres (greater than 2 millimetres). Spillage from Exxon Valdez was handled by this combustion method as the major combustion products are in gaseous form and hence easy to handle and dispose, but its dependence on climate and ecology of region, oil layer thickness, wind speed and direction limits the use of combustion method. Also this method is associated with adverse effects in the form of air pollution results off toxic gasses emission at large scale as well as water pollution with effect on aquatic organisms [24,25].

### 4.3. Booms and skimmers

Use of booms and skimmers falls under the category of natural methods of oil spill cleanup. Boomers function efficiently for both containment and recovery of spilled oil as they are used to concentrate the spilled oil on a specific area. Plastics and those materials which show oil confinement along with absorption properties are used for synthesis of booms [26]. Then, skimmers provide aid to recover the spilt oil after the action of booms. Skimmers are effective as they show affinity for oil in preference to water. Therefore, water adheres to the surface of material and then it is scraped off in the storage tank [27]. Performance of skimmers depends upon influence of winds, waves, current, natural tendency of oil to spread, thickness of oil spill layer and kind of crude oil; also, they work more effectively in calm water [27]. Literature review [27] has shown that booms are associated with some shortcomings such as oil sinking, discharge of oil by the effect of wave currents, rotation of boom by substantial amount which permits the spread of oil behind which are rectified by the development of new type of boom by Cavalli. Sayah et al. [27] tested its performance and found that new boom shows high performance against water currents and waves.

### 4.4. Bioremediation

Bioremediation falls under the class of biological method of cleaning. As oil is mix bag of hydrocarbons which are biodegradable in nature under anaerobic conditions, therefore, bioremediation is a good functioning method to eradicate the oil spillage problem. In this, microorganisms follow the mechanism of degrading and metabolizing any chemical substance. Moreover, the ability of microorganisms to consume petroleum hydrocarbons marks it as one expedient method for oil spill cleanup [28]. Additional amount of microorganisms in this process, always favours the rate enhancement of natural degradation. Different microorganisms are generally used depending upon the kind of hydrocarbons present (bacteria, fungi and yeast) and follows different degradation mechanisms [27] viz optimized nitrogen fixation, Adapted microbial consortium, tolerance to petroleum hydrocarbons and production of biosurfactant [29]. This technique was successfully used to clean the Exxon Valdez spill (Alaska, 1989) and Deep Water Horizon Spill (Gulf of Mexico, 2010) [30]. Also, bioremediation has few shortcomings viz the level of available oxygen, nutrients,

temperature pH31, specific nature of microorganisms, requirement of suitable microorganism, comparatively slow processing (needs weeks to months)[31] and incomplete mineralization of organic compounds by this process sometimes lead to natural transformation of compounds to metabolites having detrimental effects and unknown persistence [29]. Bioremediation method of cleaning can be further subcategorized as given in below Table 4.

Sr. No.	Name of Technique	Method	Advantages
1.	Humblest method ( <i>in situ</i> land treatment)	Develops standard farming measures such as plugging the oil polluted soil with a tractor, periodical irrigation and drying.	It grips the use of aerobic micro- organisms to degrade the petroleum hydrocarbons and other derivatives to carbon dioxide and water, or other less toxic intermediates.
2.	Composting technology	It involves the automatic mixing of contaminated soil or residue with compost containing <i>hydrocarbonoclastic</i> bacteria, under aerobic and warm conditions.	The microbial nitrogen fixation becomes co-optimised with the hydrocarbon degradation.
3.	Phytoremediation	In this, plants are used in clean-up of contaminated environments. Several plants used are Salt marsh plants (Spartina patens, Sagittarialancifolia, Spartinaalterniflora and Juncusroemeri-annus), black poplar, willows and miscanthus grass (elephant grass)	It is an effective, inexpensive and less disturbing clean-up process.

Table 4 Types of	Bioremediation	Techniques
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### 4.5. Solidifiers

Solidifiers are the part of chemical methods of cleanup. Solidifiers are generally of hydrophobic and granular nature possessing high oleophilic surface area [32]. Solidifiers establish physical bonds with the oil through VanderWaal's attraction based on the theory that molecules with similar structure attract each other. Therefore, solidifiers are efficient being preferably oil-wet rather than water-wet [33,34]. Addition of solidifiers to oil thickens the oil and formation of viscid, stiffen mass takes which levitates on the surface of water and can be recovered easily [32]. Further, grain size and surface area of solidifier control the rate of reaction. In view of properties of solidifiers, specific gravity of these should be less than 1.0, otherwise, the treated oil will easily sink down to bottom of sea and is dreadful for aquatic life [34]. Furthermore, they are very high costing and expensive in nature [35]. Various available forms of solidifiers are dry powder, granules and semisolid materials (pucks, cakes, balls, sponge designs) [34].

#### 4.6. Sorbents

Sorbents can be used as effective means for oil spill clean-up. They are eco-friendly, low cost and solid porous material which can skillfully recover oil from the sea surface in preference to water. Now, these insoluble materials can recuperate the oil either by absorption or adsorption or both [35]. The basic difference between the both is that adsorption is a surface phenomenon and absorption is a bulk phenomenon [1]. Sorption is an alternative method for oil spill cleanup because of the abundant presence of natural materials and gathered agriculture waste in the environment with added advantage of recycling. It further does not cause any problem regarding their disposal [35].

### 5. Oil sorption phenomenon using sorbents

Using sorbents i.e. Adsorbents and Absorbents can provide a useful resource in response to cleanup of oil spillage and also allowing oil to be recovered in situations that are unsuitable for other techniques. Sorbents are advantageous over the other oil spill clean-up methods as other methods are associated with some shortcomings like less efficiency of dispersants for heavy oils, restricted use in some European states, related environmental pollution (water and air), difficult handling of in-situ burning and linked disposal problems. Sorbents have significant oil recovery capacity, no harmful effects on environment and available in abundant form at low cost. Sorbents are comprised of three types:[36]

- INORGANIC MINERAL PRODUCT: An inorganic mineral product which includes zeolites, expanded perlites, sepialite, graphite, fly ash and organic clay. Mineral product mostly shows poor buoyancy and oil sorption capacity and therefore displays narrow use [37,38,39].
- ORGANIC NATURAL MATERIAL: Organic natural material including wool, pith bagasse, vegetable fibres, saw dust, cotton fibre, kapok fibre. Organic natural material is comparatively more proficient because of its abundance, availability, low-cost, biodegradable and is suitable for large scale production. The only limitation is relatively low sorption capacity [38,39,40].
- ORGANIC SYNTHETIC POLYMER: Organic synthetic polymers including polyester, polyurethane, polypropylene polyacrylonitrile. They possess high oleophilic and hydrophobic properties hence high sorption properties. But because of high cost, tedious fabrication process and non-biodegradability limits their use on wide level [37,38].

The extent of interaction of sorbate molecule with sorbent phase is the key to distinguish between absorbent and adsorbent. There are number of forces involved in sorbents activity like chemical, physical and electrostatic forces [42]. There are many factors like sorption time, type of sorbent, properties of medium and also thickness of the sorption material which disturbs the sorption phenomena [43]. Mechanism of sorbents involves change of liquid phase of oil to semi-solid or solid phase. Once this stage has achieved, oil-sorbent system is fetched to complete the oil cleanup process [32,44]. The productive sorbent must show some features like high hydrophobicity or oleophilicity, high rate of oil uptake capacity, retention over time, recovery of oil, amount of oil sorbed, reusability, biodegradability, buoyancy power and retention over time [39,44,45]. Oil sorption capacity of different sorbents is always different. Oil sorption capacity of the sorbent material either adsorbent or absorbent can be measured by the formula as given below: [36,37,39]

 $Oil \ sorption \ capacity \ = \ \frac{weight of \ sorbed \ oil \ (grams)}{weight \ of \ sorbent \ (grams)}$ 

Weight of sorbed oil =weight of initial crude oil -weight of remained oil

weight of remained oil =weight of oil layer -weight of dissolved components

From literature studies, several sorbents used till now are raw sugarcane bagasse, raw and fatty-acid grafted sawdust for oil, black and white rice husk ash, barley straw, banana trunk fibers, acetylated sugarcane bagasse, carbonized peat bagasse, peat-based sorbents, and hydrophobic aerogels for emulsified oil. Table 5 and Table 6 shows the adsorption and absorption power of various sorbents respectively.

Sorbent	Adsorbate	g/g adsorbed
Rice husk	Heavy crude oil	7.50
	Motor oil	6.00
	Light crude oil	9.20
Cork	Diesel oil	4.65
Hazorb	Diesel oil	9.52
Pigslimmer	Diesel oil	8.14
PAN/PS	Pump oil	194.85
	Peanut oil	131.70
	Diesel oil	66.75
	Gasoline oil	43.38
Polypropylene	Light crude oil	4.50
	Light gas oil	4.26
Wool	Motor oil	15.73

 Table 5 Adsorption Capacities of various sorbents [9,36,39,48]

		-
	Crude oil	12.46
Human hair	Crude oil(brown hair)	15.44
	Crude oil (black hair)	14.50
	Crude oil (blond hair)	16.63
Sugarcane bagasse	Crude oil	8.00
Sugarcane leaves straw	Crude oil	5.50
Kapok	Crude oil	47.82
	Diesel	38.53
Phargmites australis	Crude oil	4.50
Azolla falliculoid	Engine oil	10.20
	Crude oil	5.30
Cotton fibres	Peanut oil	34.10
	Pump oil	30.30
	Crude oil	56.00
CCFs-400	Peanut oil	57.10
	Pump oil	44.60
	Crude oil	76.60

PAN: Polyacrylonitrile; PS: Polystyrene; CFCs: Carbonized cotton fibres

# **Table 6** Oil absorption capacity of material [41,45,48,52]

Sr. No.	Material	Oil type	Oil uptake (g/g)
1.	Milkweed floss	Crude oil	40.00
2.	Cotton	Crude oil	25-30
3.	Raw kapok fibre	Waxy substance or natural oil	30.40
4.	Polypropylene	Light crude oil	10.00
5.	Unprocessed cotton (3.16 micronaire)	Motor oil	50.25
6.	Polyurethane	Diesel	46.98
		Kerosene	41.42
7.	Sisal	Crude heavy oil	03.00
8.	Leaves residue	Crude heavy oil	01.40
9.	Sponge guord	Crude heavy oil	01.90
10.	Coir fibre	Crude heavy oil	1.80
11.	Saw dust	Crude heavy oil	4.10

### 6. Fibre sorbents

#### 6.1. Sugarcane bagasse

Sugarcane bagasse is the remaining deposits of sugarcane refining process and holds good lignocellulosic content. Sugarcane bagasse consists of cellulose (32-48%), hemicellulose (19-34%), lignin (23-34%). Therefore, this lignocellulosic material can be used as an effective biosorbent material as it is present in abundance and biodegradable in nature.

But this material shows adsorption properties for both hydrophilic (water content) and hydrophobic (oil content) materials because of the presence of reactive hydroxyl groups on the surface [46]. So, to improve its adsorption capacity, material is chemically treated with more negatively charged groups of acids, bases or salts which replaces the hydroxyl functional groups of the material and provides more hydrophobic surface. This can be completed by stirring action of material along with the chemical activator, due to which there is increase in intra-particle diffusion rate and attachment of lignocellulosic groups (hydroxyl groups) with solute particles, hence, adsorption capacity [47]. Since, hydroxyl groups of lignocellulosic material behave differently because of different mode of attachment [46].

- Alcoholic hydroxyl groups in carbohydrates (either primary or secondary).
- Phenolic hydroxyl groups in lignin (attached to an aromatic ring). Therefore, order of reaction of material with chemical activator is:

#### Lignin > Hemicellulose > Cellulose

Reza Behnood et al. [48] have compared the adsorption capacity of raw and modified sugarcane bagasse. They found modified sugarcane bagasse to be more oleophilic than raw bagasse as raw bagasse adsorbs 5.4g crude oil layer per 1g sorbent, whereas, modified bagasse adsorbs 9.1g crude oil per 1g sorbent. For modification process, material was impregnated with acetic anhydride which offers a hydrophobic envelope for raw bagasse by placing a relatively hydrophobic chain on raw bagasse structure. According to the study of Reza Behnood et al [48], adsorption capacity was found to be dependent on adsorption time, crude oil layer thickness (2.4 mm layer thickness), sorbent dose and particle size (optimum particle size of 0.2 mm). Next, salinity of the water does not find to affect the rate of adsorption significantly as in the adsorption process, sorbent firstly adsorbs the oil from the oil layer formed on the water surface, therefore, is in less contact with saline water. After the completion of the application process, bagasse remains on the surface, hence, can be removed easily [48]. Recovery of the adsorbed oil from the fibre is carried out simply by squeezing process and sorbent can be reuse for many times [46] as well as the material containing oil can be used as an effective fuel for industrial heating processes [48]. It has rich oiliness and is inelastic to be spun.

#### 6.2. Kapok fibre

Hollow structure of kapok fibre with large lumen rewards it with hydrophobic and oil sorption properties. Kapok fibres are generally fluffy, lightweight, non-allergic, non-toxic, resistant to rot and odourless, excellent buoyancy. Therefore, kapok fibre is used in stuffing for bedding, upholstery, life preservers water-safety equipment and for insulation against sound and heat because of its air-filled lumen. Kapok fibre is composed of 64% cellulose, 13% lignin and 23% hemicellulose along with the waxy layer on the surface because of which, It has rich oiliness and exhibit fast oil sorption rate, high oil sorption capacity (oleophilicity or lipophilicity), low water pickup high oil retention capacity during transfer, high recovery of the absorbed oil with simple methods, good reusability, high buoyancy [49]. Capillary bridging between fiber bundle and internal lumen storage is mainly responsible for oil absorption capacity of kapok assembly. There are factors working in the mechanism [50].

- Firstly, hydrophobic nature of waxy layer of kapok assembly is responsible for the adherence of oil to kapok surface by means of interactions along with van der wall forces between oil and fibre which results into decrease in surface tension and contact angle for oil, hence, diffusion of oil to lumen structure through internal capillary movement.
- Hollow lumen structure and existence of active sites in kapok fibre helps in retention and holding up capacity of oil.
- Hydrophobicity and water repellent properties are the resultant of presence of air channel in kapok assembly which offers large contact angle for water and negative capillary entry pressure [49].

Oil sorption capacity of kapok fibre is very much dependent on the density and viscosity of oil as retention of low viscosity light oil is more. Recovery of oil can be done by simple squeezing method and fibre assembly is reused upto

four sorption/desorption cycles. Thereafter, irreversible deformation of assembly fibre causes the reduction in oil sorption capacity of reused kapok [49].

### 6.3. Cotton

Raw cotton exhibits high sorption capacity of different oils than synthetic sorbent because of the advantage of highly crystalline unique hollow tubular structure, excellent surface wettability and intrinsic porosity. Cotton owes its oleophilic behaviour to the presence of waxy components on primary wall of fibre, capillary action through its hollow tubular structure[51] and hydrophilic behaviour to cellulose as cellulose (90-95%) constitutes the major component of natural cotton fibre [36]. This intrinsic amphiphilic behaviour of cotton is responsible for poor selectivity of cotton to remove oil from water and absorbs both water and organics or oils [52]. So, raw cotton needs modification surface wettability in order to show good selectivity for oil. Bin Wang et al. [36] have treated the raw cotton in N2 atmosphere to obtain the carbonized cotton fibers with a hollow tubular structure which shows highest oil adsorption capacity upto 32-77 times of its own weight with excellent oil retention, repeatability, selectivity, and good floating ability.

### 6.4. Milkweed floss

Milkweed is lignocellulosic material with 60% cellulose, 18% lignin and 0.33-0.80% extractible oils and waxes [53]. Sorption capacity of milkweed is significantly good because of its hollow cellulosic structure (with lumen size of 90% of total diameter of the fiber) [54] with irregular scaly surfaces and crimps and high wax content present on the surface similar to kapok fibre [54]. Milkweed floss has 56% crystalline region and 44% amorphous region with0.83 intra fiber porosity. Due to low cellulosic content and their slow degradation, milkweed is efficiently applicable on fresh and marine water [55]. Higher oil sorption capacity of milkweed fibre is explainable on the basis four factors:[54]

- Presence of noncollapsing hollow lumen facilitates the capillary action.
- Vander Waals forces and hydrophobic interactions between oil- sorbent because of presence of wax content (0.4-0.8%) on surface.
- Scaly surface helps in formation of capillary bridges of oil between fibres and provides hefty and easily reachable pores.
- Crimps provide greater surface area and assists adsorption mechanism.

At room temperature, milkweed sorbs nearly 40g of crude oil/g of fibre which is higher than the sorption capacity of even polypropylene material. Furthermore, oil sorption capacity of milkweed fibre depends on viscosity of oil (inversely related), decrease of temperature decreases the rate of oil absorption and capillary diameter (directly related). Therefore, milkweed can be used as efficient sorbent because of its high oil sorption capacity and biodegradability [55].

#### 6.5. Kenaf fibre

Kenaf bast fibre is generally present in the stems of the plant [56]. Kenaf comprises upto 75% cellulose, a thick layer of lignin at the cell wall and cylindrical fibre bundles instead of single fibre [52]. When bundle fibre is separated to single fibre, it shows increase in oil sorption capacity. Lumen structure of kenaf is very irregular and becomes discontinuous and undefined which explains the low sorption capacity of the kenaf fibre. Also, absence of wax content, scaly surface and crimps adds on the low sorption capacity of kenaf fibre [54].

#### 6.6. Bamboo FIBRE

Bamboo is a generic term belongs to the taxonomic group of large woody grasses (subfamily Bambusoideae). India is the second major bamboo generating country after China and is extended over to 13% of the total forested area [58]. Bamboo has a hollow tubelike structure with longitudinally aligned fibres. Width and lumen diameter of bamboo fibre varies between 16.4-12.6 µm and 5.41-5.12 µm respectively. The main constituents of bamboo culms are cellulose (45-55%), hemi-cellulose (20-25%) and lignin (22-30%), which amount to over 90% of the total mass. The minor constituents of bamboo are resins, tannins, waxes (0.5-0.7%). Since, cellulose is nested in a lignin matrix, therefore, is a natural composite material [59]. According to Molini et al. [60], bamboo includes number of required features such as low ash content, low alkali index and it does not need to dry because of lower moisture content, therefore, can be effectively used as an energy fuel for power generation [60]. Bamboo has high value of lignin content which adds to its high heating value and calorific value, hence, can be used to produce energy [61]. Bamboo can be used as an effective oil sorbent material as it contains high lignin content value among the other fibrous materials. Literature study [61] shows that Lignin possesses high wettability, high surface energy and are light in nature. With the advantage of all these properties, it can interact with charged oil droplets and absorbs 80% of carbon introduced into water. Moreover, lignin is an aromatic polymer and presence of phenolic hydroxyl groups provides it the ability to form hydrogen bonds with the oil droplets [62]. Sudong Yang et al[63] has prepared bamboo derived low cost carbon fibre aerogel which can

significantly separate the oil droplets from the water and behave as excellent adsorbent for oil and organic solvents. Whereas, study of Mahanim et al. [91] shows that carbonisation of bamboo followed by activation into activated carbon and charcoal has been proved to act as a very efficient and economical adsorbent for waste water treatment.

Apart from these, there are two more type of sorbents exists which falls under the category inorganic mineral products and synthetic organic products.

An inorganic mineral product includes perlite, vermiculite, sorbent clay, diatomite, [65,66] zeolite, organic-inorganic hydrides, and activated carbon [65]. These are also known as "sinking sorbents" and have higher density than organic sorbents. They are not effective much because they show poor buoyancy retention, low sorption capacity, expensive, less availability, inconvenience of recycling and selectivity (have low attraction for oils) [52].

A synthetic organic product includes polypropylene, polyurethane,[52] polyester, butylrubber,[67] polydimethylsiloxane-coated material [68] and polyacrylate [50]. They show significant sorption capacity for oil spill as they possess high oil/water uptake, low density (high buoyancy), easy availability, high oleophilicity and hydrophobicity. But they are associated with some shortcomings as are non-biodegradable in nature which makes them a threat to environment.

To evaluate the efficiency of given fibre towards sorption capacity, there exists many standardised methods which are helpful in determination of various parameters of fibre viz chemical composition, sorption capacity, contact angle, moisture content, ash content, extractive contents, cellulose and hemicellulose content, lignin content and antimicrobial activity. Some of them are enlisted in Table 7.

Sr No.	Test Method Name	Name of Standard Methods
1	Absorption-water content	ASTM D95-70
2	Alpha- cellulose	TAPPI test T203 cm-74 ASTM D 1103-60
3	Antimicrobial activity	AATCC TM 30-2004 AATCC TM 81(2006) 81
4	Ash content	TAPPI test T211-cm-93 ASTM D 1102-84 TAPPI test T-264-om-88m
5	Bending length	AATCC test method 115-2005
6	Brightness of pulp	UNE 57-062
7	Chemical composition of fibre	TAPPI test T257 Sautar and Bryden scheme GB 5886-86
8	Crease recovery angle	AATCC test method 66-2003
9	Determination of contact angle	Washburn's method
10	Determination of iodine sorption	Schwertassek method
11	Effectiveness of dispersants	<i>in-situ</i> fluorimetry
12	Extractive content	TAPPI test T204 cm-88 TAPPI test T264 cm-88 TAPPI test T280 pm-99 TAPPI test T-264-om-88m
13	Fastness testing colour fastness to washing	ISO 105-C06/C25

**Table 7** Various standard methods used for estimations [22,41,55,56,59]

	colour fastness to light	ISO 105 B02
14	Fineness in tax	SRPSF.S2.212, 1963
15	Hemicellulose content	NREL
		ASTM D 1104-56
16	Kappa index of pulp	UNE 57-034
17	Lignin content	TAPPI test T222 cm-88
		ASTM D 1106-56
		Macmillan scheme
18	Moisture content	ASTM D 2654-76, 1976
		ASTM D 1776-74, 1974
		TAPPI test T-264-om-88m
19	Polymeric composite preparation	ASTM standard D790M-86
20	Sorption of oil	AATCC 106-1981
	(in wet conditions)	ASTM D95-83
21	Sorption of oil	Gravimetric methods
	(in dry conditions)	
22	Soxhlet extraction	ASTM D2257 80
23	Viscosity of pulp	UNE 57-03
24	Whiteness measurement	AATCC Test method

# 7. Conclusion

During the past decades, several oil remediation methods have been employed such as natural methods, chemical methods viz dispersants, solidifiers, in-situ burning; thermal remediation methods such as burning of oil; biological methods and physical methods viz booming, skimming, mechanical removal. All these have been proven to be costly, less available, less effective and intimidation to environment. Physicochemical method sorption is found to be comparatively cheap and considered to be best alternative with proper analysis and environmental control.

From the detailed literature review, we present the sorption method as the promising oil remediation method. In view of the dearth of the effective sorbents, the need to develop the supreme sorbent is fuelled. The literature survey revealed that although great report work is available on the use of sorbents viz cotton, wool, milkweed floss, kenaf, kapok, sugarcane bagasse etc. yet reports concerning the use of bamboo fibre is rare. The use of bamboo fibre as the oil spill cleanup materials the biggest contribution to environment as the bamboo is ingrained with properties given below:

- India is the second major bamboo generating country after China. So, it is present in abundance.
- Bamboo is a renewable grass.
- It is Eco-friendly and biodegradable.
- It has highest content of lignin.
- Lignin present in bamboo can interact with the charged oil droplets because of its high wettability, high surface energy and light nature.
- Lignin can form hydrogen bonds with the oil droplets.
- In context to its disposal, it can be used as an effective bioenergy source.

Thus, keeping in view of these observations, in the present investigation we have extracted the bamboo fibre from the raw bamboo culm for the oil spill cleanup.

#### **Compliance with ethical standards**

#### Disclosure of conflict of interest

No conflict of interest to be disclosed.

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