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PETROLEUM SLUDGE, ITS TREATMENT AND DISPOSAL : A REVIEW

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ABSTRACT

Petroleum sludge is a complex mixture containing different quantities of waste oil, waste water, sand, and mineral matter. Petroleum industries are responsible for the generation of large quantities of sludge, which is a major source of environmental pollution. Oily sludges are hazardous wastes according to Environment Protection Act and Hazardous Wastes Handling Rules. These sludges cannot be disposed off as landfill, even if they are de-oiled unless they are totally remediated. Sludges generated by petroleum industries accumulate in crude oil tanks, refinery products tanks, desalters, and elsewhere during oil production and processing. The sludges containing recoverable oil less than 40% are considered as low oil content sludges. These sludges have to be treated and made harmless before disposal. Bioremediation process can be used for this purpose.

Generally, the refinery sludges contain oil content more than 40% and several methods are used to separate the oil, water and solids. The recovered oil is pumped back into the refinery process, while the solids and water are supposed to be treated before disposal. Several methods are available for processing and disposing of slop oil such as thermal, mechanical, biological, and chemical. Each method of processing has its advantages and disadvantages, and it is a common practice to utilize a combination of the four methods to maximize the output of usable oil from sludge.

The first step in the process of disposing of the sludge is reclamation. In order to extract as much oil from the sludge as possible, a combination of chemicals and deemulsifiers is used. Topmost layers of oil are collected by the use of pumps and barges. The separation of the sludge is done with a centrifuge. The oil recovered is then delivered to a refinery or sold in the market. Hard particles, from which oil cannot be recovered, must then be disposed of. Hard particles are disposed of by the following ways:

Incinerating unusable sludge (hard hydrocarbons-based substances mixed with water and emulsions) and harnessing heat and gases. Dehydration of sludge – the cleaned water is returned to the environment, and the hard particles are buried. Use of consolidating solutions for turning the sludge into a solid state. The solids can then be used in building projects. Use of Sludge as heat source. Biological remediation. The use of surfactants and emulsifiers will break up the old sludge and allow it to be removed

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from the container. Rhamnolipids, as a natural surfactant are useful in extracting these oil sludges and recovering them for use. These recovered sludges containing the rhamnolipid surfactants have most of the main properties of the original oil except for less viscosity.

Key words: Petroleum, Sludge, Disposal, Treatment.

INTRODUCTION

Crude oil is the raw oil that is obtained from the oil wells directly and petroleum is purified form of crude oil ready to get distilled fractionally to give out the petroleum products. Crude oil is a mixture of hydrocarbons that exists as a liquid in natural underground reservoirs and remains liquid, when brought to the surface. Petroleum products are produced from the processing of crude oil at petroleum refineries and the extraction of liquid hydrocarbons at natural gas processing plants. Petroleum is the broad category that includes both; crude oil and petroleum products. The terms "oil" and "petroleum" are sometimes used interchangeably.

Petroleum or crude oil is a naturally occurring flammable liquid consisting of a complex mixture of hydrocarbons of various molecular weights and other liquid organic compounds, that are found in geologic formations beneath the Earth's surface. Most petroleum is a fossil fuel. A fossil fuel is formed, when large quantities of dead organisms, usually zooplankton and algae, are buried underneath sedimentary rock and undergo intense heat and pressure. Technically, the term petroleum only refers to crude oil, but sometimes it is applied to describe any solid, liquid or gaseous hydrocarbons.

Petroleum is recovered mostly through oil drilling. This comes after the studies of structural geology (at the reservoir scale), sedimentary basin analysis, and reservoir characterization (mainly in terms of porosity and permeable structures). It is refined and separated, most easily by boiling point, into a large number of consumer products, from petrol (or gasoline) and kerosene to asphalt and chemical reagents used to make plastics and pharmaceuticals. Petroleum is used in manufacturing a wide variety of materials, and it is estimated that the world consumes about 88 million barrels each day.

EXPERIMENTAL

Composition of petroleum

In its strictest sense, petroleum includes only crude oil, but in common usage, it includes all liquid, gaseous, and solid (e.g., paraffin) hydrocarbons. Under surface pressure and temperature conditions, lighter hydrocarbons methane, ethane, propane and butane occur as gases, while pentane and heavier ones are in the form of liquids or solids. However, in an underground oil reservoir the proportions of gas, liquid, and solid depend on subsurface conditions.

An oil well produces predominantly crude oil, with some natural gas dissolved in it. Because the pressure is lower at the surface than underground, some of the gas will come out of solution and recovered (or burned) as associated gas or solution gas. A gas well produces predominantly natural gas. However, because the underground temperature and pressure are higher than at the surface, the gas may contain heavier hydrocarbons such as pentane, hexane, and heptane in the gaseous state. At surface conditions, these will condense out of the gas to form natural gas condensate, often shortened to condensate. Condensate resembles petrol in appearance and is similar in composition to some volatile light crude oils.

The proportion of light hydrocarbons in the petroleum mixture varies greatly among different oil fields, ranging from as much as 97 per cent by weight in the lighter oils to as little as 50 per cent in the heavier oils and bitumens.

The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. The exact molecular composition varies widely from formation to formation.

The composition of oily sludge is very complex. It comprises of oil in water, water in oil emulsion and suspended solids[1]. Oily sludge contains toxic substances like aromatic hydrocarbons, polyaromatic hydrocarbons[2] and high total hydrocarbons content[3]. Oily sludge is difficult to be hydrated due to its high viscosity. Oily sludge is a hazardous solid waste. Oily sludge basically comprises of about 55.13% of water, 9.246% of sediments, 1.9173% of asphaltenes, 10.514% of wax and 23.19% of light hydrocarbons and also a high concentration of heavy metals for instance vanadium is 204 ppm, Fe is 0.6% and nickel is 506 ppm[4], which makes the oily sludge harmful for the environment and organisms, which need to be dealt with, for environmental protection[4].

Petroleum is used mostly, by volume, for producing fuel oil and petrol, both important "primary energy" sources. 84 per cent by volume of the hydrocarbons present in petroleum is converted into energy-rich fuels (petroleum-based fuels), including petrol, diesel, jet, heating, and other fuel oils, and liquefied petroleum gas. Due to its high energy density, easy transportability and relative abundance, oil has become the world's most important source of energy since the mid-1950s. Petroleum is also the raw material for many chemical products, including pharmaceuticals, solvents, fertilizers, pesticides, and plastics.

Chemistry of petroleum

Petroleum is a mixture of a very large number of different hydrocarbons; the most commonly found molecules are alkanes (linear or branched), cycloalkanes, aromatic hydrocarbons, or more complicated chemicals like asphaltenes. Each petroleum variety has a unique mix of molecules, which define its physical and chemical properties, like color and viscosity.

The alkanes, also known as paraffins, are saturated hydrocarbons with straight or branched chains, which contain only carbon and hydrogen and have the general formula C_nH_{2n+2}. They generally have 5 to 40 carbon atoms per molecule, although trace amounts of shorter or longer molecules may be present in the mixture.

The alkanes from pentane (C_5H_{12}) to octane (C_8H_{18}) are refined into petrol, and from nonane (C_9H_{20}) to hexadecane ($C_{16}H_{34}$) into diesel fuel, kerosene and jet fuel. Alkanes with more than 16 carbon atoms can be refined into fuel oil and lubricating oil. At the heavier end of the range, paraffin wax is an alkane with approximately 25 carbon atoms, while asphalt has 35 and up, although these are usually cracked by modern refineries into more valuable products. The shortest molecules, those with four or fewer carbon atoms, are in a gaseous state at room temperature. They are the petroleum gases. Depending on demand and the cost of recovery, these gases are either flared off, sold as liquified petroleum gas under pressure, or used to power the refinery's own burners. During the winter, butane (C_4H_{10}), is blended into the petrol pool at high rates, because its high vapor pressure assists with cold starts. Liquified under pressure slightly above atmospheric, it is best known for powering cigarette lighters, but it is also a main fuel source for many developing countries. Propane can be liquified under modest pressure, and is consumed for just about every application relying on petroleum for energy, from cooking to heating to transportation.

The cycloalkanes, also known as naphthenes, are saturated hydrocarbons, which have one or more carbon rings, to which hydrogen atoms are attached according to the formula C_nH_{2n}. Cycloalkanes have similar properties to alkanes but have higher boiling points.

The aromatic hydrocarbons have one or more planar six-carbon rings called benzene rings, to which hydrogen atoms are attached with the formula C_nH_n. They tend to burn with a sooty flame, and many have a sweet aroma. Some are carcinogenic.

These different molecules are separated by fractional distillation at an oil refinery to produce petrol, jet fuel, kerosene, and other hydrocarbons. For example, 2,2,4-trimethylpentane (isooctane), widely used in petrol, has a chemical formula of C_8H_{18} and it reacts with oxygen exothermically[5].

$$2\ C_8H_{18(l)} + 25\ O_{2(g)} \rightarrow 16\ CO_{2(g)} + 18\ H_2O_{(g)}\ (\Delta H = -10.86\ \text{MJ/mol of octane})$$

Incomplete combustion of petroleum or petrol results in production of toxic by products. Too little oxygen results in carbon monoxide. Due to the high temperatures and high pressures involved, exhaust gases from petrol combustion in car engines usually include nitrogen oxides, which are responsible for creation of photochemical smog.

Crude oil is an important energy source as well as feed stock of oil refineries.

During the processing of crude oil, various kinds of waste are generated; of this, oily sludge and chemical sludge, biosludge are of special environmental concern because many of the constituents of this sludge are of hazardous nature. Hazardous waste is generated in significant amounts in petroleum refineries worldwide. In India, oil refineries generate approximately 20,000 tonnes of oily sludge per annum. One of the major problems faced by oil refineries is the safe disposal of this oily sludge.

Uncontrolled handling of these sludges often leads to environmental pollution and also affects the aesthetic quality. Recycling of sludges in an environment friendly manner is one of the appropriate solutions of sludge management problem. The treatment technologies developed can be grouped as physical remediation, chemical remediation and biological remediation.

Petroleum sludge is classified as hazardous waste (usually due to the oil content) and in most cases, it is also classified as a liquid, which means that it cannot be disposed of directly to a landfill.

The two attributes that make oil sludge such a problem are that it is classified as hazardous waste (usually due to the oil content) and in most cases, it is also classified as a liquid, which means, it cannot be disposed of directly to a landfill.

All of the more traditional methods for waste disposal and treatment don't really work on oil sludge:

Typically, oil sludge can't be incinerated because it contains too much oil and water, making it almost impossible to incinerate.

In most of the cases, it is not cost effective to apply thermal treatment because the waste contains too much oil and water.

The oil sludge can't be filtered because the solids content is too high, and attempts at filtering will just clog the filtration systems.

The oil sludge can't be pumped to a waste water treatment facility because of the high oil and solid content, and the waste has too high COD/BOD. Because it is a liquid, the oil sludge can't be disposed of, in traditional hazardous waste landfills, only solids can go to landfills. Due to the fact that there simply haven't been many good options for dealing with this type of waste, it has been accumulating at an alarming rate. To date, there is an estimated 9 billion tonnes of oil sludge waste on the planet, and this volume is growing every minute.

There have been many attempts at providing a viable long term solution for the industry to treat oil sludge. So far, the industry has only made small advances. In reality, this is not due to a lack of possible solutions or resources, but it's more down to a lack of will and desire by the industry to tackle this issue head on. The petroleum industry in its production, refining, transport and storage processes, generate oily residues, which have been stored in pits, marshes or open earth pools for many years, causing a high degree of contamination, not only in the storage areas but also in nearby areas.

The appropriate treatment and correct disposal of this type of wastes prevents the contamination of superficial and ground water, the contamination of the surrounding air; and reduces the risk of fires, explosions, poisoning of the food chain and destruction of green areas.

Due to the continuous treatment and the processes implemented, no significant areas for temporary storage are needed. The risk for potential contamination of air and water resources is significantly decreased.

A considerable amount of oily sludge can be generated from the petroleum industry during its crude oil exploration, production, transportation, storage, and refining processes[6,7]. In particular, the sludge generated during the petroleum refining process has received increasing attention in recent years. It contains a high concentration of petroleum hydrocarbons (PHCs) and other recalcitrant components. As being recognized as a hazardous waste in many countries, the improper disposal or insufficient treatment of oily sludge can pose serious threats to the environment and human health[6-10]. The major sludge generated by the petroleum refineries are oily sludge, bio-sludge and chemical sludge[11].

Most of the crude oils have a property to separate into the heavier and lighter hydrocarbons during their storage and transportation. In refineries, hydrocarbon sludge is usually generated during cleaning up of crude oil storage tanks, maintenance of associated facilities and pre-export processing i.e. tank farms, desalter failure, oil draining from tanks and operation units, pipeline ruptures and processing of oil[12]. The composition of oily sludge varies due to the large diversity in the quality of crude oils, differences in the processes used for oil-water separation, leakages during industrial processes and also mixing with the existing oily sludge. The effective remediation of oily sludge has become a worldwide problem due to its hazardous nature and increasing production quantity around the world. Because of the hazardous nature of oily sludge, disposal of excess sludge will be forbidden in the near future; thus, increased attention has been turned to look into potential technology for sludge treatment. Oil production companies and the refiners are looking for the technologies, which are aimed to extract the hydrocarbons from the sludge to the maximum extent and thus to minimize the final treated sludge quantity, which can be disposed in a much economical, fast and eco-friendly ways. During the past years, a variety of oily sludge treatment methods have been developed, such as landfarming, incineration, solidification/stabilization, solvent extraction, ultrasonic treatment, pyrolysis, photocatalysis, chemical treatment, and biodegradation[6,8-14]. By employing these technologies, the contents of hazardous constituents can be reduced or eliminated, and its deleterious environmental and health impacts can thus be mitigated.

Classification of refinery sludge

Based on source and chemical composition the waste generated in refineries can be broadly classified as follows:

Hydrocarbon Wastes: It includes API separator sludge, dissolved air floatation float, slop oil emission solids, tank bottoms, FFU sludge, desalter bottoms and waste oils/solvents.

Spent Catalysts: It includes fluid cracking catalyst, hydro-processing catalyst and other spent inorganic clays.

Chemical/Inorganic Wastes: It includes spent caustic, spent acids and waste amines.

Contaminated Soils and Solids: It includes heat exchanger bundle cleaning sludge, waste coke/carbon/charcoal, waste sulphur and miscellaneous contaminated soils.

Aqueous Waste: It includes biomass, oil contaminated water (not wastewater), high/low pH water and spent sulphide solutions.

Oily sludge source

Both the upstream and downstream operations in petroleum industry can generate a large amount of oily wastes. The upstream operation includes the processes of extracting, transporting, and storing crude oil, while the downstream operation refers to crude oil refining processes. In the upstream operation, the related oily sludge sources include slop oil at oil wells, crude oil tank bottom sediments, and drilling mud residues[15]. A variety of oily sludge sources exist in downstream operation, including (a) slop oil emulsion solids; (b) heat exchange bundle cleaning sludge; (c) residues from oil/water separator, such as the American Petroleum Institute (API) separator, parallel plate interceptor, and corrugated plate interceptor (CPI); (d) sediments at the bottom of rail, truck, or storage tanks; (e) sludge from flocculation-flotation unit (FFU), dissolved air flotation (DAF), or induced air flotation (IAF) units, and (f) excess activated sludge from on-site wastewater biological treatment plant[16]. Prior to being refined to petroleum products, crude oil is temporarily housed in storage tanks, where it has a propensity to separate into heavier and lighter petroleum hydrocarbons (PHCs). The heavier PHCs often settle along with solid particles and water[17]. This mixture of oil, solids, and water deposited at the storage tank bottom is known as oily sludge[18]. It is removed during tank cleaning operations and sent for further treatment or disposal[19].

The sludge quantity generated from petroleum refining processes depends on several factors such as crude oil properties (e.g., density and viscosity), refinery processing scheme, oil storage method, and most importantly, the refining capacity. Generally, a higher refining capacity is associated with a larger amount of oily sludge production. It has been estimated that one ton of oily sludge waste is generated for every 500 tons of crude oil processed[16]. It is estimated that more than 60 million tons of oily sludge can be produced every year and more than 1 billion tons of oily sludge has been accumulated worldwide[20-22]. It is also expected that the total oily sludge production amount is still increasing as a result of the ascending demand on refined petroleum products worldwide[21-23].

The formation of crude oil sludge

Most of the oils have a property to separate into the heavier and lighter hydrocarbons during their storage and transportation. The heavy ends of crude oil are deposited on the bottom of storage tank.

Paraffin based crude oil sludge forms, when the molecular orbital of individual straight chain hydrocarbons are blended by proximity, producing an induced dipole force that resists separation. As the heavier straight chain hydrocarbons flocculate (heavier meaning predominantly the C_{20+} hydrocarbon molecules), they tend to fall out of suspension within a static fluid, as in the case of storage tanks, where they accumulate at the bottom as viscous gel commonly known as sludge or wax. This newly formed profile stratifies over time as the volatile components within the sludge are expelled with changes in temperature and pressure. The departure of such volatile components results in a concentrated heavier fractions within the sludge, accompanying with increased in density and viscosity, and decreased fluidity[24].

Asphaltic sludge is formed due to the formation of the tendency of asphaltenes, resins and polymeric compounds to precipitate. Neutral resins are high molecular weight aromatic hydrocarbons. These resins are insoluble in alkalies and acids but are completely miscible with petroleum oils, including light fractions.

Asphaltenes are similar to the neutral resins but they are insoluble in light gasoline and petroleum ether. Asphaltenes are precipitated in presence of an excess of petroleum ether. Asphaltenes and neutral resins are soluble in benzene, chloroform and carbon disulphide.

Inorganic salts, sediments, sands, scale and dust are also present in the sludge.

Sludge treatment methods

The various technologies for oil recovery and redemption of the crude sludge include chemical treatments, various distillation processes, cracking, hydro-treating, solvent treatment and bioremediation. Some of the conventional methods of sludge treatment are as follows:

Manual cleaning and incineration

Manual cleaning is the low cost method. The cleaning is done by entering in the tank. The sludge is moved out of the tank manually or to pumps present in the tanks. This method takes long time. It is difficult to recover the usable hydrocarbons from the sludge by using this method.

Solvent extraction method

Various solvents are used in this method, which are able to break down complex molecules present in the sludge into their basic constituents - water, crude oil and particulate. This method requires mixing and agitation apparatus (Fig. 1). Sludge has waxy and non waxy (asphaltenes) organic components along with salt, oxides and other inorganic materials. These may be dissolved by selecting appropriate solvent[25].

Oily sludge waste is firstly mixed in the reactor column with a solvent, which selectively dissolves the oil fraction of sludge and leaves the less soluble impurities at the column bottom. The oil solvent solution is then transferred to a solvent distillation system where the solvent is separated from oil. The separated oil is considered as oil recovery, while the separated solvent vapour can be liquefied through a compressor and cooling system and sent to a solvent recycling tank. The solvent can be used for repeating the extraction cycle. The bottom impurities from reactor column are pumped to a second distillation system, and the solvent contained in the impurities is separated and then sent to the solvent recycling tank, while the waste residues after separation may need further treatment.

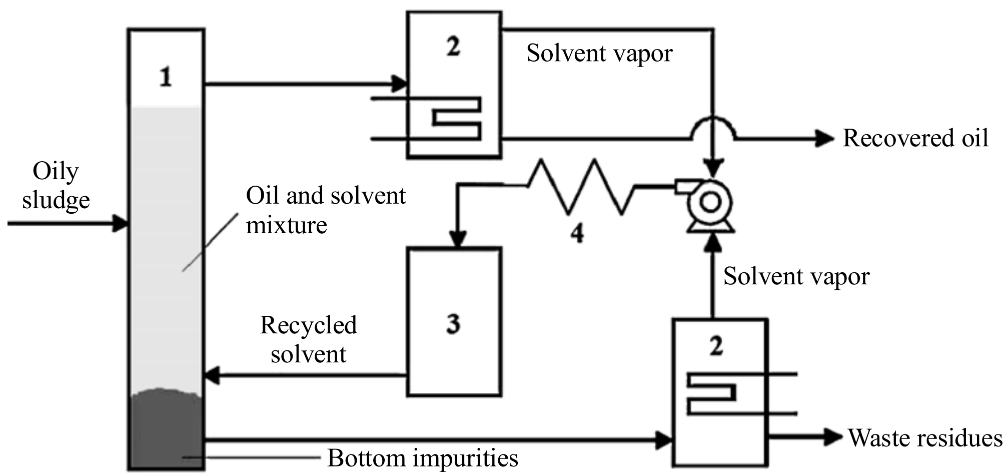

Fig. 1: Block flow diagram of solvent extraction method

1. Reactor column; 2. Distillation; 3. Solvent recycling tank; 4. Compressor and cooling system

Ultra high temperature gasification

In this method, thermal oxidation of sludge is carried out. The sludge is heated to a very high temperature (1000^{o}C) using plasma arc without oxygen. The sludge is converted to pyrogas by this method and this can be used as fuel[26].

Oil sludge separation using cyclone

By this method, oil is recovered from the oily sludge and residue is separated[27] (Fig. 2).

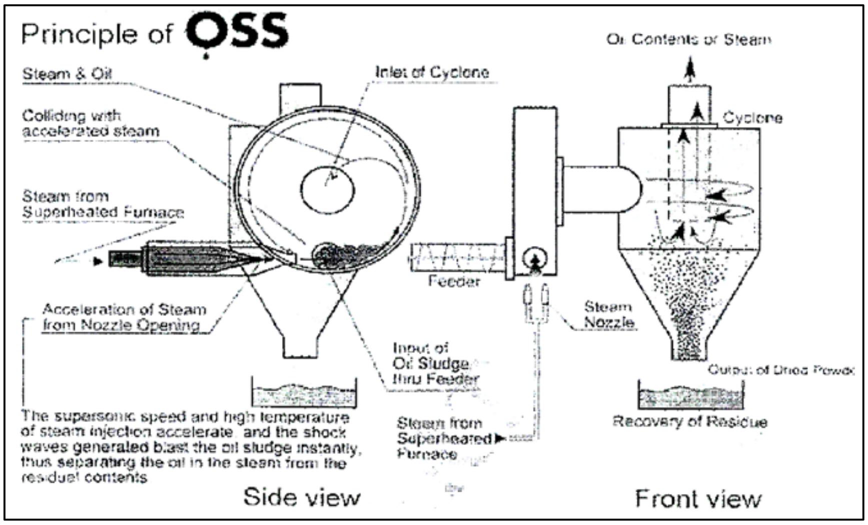

Fig. 2: Oily sludge separation by cyclone

Oily sludge treatment by application of thermochemistry

In this method, oily sludge is diluted by water and heated, and then certain chemicals are added for extraction of oil from solid phase.

Microwave heating method

Microwave heating has more advantages than conventional heating. This method is used for waste management. Microwave heating technology for demulsification of sludge-oil was first introduced by Klaila (1983) and Wolf (1986)[28,29]. In conventional thermal heating, heat is transferred to the material through convection, conduction, and radiation of heat from the surfaces of the material. Whereas microwave energy is reached directly to the materials through molecular interaction with the electromagnetic field. In heat transfer, energy is transferred due to thermal gradients, but microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion, rather than heat transfer. This results in many advantages for using microwaves for processing of materials. Microwaves can penetrate materials and deposit energy so heat can be generated throughout the volume of the material. The transfer of heat energy does not rely on diffusion of heat from the surface and it is possible to achieve rapid and uniform heating of thick materials[30].

Centrifugation method

In this method, components are separated on the basis of their densities (such as water, solids, oil and pasty mixtures in oily sludge) by generating centrifugal force. This method uses a special high speed rotation equipment by reducing viscosity of oily sludge by adding organic solvents, demulsifying agents & tensioactive chemicals and the injection of steam and direct heating[12,31-33]. The performance of centrifugation method is enhanced and energy consumption is reduced. Conway[31] reported that after viscosity reduction using heat pre-treatment, the less viscous petroleum sludge could be effectively treated by a disc/bowl centrifuge, with more than 80% of the waste volume being obtained as liquid effluent from the first centrifugation, and residue from centrifugation was then mixed with hot water and centrifuged again. The effluent from two centrifugations was combined and sent to refinery for processing[31]. According to Cambiella et al.[32], a small amount of a coagulant salt $CaCl_2$ (0.01-0.5 M) can improve the water-oil separation process by centrifugation, with a high oil separation efficiency of 92-96%.

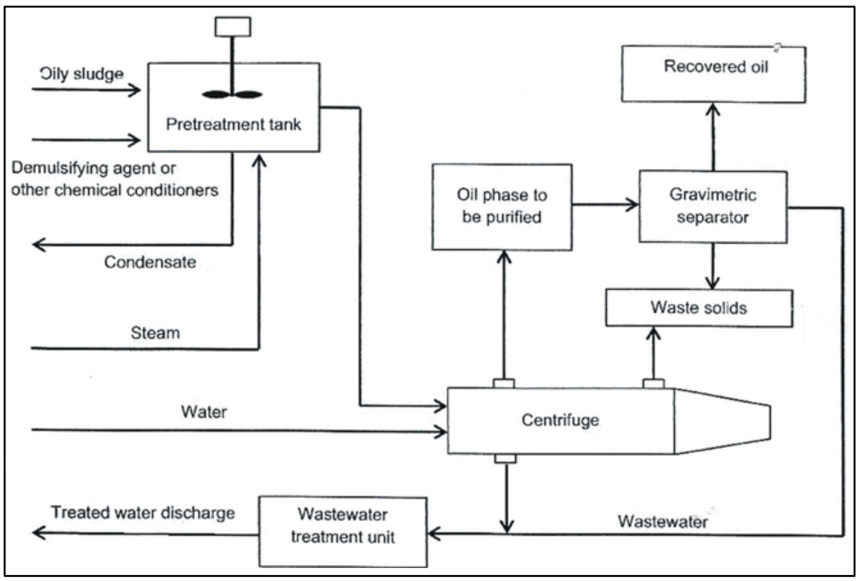

Fig. 3: Schematic diagram of centrifugation method

Oily sludge is mixed with demulsifying agent or other chemical conditioners. The mixture is then treated by hot steam in a pre-treatment tank in order to reduce the viscosity. This less viscous petroleum is mixed with water for high speed centrifugation. The separated water after centrifugation containing high concentration of PHCs drained for further wastewater treatment. The separated oil containing water and solids is sent to a gravimetric separator for further separation to obtain the recovered oil. The separated water from the separator is sent to wastewater treatment. The sediments from centrifugation and separator are collected as solid residue for further treatment. Centrifugation is a relatively clean and mature technology for oily sludge treatment, and its oil separation from sludge is effective.

Centrifugation equipment does not occupy large space[20]. However in this method a high energy consumption is required to produce high centrifugal force to separate oil from petroleum sludge. High equipment investment is responsible for the limited use of centrifugation method. The addition of demulsifying agents and tensioactive chemicals for pre-treatment increases the processing cost. Centrifugation process creates high noise.

Electrokinetic method

In this method, an electrode pair is used on two sides of a porous medium and a low direct current is passed through the medium causing the electro-osmosis of liquid phase, migration of ions and electrophoresis of charged particles in a colloidal system to the respective electrode[34, 35]. The separation of water, oil, and solids from oily sludge can be carried out by electrokinetic method and this separation is based on three mechanisms. Colloidal aggregates in oily sludge can be broken due to electric field and this leads to the movement of colloidal particles and solid particles of oily sludge towards the anode as a result of electrophoresis. Water and oil move towards the cathode as a result of electro-osmosis. The electro-coagulation of the separated solid phase occurs near the anode, this increases the concentration of solid phase and the sediments. The separated liquid phase (water and oil, without colloidal particles and fine solids) can form an unstable secondary oil-in-water emulsion, which could be gradually electro-coalesced near the cathode through charging and agglomeration of droplets; thus, forming two separated phases of water and oil[36].

Ultrasonic irradiation

Ultrasonic waves generate compressions and rarefactions in the medium through, which they are passed. The compression cycle exerts a positive pressure on the medium by pushing molecules together. The rarefaction cycle exerts a negative pressure by pulling molecules from each other. Microbubbles are produced in the medium and these will be grown due to negative pressure. These microbubbles grow to unstable dimension and collapse violently generating shock waves, which results in high pressure and temperature immediately[37]. This increases the temperature of the emulsion system and decreases its viscosity, increases the mass transfer of liquid phase, and thus leads to destabilization of W/O emulsion[38]. Smaller droplets in emulsion move faster than the larger ones under the influence of ultrasonic irradiation. This can increase their collision frequency to form aggregates and coalescence of droplets, which then promotes the separation of water/ oil phases[39,40].

Froth flotation method

This method involves the capture of oil droplets or small solids by air bubbles in an aqueous slurry followed by their levitation and collection in a froth layer[41]. Froth flotation process can be used for the treatment of oily wastewater from the refineries and oily sludge[19]. In this method, water is mixed with oily sludge to form oily sludge slurry. Air is passed through the sludge slurry, which form air bubbles in the water sludge mixture. These air bubbles approach oil droplets in the slurry mixture. The water film between oil and air bubble becomes very thin and then it is ruptured causing spreading of oil in the air bubbles. The conglomerate of oil droplets with air bubbles can quickly rise to the top of water-oil mixture, and the accumulated oil can be skimmed off and collected for further purification[42].

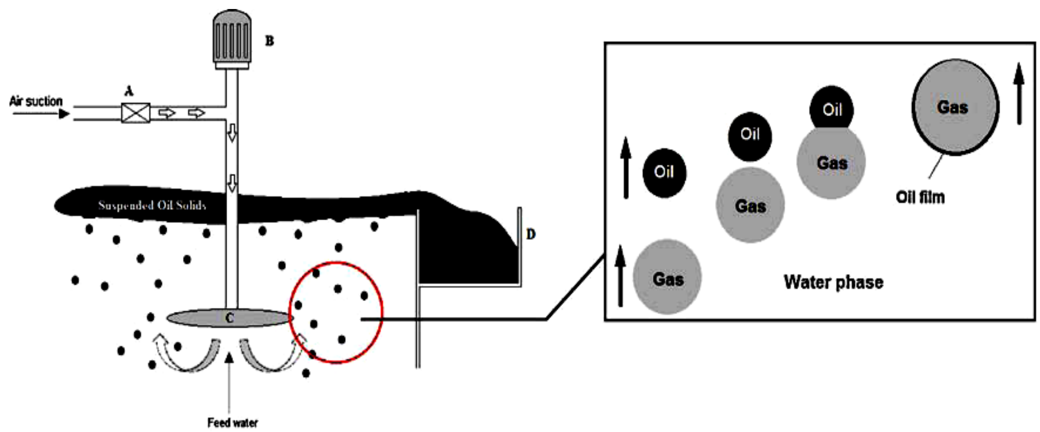

Fig. 4: Schematic diagram of froth flotation process

Oily sludge disposal method

Oily sludge after the recovery of oil should be disposed of by a number of methods such as incineration, stabilization/solidification, oxidation and biodegradation.

Incineration

In this method, complete combustion of oily wastes is carried out in presence of excess air and auxiliary fuels. The commonly used incinerators are rotary kiln and fluidized bed incinerator. The combustion temperature range for rotary Kelvin is 980-1200^{o}C and residence time is around 30 min. In fluidized bed incinerator, the combustion temperature can be in the range of 730-760^{o}C and the residence time can be in the order of days[43]. Fluidized bed incinerator is more effective for low quality sludge due to its fuel flexibility, high mixing efficiency, high combustion efficiency and relatively low pollutant emissions[44].

Stabilization/solidification

By this method, contaminants are immobilized by converting them into a less soluble or less toxic form (stabilization). The contaminants can be encapsulated by creating a durable matrix (solidification)[45]. Inorganic wastes are easily disposed of by this method. This method is less compatible with organic wastes.

Oxidation method

Oxidation treatment is useful method to degrade a number of organic contaminants through chemical or other oxidation processes. Chemical oxidation is carried out by adding reactive chemicals into oily wastes, which oxidize organic compounds to carbon dioxide and water or transform them to other non-hazardous substances such as inorganic salts[46]. The oxidation can be carried out by Fenton's reagent, hypochlorite, ozone, ultrasonic irradiation, permanganate and persulphate, by generating a sufficient amount of radicals such as hydroxyl radicals (OH^*), which can quickly react with most organic and many inorganic compounds[47].

Bioremediation

Refineries produce oil sludge as waste by the processing of crude oil. This sludge is poorly biodegradable. One of the major problems faced by oil refinery is the safe disposal of oily sludge in the environment. Many of the constituents of oil sludge are carcinogenic and potent immuno-toxicant[48]. This technique uses living organisms (bacteria, fungi, some algae, and plants) to reduce or eliminate toxic pollutants. These organisms may be either naturally occurring or may be cultivated in the laboratory. They either eat up the contaminants (organic compounds) or assimilate within them all harmful compounds (heavy metals) from the surrounding; thereby, rendering the region contaminant free. Bioremediation can be enhanced with the use of fertilizers, compost, bulking agents and some chemicals including oil dispersant. Bioremediation of waste oil in soil (land farming) or also land spreading had been carried out in different parts of the world. Dotson et al.[49] and Kincannon[50] published early studies in USA. By mid 70's, other authors reported on oily sludge land farming including Fusey[51] in USA. More studies on bioremediation by land farming were reported by a number of authors namely Grove[52] in UK, Dibble and Bartha[53] in South Africa in the late 70's.

Land farming is cheaper and environmentally safe method. In land spreading, the sludge is evenly dispersed over a plot of land, where it can be degraded by native microbial flora over a period of months or years. The sludge is blended into the soil with tilling equipment, and the rate of degradation in the land farming is increased with the addition of fertilizers. The primary mechanisms involved in the disappearance of hydrocarbons in land spreading and land farming are biodegradation, vaporization, oxidation, and to some extent, degradation by sunlight and leaching. When the sludge has been substantially degraded, the plot of land can be used again for further sludge treatment.

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