



## Recent development in the treatment of oily sludge from petroleum industry: A review



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### HIGHLIGHTS

- A comprehensive review of recent oily sludge treatment methods is provided.
- Oily sludge treatment is divided into oil recovery and sludge disposal approaches.
- The advantages and limitations of each treatment method are discussed.
- Issues of both petroleum hydrocarbons and heavy metals in oily sludge are discussed.

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### ABSTRACT

Oily sludge is one of the most significant solid wastes generated in the petroleum industry. It is a complex emulsion of various petroleum hydrocarbons (PHCs), water, heavy metals, and solid particles. Due to its hazardous nature and increased generation quantities around the world, the effective treatment of oily sludge has attracted widespread attention. In this review, the origin, characteristics, and environmental impacts of oily sludge were introduced. Many methods have been investigated for dealing with PHCs in oily sludge either through oil recovery or sludge disposal, but little attention has been paid to handle its various heavy metals. These methods were discussed by dividing them into oil recovery and sludge disposal approaches. It was recognized that no single specific process can be considered as a panacea since each method is associated with different advantages and limitations. Future efforts should focus on the improvement of current technologies and the combination of oil recovery with sludge disposal in order to comply with both resource reuse recommendations and environmental regulations. The comprehensive examination of oily sludge treatment methods will help researchers and practitioners to have a good understanding of both recent developments and future research directions.

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### 1. Introduction

A considerable amount of oily sludge can be generated from the petroleum industry during its crude oil exploration, production, transportation, storage, and refining processes [1,2]. 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 [1–5]. The effective remediation of oily sludge has become a worldwide problem due to its hazardous nature and increasing production quantity around the world. 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 [1,3–9]. 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. However, due to the recalcitrant nature of oily sludge, few technologies can reach a compromised balance between satisfying strict environmental regulations and reducing treatment costs. As a result, there is a need for a comprehensive discussion of current oily sludge treatment methods to identify their advantages and limitations. The main objectives of this review are (a) to introduce the source, characteristics, and environmental impact of oily sludge in the petroleum industry, (b) to summarize current treatment methods available for dealing with oily sludge, (c) to discuss the advantages and limitations of these methods, and (d) to discuss future development needs to meet resource recycling and waste disposal standards.

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## 2. Source, characteristics, and toxicity of oily sludge

### 2.1. 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. The oily waste generated in petroleum industry can be categorized as either simple oil or sludge depending on the ratio of water and solids within the oily matrix [10]. Simple waste oil generally contains less water than sludge that is highly viscous and contains a high percentage of solids. Stable water-in-oil (W/O) emulsion is a typical physical form of petroleum sludge waste [11]. In the upstream operation, the related oily sludge sources include slop oil at oil wells, crude oil tank bottom sediments, and drilling mud residues [12]. 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 [13]. In particular, the bottom sediments in crude oil storage tanks represent the most intensively studied oily sludge in literatures. 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 [14]. This mixture of oil, solids, and water deposited at the storage tank bottom is known as oily sludge [15]. It is removed during tank cleaning operations and sent for further treatment or disposal [16].

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. According to an investigation conducted by US EPA, each refinery in the United States produces an annual average of 30,000 tons of oily sludge [17]. In China, the annual production of oily sludge from petrochemical industry is estimated to be 3 million tons [18]. 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 [13]. Fig. 1

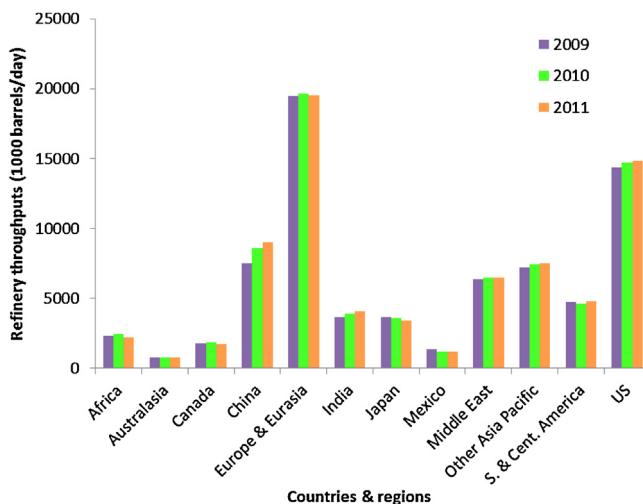


Fig. 1. Worldwide daily refining throughputs in recent years [20].

shows the global refining throughputs in recent years, and 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 [19–21]. 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 [20,22].

### 2.2. Characteristics of oily sludge

In general, oily sludge is a recalcitrant residue characterized as a stable W/O emulsion of water, solids, PHCs, and metals [23]. The stability of W/O emulsions depends mainly on a protective film that inhibits water droplets from coalescing with each other. This interfacial film is composed of many natural emulsifiers such as some PHCs constituents (e.g., asphaltenes and resins), fine solids, oil soluble organic acids, and other finely divided materials [24,25]. The pH value of oily sludge is usually in a range between 6.5 and 7.5 and its chemical composition varies over a wide range, depending on crude oil source, processing scheme, and equipment and reagents used in refining process. For example, the total petroleum hydrocarbon (TPH) contents in oily sludge can range from 5% to 86.2% by mass, but more frequently in the range of 15–50%, whereas the contents of water and solids are in the range of 30–85% and 5–46%, respectively [16,21,26–29]. The PHCs and other organic compounds in oily sludge can be generally classified into four fractions, including aliphatics, aromatics, nitrogen sulphur oxygen (NSO) containing compounds, and asphaltenes [2,30]. The aliphatics and aromatic hydrocarbons usually account for up to 75% of PHCs in oily sludge [31], and their most common compounds include alkanes, cycloalkanes, benzene, toluene, xylenes, naphthalene, phenols, and various polycyclic aromatic hydrocarbons (PAHs) (e.g., methylated derivatives of fluorine, phenanthrene, anthracene, chrysene, benzofluorene, and pyrene) [32]. The NSO fraction contains polar compounds such as naphthenic acids, mercaptans, thiophenes, and pyridines [32]. The nitrogen (N) content accounts for less than 3% in oily sludge, and most of them are contained in the distillate residue as part of asphalt and resin fraction. The sulphur (S) content can be in the range of 0.3–10% whereas the oxygen (O) content is usually less than 4.8% [32]. Asphaltenes are mixtures of pentane-insoluble and colloidal compounds including polyaromatic and alicyclic molecules with alkyl substitutes (usually methyl groups), and they vary in molecular weight between 500 and several thousand [33]. Asphaltenes and resins can be responsible for the stability of oily sludge emulsion since these constituents contain hydrophilic functional groups and consequently can act as lipophilic emulsifiers [34]. Usually, oily sludge is composed of 40–52% alkanes, 28–31% aromatics, 8–10% asphaltenes, and 7–22.4% resins by mass [35,36].

As a result of diverse chemical compositions in oily sludge, its physical properties such as density, viscosity, and heat value can vary significantly. The property measurements obtained from one oily sludge source cannot be applied to another source or to another sludge sample of the same source but collected on a different day or different location [37,38]. However, a key factor affecting the physical properties of oily sludge is the polarity and molecular weight of chemical constituents in sludge, and it is possible to make an empirical estimation of physical properties based on the chemical compositions of sludge [38,39]. In addition to organic chemical components, oily sludge also contains a variety of heavy metals resulted from different sources. The species and concentrations of these heavy metals could vary over a wide range as similar to organic compounds. According to a report from American Petroleum Institute (API) [40], metal concentrations in oily sludge obtained from petroleum refineries are generally 7–80 mg/kg for zinc (Zn), 0.001–0.12 mg/kg for lead (Pb), 32–120 mg/kg for copper

(Cu), 17–25 mg/kg for nickel (Ni), and 27–80 mg/kg for chromium (Cr). It is possible that a very high concentration of heavy metals could be found in oily sludge. For example, the metal concentration in oily sludge from refineries was reported in recent literatures as 1299 mg/kg for Zn, 60200 mg/kg for iron (Fe), 500 mg/kg for Cu, 480 mg/kg for Cr, 480 mg/kg for Ni, and 565 mg/kg for Pb, respectively [5,6,41,42].

### 2.3. Toxicity and impact of oily sludge

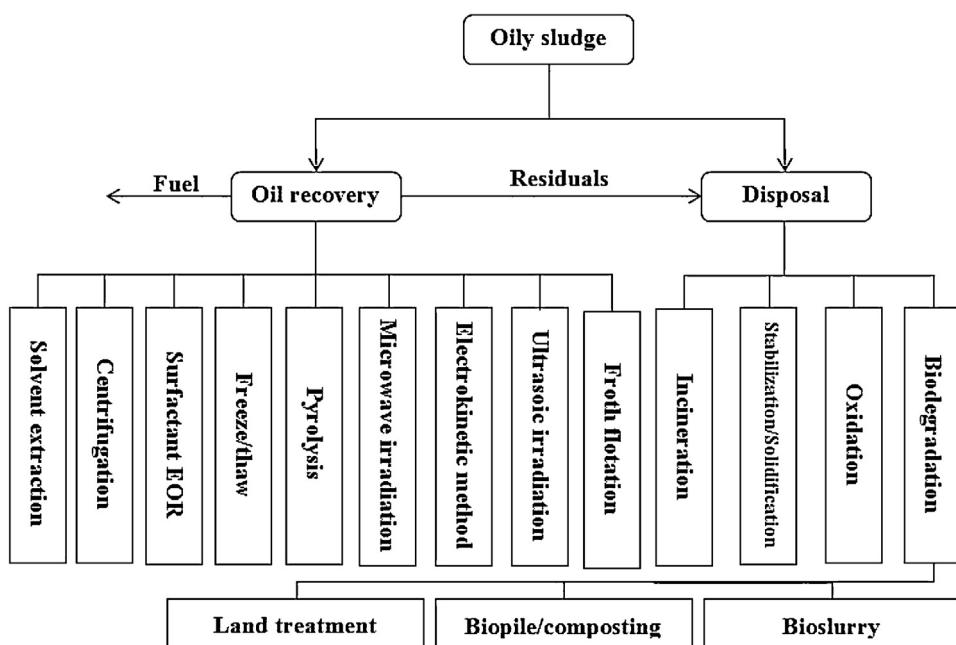
Due to the existence of high-concentration toxic substances, the improper disposal of oily sludge can pose serious threats to the receiving environment. After entering the terrestrial environment, oily sludge can disturb the physical and chemical properties of receiving soils, leading to soil morphological change [43]. The oily sludge contaminated soils may create nutrient deficiency, inhibit seed germination, and cause restricted growth or demises of plants on contact [44]. Due to its high viscosity, oily sludge components can be fixed in soil pores, adsorbed onto the surface of soil mineral constituents, or form a continuous cover on soil surface [45]. These would lead to reduced hygroscopic moisture, hydraulic conductivity, and water retention capacity (i.e. wettability) of soils [45,46]. In particular, the components with higher molecular weight in sludge and their degradation products could remain near soil surface and form hydrophobic crusts that decrease water availability and limit water/air exchange [47]. A long-term (i.e. several years) hydrophobicity of oily wastes contaminated agricultural soils has been reported in western Canada although many PHCs-contaminated soils eventually take up water [43].

The disposal of oily sludge to the environment could lead to various toxic effects caused by PHCs and heavy metals. Most of the heavy metals have a cumulative effect and are of particular hazard. In terms of PHCs, the polycyclic aromatic hydrocarbons (PAHs) are of major concerns since they are genotoxic to humans and other ecological receptors [43]. The PHCs in oily sludge could migrate down through the soil profile and enter groundwater that is linked with other aquatic systems, causing serious adverse consequences such as reduced diversity and abundance of fish in the aquatic

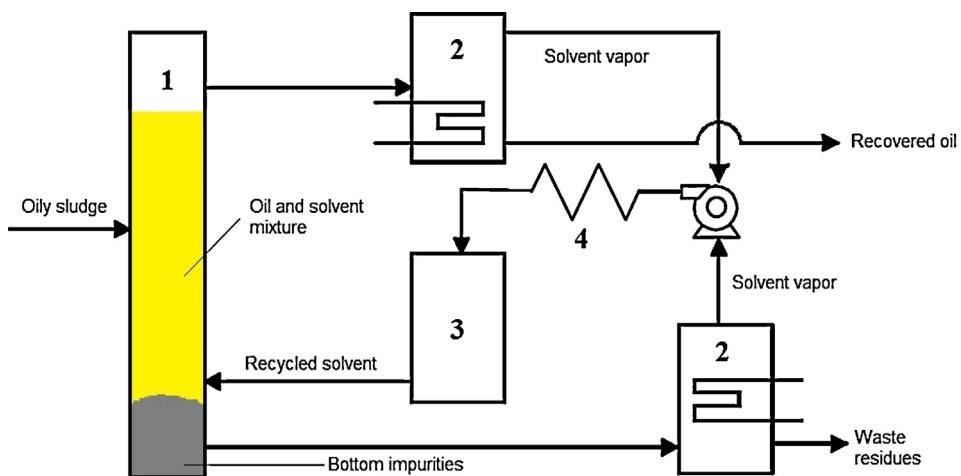
system [45,48]. PHCs in oily sludge could also decrease the activity of soil enzymes (i.e. hydrogenase and invertase) and pose toxic effects on the soil microorganisms [46]. Moreover, after remaining in the terrestrial environment for an extended period of time, the weathered (or aged) chemical residues may appear to resist de-sorption and degradation, and they have considerable time to interact with soil components [47]. Covalent bonding between organic compounds in sludge residues and humic polymers (e.g., humin, fulvic acid, and humic acid) in soil could form stable dialkylphthalates, long-chain alkanes, and fatty acids that are resistant to microbial degradation [49,50]. Due to the hazardous nature of oily sludge, many regulations in the world such as the *Resource Conservation and Recovery Act* (RCRA) in USA have established strict standards for its handling, storage, and disposal [51]. For example, it was regulated that all surface impoundments which treat or store hazardous wastes must either be double lined or taken out of service [38]. Even if oily sludge is disposed of in lagoon which is lined with cement and bricks, problems of odour, and fire hazard would still be created [22]. Refinery oily sludge deposited in lagoons or landfills has also been identified as a stationary source of atmospheric volatile organic compounds (VOCs) pollution [52]. Such air pollutant emissions can create health risks to facility workers and surrounding communities [53].

## 3. Overview of sludge treatment methods

Generally, a three-tiered oily sludge waste management strategy should be applied [10]. This includes (1) employing technologies to reduce the quantity of oily sludge production from petroleum industry, (2) recovering and reclaiming valuable fuel from existing oily sludge, and (3) disposing of the unrecoverable residues or oily sludge itself if neither of the first two tiers is not applicable [19,54]. The first tier is to prevent the generation of oily sludge and reduce its volume of generation, while the next two tiers are more concerned about the effective treatment of existing oily sludge which is the focus of this review. A variety of methods have been developed for the treatment of oily sludge as discussed below (Fig. 2).



**Fig. 2.** Overview of oily sludge treatment methods.



**Fig. 3.** Flow diagram of solvent extraction process (1: reactor column; 2: distillation system; 3: solvent recycling tank; 4: compressor and cooling system). Revised from Ref. [62].

#### 4. Oil recovery from sludge

Recycling is the most desirable environmental option for handling oily sludge since it enables petroleum industry to reuse valuable oil for reprocessing and reformulating or energy recovery. Moreover, recycling of oily sludge can reduce the disposal volume of hazardous waste outside the industrial zone, prevent the extent of contamination, and decrease the use of non-renewable energy resources. According to API [40], the primary environmental consideration in handling oily sludge should be the maximization of hydrocarbon recovery. It was reported that in the USA, more than 80% of PHCs wastes generated within a refinery is recycled, with the remaining 20% managed by an acceptable disposal method [38]. In general, oily sludge with a high concentration (>50%) of oil and a relatively low concentration of solids (<30%) are preferable to be recycled [55]. Other studies suggested that oily sludge even containing a relatively low oil content (>10%) still merits an treatment of oil recovery [16]. A number of methods have been available for recycling hydrocarbons from oily sludge.

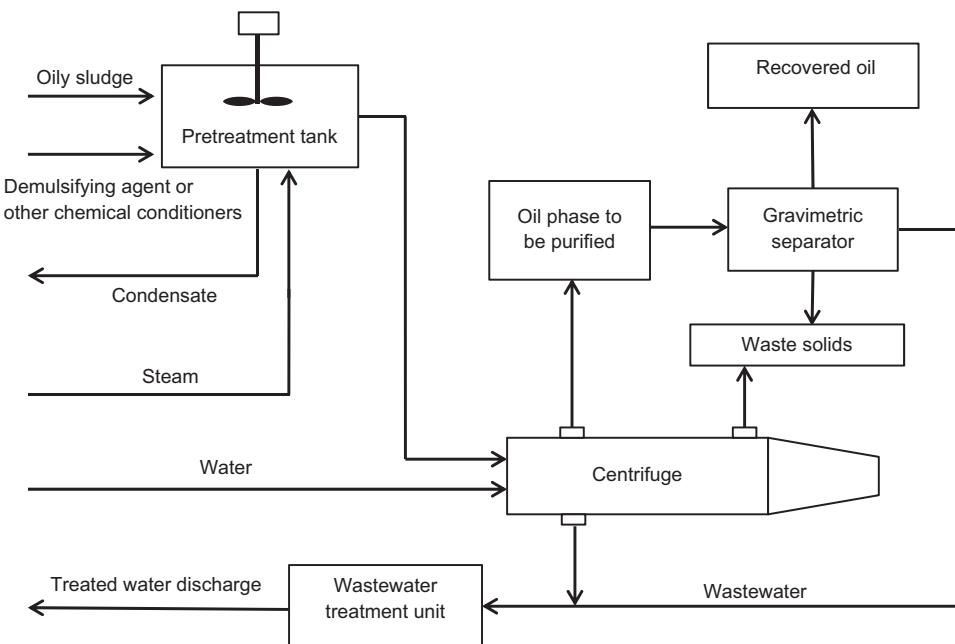
##### 4.1. Solvent extraction

Solvent extraction has been widely used for removing semi-volatile and non-volatile organic compounds from soil/water matrices. It mixes oily wastes with solvent at desired proportions to ensure complete miscibility, while the water, solid particles and carbonaceous impurities are rejected by extraction solvent. The solvent/oil mixture is then sent for distillation to separate oil from solvent [56]. Various solvents have been reported for oily sludge treatment. Gazineu et al. [57] used turpentine as a solvent for oil extraction, and they found that the extracted oil accounted for 13–53% of the original sludge mass. Zubaidy and Abouelnasr [7] compared the effects of several organic solvents such as methyl ethyl ketone (MEK) and liquefied petroleum gas condensate (LPGC), and they found that at a solvent-to-sludge ratio of 4:1, the highest oil recovery rate of 39% and 32% was obtained by MEK and LPGC extraction, respectively. Their results indicated that the ash, carbon residue, and asphaltene levels in the recovered oil were mostly improved when using MEK as the solvent, but the recovered oil still contained high levels of sulfur and carbon residue, thus the recovered oil would require further purification prior to be used as a fuel. El Naggar et al. [58] used several solvents such as naphtha cut, kerosene cut, n-heptane, toluene, methylene dichloride, ethylene dichloride, and diethyl ether to recover oil from dry and semi dry petroleum sludge, while toluene gave the highest PHCs

recovery rate of 75.94%. Meyer et al. [59] found that petroleum solvent oil with a high percentage of ring compounds (e.g., naphthenics and aromatics) such as catalytic cracking heating oil was highly effective in dissolving asphaltenic components in oily sludge, and the solvent oil with paraffinic character like virgin paraffinic diesel was effective for sludge with more paraffinic (waxy) components. Hexane and xylene have also been used as solvents to recover hydrocarbons from petroleum sludge, and it was reported that 67.5% of PHCs in sludge could be recovered, with most of them in the range of C<sub>9</sub> to C<sub>25</sub> [60].

Fig. 3 presents a simplified conceptual diagram for a field-scale solvent extraction process. 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. In general, the performance of solvent extraction is affected by a number of factors such as temperature and pressure, solvent-to-sludge ratio, mixing, and solvent itself. Mixing and heating are usually required to improve the dissolution of sludge organic components in solvent [59,60]. High temperature can accelerate the extraction process but it can result in the loss of PHCs and solvent through evaporation, while low temperature would decrease the cost of extraction process but it can lead to lower oil recovery efficiency [61]. Lower pressure is favoured during distillation since solvent evaporation could occur at a relatively lower distillation temperature. A lower distillation temperature can not only save heating cost, but also prevent thermo degradation of solvents. Moreover, the quantity and quality of recovered oil can be improved with increasing solvent-to-sludge ratio. For example, it was observed that the amount of ash and high-molecular-weight hydrocarbons in the recovered oil decreased with the increasing amount of solvents [7].

Generally, solvent extraction represents a simple but efficient method to separate oily sludge into valuable hydrocarbon and a solid or semi-solid residue with reduced volume. The extraction treatment can be completed within a relatively short period, and has the potential to treat a large volume of oily sludge depending



**Fig. 4.** Schematic view of centrifugation used in oily sludge treatment.

on the extraction column design. In order to prevent the emission of solvent vapour, a closed and continuous process capable of retaining the evaporated solvent is usually desired. Heating is also required for solvent recycling, and this could increase the energy cost of application. One major obstacle of applying solvent extraction to field-scale oily sludge treatment is that a large volume of organic solvents are required. This could result in significant economic and environmental concerns. Some alternative methods have been developed to improve the performance of solvent extraction. For example, supercritical fluid extraction (SFE) can extract PHCs in soil matrices more rapidly than conventional solvent extraction, and more importantly, it can eliminate the use of organic solvents [63]. However, when this method is used for extracting oil from a large volume of oily sludge, it may be subject to low efficiency and high variability [64].

#### 4.2. Centrifugation treatment

Centrifugation has been widely applied to field-scale oily sludge treatment although few scholarly literatures have been reported in recent years. It utilizes a special high-speed rotation equipment to generate a strong centrifugal force which can separate components with different densities (such as water, solids, oil, and pasty mixtures in oily sludge) within a short time. In order to enhance the centrifugation performance and reduce energy consumption, the viscosity of oily sludge needs to be reduced through sludge pre-treatment, such as the addition of organic solvents, demulsifying agents and tensioactive chemicals, the injection of steam, and direct heating [7,65–67]. For example, Conaway [65] 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 the 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 [65]. Cambiella et al. [66] found that a small amount of a coagulant salt ( $\text{CaCl}_2$ , in the concentration range of 0.01–0.5 M) could improve the water–oil separation process by centrifugation, with a high oil separation efficiency of 92–96% being obtained. One recent US patent reported an approach

of recovering crude oil from oily sludge through centrifugation, with oily sludge being mixed with demulsifying reagents at pre-defined ratio and then agitated to allow homogenization, while the processed mixture is centrifuged to separate PHCs, water and solids [67].

Fig. 4 presents a process of using centrifugation for oily sludge treatment. Oily sludge is firstly 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 its viscosity. The less viscous sludge is mixed with water at a certain sludge/water ratio for high-speed centrifugation. After centrifugation, the separated water containing high concentration of PHCs is drained for further wastewater treatment, and the separated oil (still 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 residues for further treatment. In general, centrifugation is a relatively clean and mature technology for oily sludge treatment, and its oil separation from sludge is effective. Another advantage is that centrifugation equipment usually does not occupy much space [19]. However, this process requires high energy consumption to generate strong enough centrifugation force to separate oil from petroleum sludge. The use of centrifugation has been limited to small scales because of the high equipment investment and limitations [68]. In addition, centrifugation can bring noise problems [19]. Moreover, the introduction of demulsifying agents and tensioactive chemicals for sludge pre-treatment not only increase the processing cost, but also bring environmental concerns.

#### 4.3. Surfactant enhanced oil recovery (EOR)

The application of surfactant for removing organic pollutants from solid matrices is a cost effective and relatively fast process, and it has the potential to treat a large volume of contaminants. Surfactant is usually an amphiphilic compound, and its molecule consists of a hydrophobic tail and a hydrophilic tail. The hydrophilic tail makes surfactant molecule dissolve in the water phase and increase solubility of PHCs, while the hydrophobic tail makes it tend to gather at the interfaces to decrease

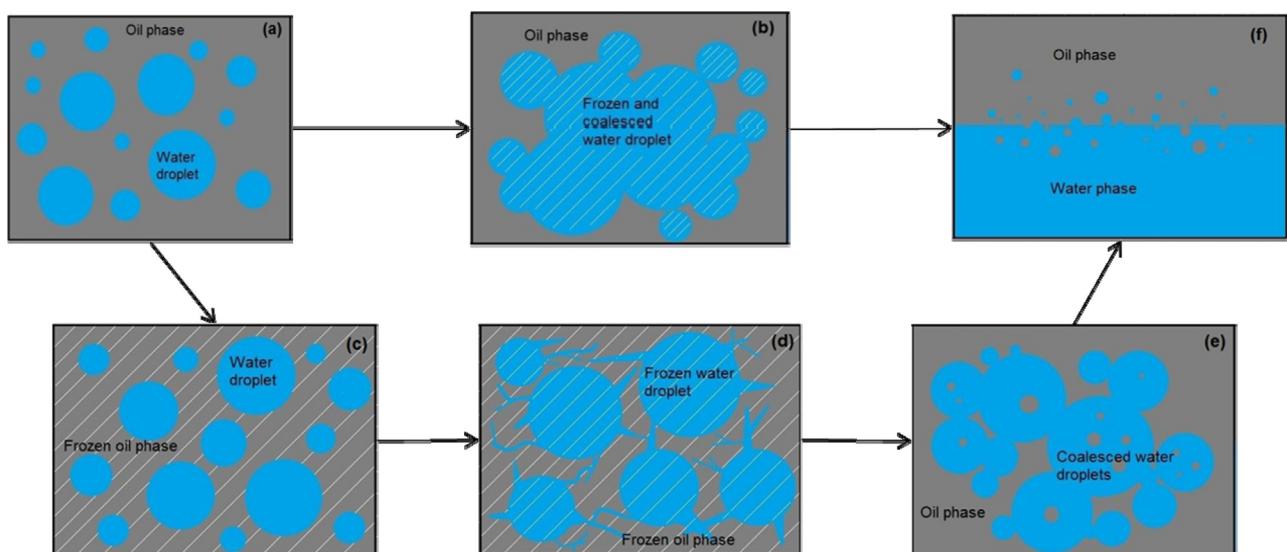
the surface or interfacial tension and thus enhance the mobility of PHCs [69]. It was reported that chemical surfactants, such as sodium dodecyl sulphate (SDS), Corexit 9527, Triton X-100, Tween 80 and Afonic 1412-7, can be used to increase the concentration of PHCs in aqueous phase [70–73]. Abdel-Azim et al. [74] used three sets of surfactant (nonyl phenol ethoxylates) based demulsifier mixture to break down petroleum sludge emulsion, and they found that more than 80% of water can be separated from oily sludge. Similar results can be found in Dantas et al.'s research [75]. However, using chemical surfactants can be associated with a range of problems such as environmental toxicity and resistance to biodegradation [70,76–78]. As compared to chemical surfactant, bio-surfactant has received increasing attention since it exhibits greater environmental compatibility, more diversity, better surface activity, lower toxicity, higher emulsification ability, higher selectivity, and higher biodegradability [79–84]. For instance, Lima et al. [85] compared the toxicity of five bio-surfactants and one chemical surfactant called SDS to petroleum degrading microorganisms, and their results showed that bio-surfactants had a significantly lower toxicity than SDS. Edwards et al. [86] also found that the toxicity of bio-surfactants to estuarine invertebrate species were much lower than that of chemical surfactants.

Bio-surfactants are produced by yeast or bacterial from various substrates including sugars, oils, alkanes, and wastes. They can be grouped into five categories, including (1) glycolipids, (2) lipopeptides, (3) phospholipids, fatty acids, and neutral lipids, polymetric bio-surfactant, and particulate bio-surfactant [69]. Most of the bio-surfactants are either anionic or neutral, and only a few are cationic such as those containing amine groups. Their structures include amphiphilic molecules with a hydrophobic moiety (i.e. fatty acid) and a hydrophilic moiety (e.g., carbohydrate, carboxylic acid, phosphate, amino acid, cyclic peptide or alcohol) [82]. A very wide spectrum of microbial species can be used to produce bio-surfactants, and three groups of bio-surfactants have been extensively studied, including (1) rhamnolipids (i.e. a type of glycolipids) produced from *Pseudomonas aeruginosa*, (2) sorphorolipids (i.e. a type of glycolipids) produced from *Candida bombicola*, and (3) surfactins (i.e. a type of Lipopeptides) produced from *Bacillus subtilis* [87–92]. Various laboratory- and field-scale studies have

been conducted to use bio-surfactants in oily sludge treatment. For example, Lima et al. [93] isolated five bacterial strains for bio-surfactant production, and they found that bio-surfactants produced by *Dietzia maris* sp., *Pseudomonas aeruginosa*, and *Bacillus* sp. respectively recovered up to 95%, 93%, and 88% of the total oily sludge as oil, but only 2% of the oil present in oily sludge was recovered when not using bio-surfactant. Yan et al. [9] proved the promising oil recovery performance of bio-surfactant produced by *Pseudomonas aeruginosa*, and an oil recovery rate of up to 91.5% was obtained when using bio-surfactant and centrifugation for oil separation from refinery oily sludge. Long et al. [94] also applied rhamnolipid to a pilot-scale (100 L) waste crude oil treatment, and their results indicated that rhamnolipid could recover over 98% of crude oil from the wastes, while the recovered oil contained less than 0.3% of water. In general, surfactant enhanced oil recovery method is a simple but a relatively fast and effective process, and it has a potential to treat a large volume of oily sludge. In spite of the successful application of surfactants, several factors should be taken into account when selecting surfactants for oil recovery, including effectiveness, cost, public and regulatory acceptance, biodegradability, degradation products, toxicity, and ability to recycle. In particular, the costs of producing bio-surfactants may limit their commercial applications. The related costs can be reduced by improving yields, recovery, and using inexpensive or waste substrates [95].

#### 4.4. Freeze/thaw treatment

One important process of oil recovery from oily sludge is to remove water from a W/O emulsion by separating oil and water into two phases, and this process is called demulsification. Freeze/thaw treatment used for sludge dewatering in cold regions has been reported as an effective demulsification method [96–98]. As shown in Fig. 5, two different mechanisms are responsible for the demulsification. The first one occurs when water phase in emulsion becomes frozen ahead of oil phase. The volume expansion of frozen water droplets leads to their coalescence and cause the inner disarrangement of emulsion, and the oil phase is gradually frozen with temperature dropping (Fig. 5b). During the thawing process, the oil phase coalesces as a result of interfacial tension, and the



**Fig. 5.** Schematic diagram of the mechanism of freeze/thaw-induced demulsification for W/O emulsion: (a) original emulsion, (b) water droplets freezing, expansion and coalescing, (c) oil phase freezing to form a solid cage, (d) water droplets freezing and expanding to break the cage, (e) emulsion thawing and water droplets coalescing, and (f) gravitational delamination.

Revised from Ref. [99].

oil–water mixture can thus be delaminated into two bulk phases driven by gravitational force (Fig. 5f) [99]. The second mechanism occurs when oil phase becomes frozen ahead of water phase. This would form a solid cage that encapsulates water droplets during the freezing process (Fig. 5c). These water droplets are gradually frozen with temperature dropping, and the volume expansion of frozen droplets breaks the oil cage. This could produce fine crevices that allow the unfrozen water droplets to permeate and contact with each other, forming a large network of micro-channels (Fig. 5d). During the thawing process, this network fuses with water droplet coalescence that leads to phase inversion (Fig. 5e), and such unstable oil–water mixture can then be delaminated into two bulk phases driven by gravitational force (Fig. 5f) [99].

Jean et al. [37] found that over 50% of oil can be separated from refinery oil-in-water emulsions by freeze/thaw method. Chen and He [95] reported that freeze/thaw treatment removed nearly 90% of water from a high-water-content oily sludge. In another research [100], freeze/thaw showed satisfactory performance on the dewatering of lubricating oily sludge, and over 90% of water was removed using this method. Lin et al. [98] applied freeze/thaw treatment to break water/oil emulsions, and the volume expansion of water turning to ice and interfacial tension of oil–water interface were determined as the main driving forces of demulsification. They investigated the effect of four different freezing methods (i.e. freezing in a refrigerator, cryogenic bath, dry ice and liquid nitrogen), and found that the best freezing method was freezing in cryogenic or dry ice, with over 70% dehydration efficiency being achieved for the emulsions containing 60% of water. Zhang et al. [101] found that freeze/thaw worked effectively for oil recovery from refinery sludge with an oil recovery rate of 65.7%. In general, the performance of freeze/thaw on demulsification can be affected by a number of factors, such as freezing and thawing temperatures, treatment duration, water content, salinity of aqueous phase, presence of surfactants, and solid contents in emulsion [98,101]. For example, Chun et al. [102] found that the dewatering rate at  $-40^{\circ}\text{C}$  was obviously higher than that at  $-20^{\circ}\text{C}$ , and the lower thawing temperature was also beneficial to dewatering process. At high thawing temperature, the frozen sludge could be melted rapidly which may break down the aggregated flocs of oil/solids, thus leading to poor dewaterability. Yang et al. [24] compared the effect of three thawing approaches on W/O demulsification, and they found that rapid thawing (i.e. microwave heating) could significantly enhance the water–oil separation efficiency, with more than 90% (v/v) of emulsion being separated. Similar results can be found in Rajaković and Skala [103]. Oh and Deo [104] also proved that water content can affect oil recovery, with higher yield stresses being observed in W/O emulsion with lower water content. In summary, freeze/thaw treatment is a promising method for dewatering and oil recovery from oily sludge. However, its industrial application should consider the required freezing time and related costs. Chun et al. [102] suggested that 8 h was almost sufficient for freezing at  $-20^{\circ}\text{C}$ . In addition, freezing could be a relatively slow process that requires intensive energy and high cost [97]. Thus, the application of freeze/thaw treatment for oil recovery from oily sludge might be more promising for cold regions where natural freezing is possible.

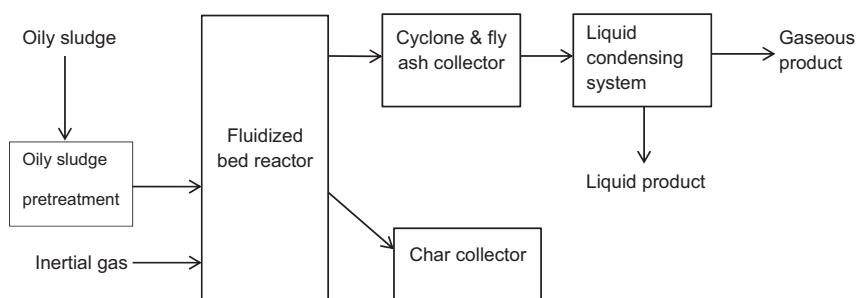
#### 4.5. Sludge pyrolysis

Pyrolysis is the thermal decomposition of organic materials at elevated temperatures ( $500\text{--}1000^{\circ}\text{C}$ ) in an inert environment. It is different from gasification which transforms organic materials to combustible gas or syngas with the existence of 20–40% of oxygen. The pyrolysis process produces hydrocarbons with lower molecular weight in condensation (i.e. liquid) and/or non-condensable gases. It also generates a solid product called char [105].

Depending on the operational conditions, the main product of pyrolysis can be either char, liquid, or gas, and they may have a more elevated heating value than the raw oily sludge [106]. For example, the major product of fast pyrolysis treatment (i.e. a pyrolysis process that rapidly heats feedstock to a controlled temperature and then very quickly cools the volatile products formed in the reactor) can be a liquid (i.e. pyrolysis oil), which could be used as a fuel or a source of other valuable chemical products [107,108]. Several studies have been reported to use pyrolysis for fuel recovery from oily sludge. Shen and Zhang [109] observed that oil yield increased initially with pyrolysis temperature with a maximum oil yield (30 wt.% of the feed oily sludge) occurring at  $525^{\circ}\text{C}$ , but decreased when the temperature was above  $525^{\circ}\text{C}$  due to secondary decomposition reactions which could break the oil into lighter and gaseous hydrocarbons. Liu et al. [3] found that about 80% of total organic carbon content (TOC) in oily sludge could be converted into usable hydrocarbons when using a pyrolysis process, with a significant hydrocarbon yield occurring in the temperature range of  $327\text{--}450^{\circ}\text{C}$ . Schmidt and Kaminsky [110] found that the separation of oil from oily sludge occurred from  $460$  to  $650^{\circ}\text{C}$ , and 70–84% of the oil could be separated from sludge by a fluidized bed reactor. Chang et al. [111] applied the pyrolysis process to treat oily sludge, and they observed a maximum production rate of hydrocarbons (mainly low-molecular-weight paraffins and olefins, 51.61 wt.% of PHCs) at  $440^{\circ}\text{C}$ , and the distillation characteristics of liquid product from pyrolysis were close to that of diesel oil. Their results also indicated that the major gaseous products from pyrolysis excluding  $\text{N}_2$  are  $\text{CO}_2$  (50.88 wt.%), hydrocarbons (25.23 wt.%),  $\text{H}_2\text{O}$  (17.78 wt.%), and  $\text{CO}$  (6.11 wt.) [111]. Karayildirim et al. [112] illustrated that the main decomposition of oily sludge occurred in the temperature range of  $100\text{--}350^{\circ}\text{C}$ , while the inorganic materials started decomposition when the temperature rose to  $400^{\circ}\text{C}$ , and the carbonaceous residues accounted for 38 wt.% of the original sludge at the final pyrolysis temperature of  $900^{\circ}\text{C}$ . Wang et al. [113] found that pyrolysis of oily sludge started at a low temperature of  $200^{\circ}\text{C}$ , and the maximum hydrocarbon production occurred in the range of  $350\text{--}500^{\circ}\text{C}$ , with improved oil yield and quality being observed by maintaining temperature at  $400^{\circ}\text{C}$  for 20 min.

Pyrolysis can be affected by a number of factors, such as temperature, heating rate, characteristic of oily sludge, and chemical additives. Punnaruttanakun et al. [114] investigated the influence of different heating rate (i.e. 5, 10, and  $20^{\circ}\text{C}/\text{min}$ ) on the pyrolysis of API separator sludge, and they found a lower pyrolysis rate at a heating rate of  $20^{\circ}\text{C}/\text{min}$  than those at 5 and  $10^{\circ}\text{C}/\text{min}$ , but the heating rate did not affect the amount of solid products. Shie et al. [115] found that chemical additives (such as sodium and potassium compounds) in the pyrolysis process could enhance the reaction rate within a pyrolysis temperature range of  $377\text{--}437^{\circ}\text{C}$ , and the highest fuel yield was obtained as 73.13 wt.% with the addition of  $\text{KCl}$ , while the maximum improvement effect on the quality of pyrolysis oil was achieved by  $\text{KOH}$ , then followed by  $\text{KCl}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaCl}$ . Results from other studies also indicated that additives of metal compounds (i.e. aluminum and iron compounds) and catalytic solid wastes (i.e. fly ash, oily sludge ash, waste zeolite, and waste polymer of polyvinyl alcohol) could affect the conversion, reaction rate, yield and quality of oil products from oily sludge pyrolysis process [116,117]. In terms of application, three types of pyrolysis configuration can be used, including ablative pyrolysis, fluid bed and circulating fluid bed pyrolysis, and vacuum pyrolysis. The commercial-scale oil recovery application has mainly adopted the fluid beds or circulating fluid beds and the associated auxiliary systems, such as sludge and nitrogen feeding, char collection, and vapor condensation (Fig. 6) [105].

Pyrolysis has the advantages of producing a liquid product that can be easily stored and transported, and the recovered oil was proved to be comparable to low-grade petroleum distillates from



**Fig. 6.** Typical schematic view of fluidized bed systems used in sludge pyrolysis treatment.

commercial refineries and could be directly used in diesel fuelled engines [118,119]. As compared to the incineration process, pyrolysis of oily sludge generates a lower emission of NO<sub>x</sub> and SO<sub>x</sub>, and it also enables heavy metals in oily sludge to be concentrated in the final solid product (i.e. char) [109]. The char usually accounts for 30–50 wt.% of the original oily sludge, and it can be applied as an adsorbent for the removal of different pollutants such as H<sub>2</sub>S or NO<sub>x</sub> in gaseous streams [105]. It can also be used as a soil conditioner to increase the nutrient availability for plants [120]. The metals enriched in solid char can be more resistant to leaching than those concentrated in the ash obtained from incineration [121]. In spite of these advantages, the large-scale implementation of pyrolysis could be restricted by the low economic value of liquid products and the relatively complex processing equipments [122,123]. The high operational cost is mainly due to the large amount of external energy required for the endothermic reaction to take place [105]. In addition, oily sludge usually contains a relatively high water content, and thus the dewatering of oily sludge before pyrolysis treatment may significantly increase the overall cost of pyrolysis [124]. Additional concern may include that PAHs, the well-known highly carcinogenic substances, could be existed as a large portion in the liquid products of sludge pyrolysis [125].

#### 4.6. Microwave irradiation

The microwave frequency ranges from 300 MHz to 300 GHz, but the industrial application is usually performed at a frequency either close to 900 MHz or near 2450 MHz [126]. Microwave energy can directly penetrate the material through molecular interaction with the electromagnetic field, and provide a quick heating process at improved heating efficiencies as compared with conventional techniques. Such heating effect can be used for the demulsification of W/O emulsion by rapidly increasing the temperature of emulsions, leading to the reduction of viscosity which could accelerate the settlement of water droplets in emulsion [127]. The rapid temperature increase can also break heavy hydrocarbons into lighter ones. For materials with low dielectric loss, microwave can pass through them with little energy absorption. For materials with high dielectric loss, microwave energy can be absorbed based on the electric field strength and the dielectric loss factor. When using microwave for treating a mixture of materials with different dielectric properties, a selective heating could occur [128,129]. For W/O emulsion such as oily sludge, the inner phase is water with a relatively higher dielectric loss, and it can absorb more microwave energy than oil. Such energy absorption could result in the expansion of water and press the water–oil interfacial film to become thinner, which could facilitate water/oil separation [127]. Moreover, microwave irradiation could lead to molecular rotation by rearranging the electrical charges surrounding water molecules. This could destroy the electric double layers at the oil/water interface, resulting in the reduction of zeta potential. Under reduced zeta potential, water and oil molecules can move more freely in

the emulsion so that the water or oil droplets can collide with each other to form coalescence [127]. The above mechanisms can lead to the separation of an emulsion [130]. Several laboratory- and field-scale studies have demonstrated the benefits of using microwave irradiation for W/O emulsion treatment. Xia et al. [131] observed a nearly 100% of demulsification efficiency within a very short time by using microwave radiation for treating W/O emulsions, which is much higher than that when using conventional heating approaches. Fang and Lai [132] applied microwave irradiation for a field test to demulsify 188 barrels of W/O emulsion in tanks, and their results showed that the emulsion was separated into 146 barrels of oil and 42 barrels of water, while the water separation efficiency from emulsions was higher than that when using conventional heating. They also illustrated that microwave irradiation could have particular effect on the partial removal of polar compounds [132].

The performance of microwave irradiation on oily sludge demulsification can be affected by many factors such as microwave power, microwave duration, surfactant, pH, salt, and other properties of oily sludge such as water–oil ratio [133]. The increase of pH could decrease the stability of sludge W/O emulsion due to the increase in hydrophilicity [133]. On the other hand, the salt-assisted microwave irradiation has been found to be effective due to increased conductivity of water phase that could accelerate the heating rate [134]. For example, Chan and Chen [128] found that electrolyte could lower the Zeta potential of oil droplets and result in the destabilization of W/O emulsions, and they observed that the demulsification rate increased with electrolyte concentration (NaCl, KCl, NaNO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub>) in the range of dilute solutions (<0.5 M) when using microwave irradiation. The optimum microwave irradiation power and treatment time were suggested to be 420 W and 12 s in their research [128]. Fortuny et al. [133] investigated the demulsification effect of salt (NaCl) on a crude oil emulsion by microwave irradiation, and they found that the dissolved salts significantly increased the heating efficiency and destabilization of emulsions. Tan et al. [127] found that the performance of microwave treatment on W/O emulsions could be improved by the addition of chemical demulsifiers, and a satisfactory water–oil separation efficiency (95 v/v%) was achieved by adding 50 ppm of demulsifier when using microwave irradiation (700 W, 2450 MHz). Abdulbari et al. [135] combined microwave heating (900 W, 2450 MHz) with synthetic surfactants (i.e. Triton X-100, low-sulfur wax residue, sorbitan monooleate, and SDS) to separate water from petroleum emulsions, and their results indicated that over 90% of water can be separated. In general, as compared to other heating methods, microwave irradiation can more rapidly raise the energy of molecules inside the medium, leading to higher reaction rates and superheating within several minutes [136]. The short heating time makes microwave irradiation a high energy-efficient and easy-to-control approach for breaking emulsions. In addition to its high demulsification efficiency, the low temperature of reactor wall during the direct heating inside

the bulk medium caused by microwave irradiation could lead to an extended aromatization reaction. This could result in an increased yield of light aromatic compounds. These light compounds can have a much lower toxicity as compared to PAHs with high molecular weight in the liquid products generated during the pyrolysis process [137]. However, the application of microwave irradiation to industrial-scale oily sludge treatment is limited due to the specific equipment required and possible high operating costs.

#### 4.7. Electrokinetic method

Electrokinetic process utilizes a low-intensity direct current across an electrode pair on each side of a porous medium, causing the electro osmosis of liquid phase, migration of ions and electrophoresis of charged particles in a colloidal system to the respective electrode [130,139]. The separation of different phases (water, oil, and solids) from oily sludge using electrokinetic process can be based on three main mechanisms. Firstly, colloidal aggregates in oily sludge can be broken under the influence of an electrical field, leading to the movement of colloidal particles of oily sludge and solid phase towards the anode area as a result of electrophoresis, and the movement of the separated liquid phase (water and oil) towards the cathode area as a result of electro-osmosis [139]. As mentioned before, oily sludge is a W/O emulsion stabilized by several kinds of emulsifiers such as asphaltenes, resins, organic acids, and finely divided solids. These emulsifiers usually occur as a film on the surface of dispersed water droplets, and the fine particles can be adsorbed at the water droplet surface and act as a barrier to prevent droplet coalescence [140]. The separation of colloidal particles and fine solids from W/O emulsion could remove such barrier and thus accelerate the coalescence of water droplets in continuous oil phase. Secondly, following this process, the electro-coagulation of the separated solid phase could occur near the anode area, leading to increased solid phase and sediments concentration. Lastly, the separated liquid phase (water and oil, without colloid particles and fine solids) can produce an unstable secondary oil-in-water emulsion which could be gradually electro-coalesced near the cathode area through charging and agglomeration of droplets, thus forming two separated phases of water and oil [141].

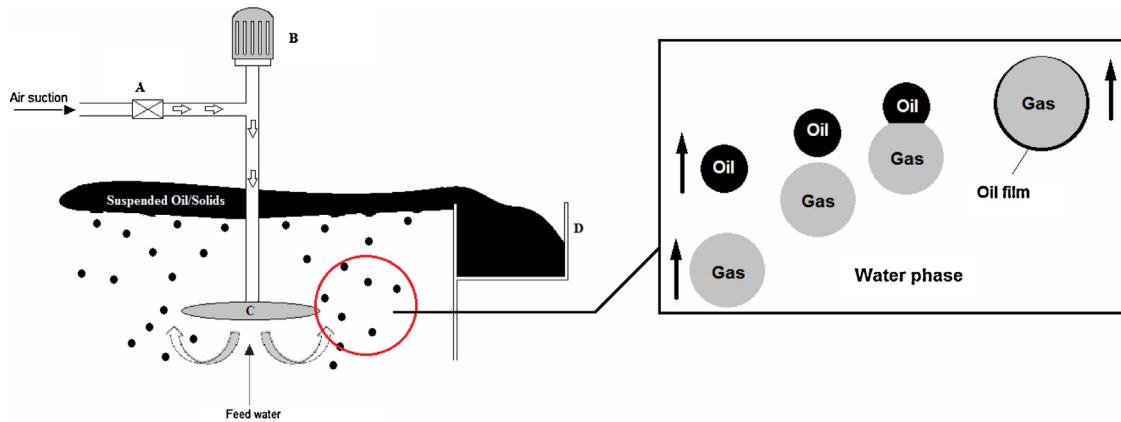
The electrokinetic treatment performance can be affected by several factors such as resistance, pH, electrical potential, and spacing between electrodes. This process may be improved through the use of surfactants or reagents to increase the contaminant removal rates at the electrodes [142]. Elektorowicz and Habibi [11] applied electrokinetic process to treat oily sludge, and they found that this process could reduce the amount of water by nearly 63% and light hydrocarbon content by about 43%, and the light hydrocarbon content was removed by 50% when combining electrokinetic treatment with surfactant. Yang et al. [139] conducted an oily sludge dewatering study using electrokinetic treatment, and their results showed that the water removal efficiency reached to 56.3% at a 4 cm electrode spacing and an electric potential of 30 V, while the solids content at the anode area increased from 5% to 14.1%. A large-scale experimental study (i.e. a capacity of 4 L) revealed that more than 40% of water was removed and a very efficient oil separation from oily sludge was achieved using electrokinetic process at 60 V with an initial spacing of 22 cm [139], and the temperature in the system was observed to increase significantly in a short time due to the application of high electric current. In general, the application of electrokinetic process for oil recovery from oily sludge requires less amount of energy than other oil recovery methods such as centrifugation and pyrolysis. However, most of the electrokinetic studies on oily sludge have been conducted at the laboratory level, and the performance and costs at a large scale still need further investigation. It is expected that using oily sludge storage pools as the

electrokinetic cell at the field scale could considerably reduce the treatment cost [139].

#### 4.8. Ultrasonic irradiation

Ultrasonic irradiation has proved to be effective for removing adsorbed materials from solid particles, separating solid/liquid in high-concentration suspensions, and decreasing the stability of W/O emulsion [143–146]. When ultrasonic wave propagates in the treatment medium, it generates compressions and rarefactions. 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, and microbubbles can be generated and grow due to such negative pressure. When these microbubbles grow to an unstable dimension, they can collapse violently and generate shock waves, resulting in very high temperature and pressure in a few microseconds [147]. Such cavitation phenomenon can increase the temperature of the emulsion system and decrease its viscosity, increase the mass transfer of liquid phase, and thus lead to destabilization of W/O emulsion [148]. Other studies suggested that under the influence of ultrasonic irradiation, smaller droplets in emulsion can move faster than the larger ones, and this can increase their collision frequency to form aggregates and coalescence of droplets, which then promotes the separation of water/oil phases [149,150]. Ultrasonic irradiation can not only clean the surface of solid particles but also penetrate into different regions of a multiphase system that are inaccessible when using other separation methods [151]. This mechanism is called ultrasonic leaching which enables solvents or leaching reagents to more readily enter the interior of solids pores, and increases the mass transfer of contaminants through the solids matrix [152]. A number of studies have been conducted to investigate the efficiency of ultrasonic irradiation for oil recovery from oily sludge. Xu et al. [1] applied ultrasonic cavitation with a frequency of 28 kHz in an ultrasonic cleaning tank to strip oil constituents from the surface of solid particles in oily sludge, and an overall oil separation rate of 55.6% was obtained. They also found that the optimal temperature, acoustic pressure, and ultrasonic power for oil recovery from sludge were 40 °C, 0.10 MPa, and 28 kHz, respectively, while both too high or too low ultrasonic energy input could inhibit oil recovery process since high ultrasonic energy input can prevent oil droplets from merging and low ultrasonic energy input makes it difficult to detach oil from solid particles. Zhang et al. [101] reported an oil recovery rate of up to 80% from oily sludge–water matrix (sludge/water ratio of 1:2) after 10 min of ultrasonic treatment using a 20 kHz ultrasonic probe system at a power of 66 W.

In general, the performance of oil recovery from oily sludge using ultrasonic treatment can be affected by a variety of factors, such as ultrasonic frequency, sonication power and intensity, water content in emulsion, temperature, ultrasonic treatment duration, solid particle size, initial PHCs concentration, salinity, and presence of surfactant [145,152,153]. For example, Xu et al. [1] found that lower ultrasonic frequency is more favorable for oily sludge treatment since cavitation is more difficult to occur under high frequency ultrasound than that under low frequency ultrasound, and they also indicated that too high or too low temperature is not suitable for oily sludge treatment by ultrasound. In the research by Jin et al. [154], a high oil recovery rate (above 95%) was achieved when the ultrasonic treatment parameters were 28 kHz, 15 min, 400 W, and 60 °C, respectively, and no further enhancement of oil recovery was observed when the ultrasonic power and treatment duration increased beyond 400 W and 15 min. Overall, ultrasonic irradiation is a “green” treatment method which can process oily sludge within a relatively short time. In spite of its high efficiency of oil recovery and no secondary pollution, the application of ultrasonic irradiation to field-scale oil recovery from sludge has rarely been reported,



**Fig. 7.** Schematic view of froth flotation in oil/water separation process.

Revised from Ref. [157].

while the most commonly used laboratory ultrasonic irradiation system was the ultrasonic probe system which can only be effective when treating a small volume of oily sludge. The utilization of large ultrasonic cleaning tank could be more promising in terms of treating a large amount of oily sludge, but its oil recovery performance might be compromised due to the resulted low ultrasonic intensity [155]. The high cost of equipment and maintenance could also inhibit the industrial application of this technology.

#### 4.9. Froth flotation

Froth flotation is a surface chemistry-based unit operation for separating fine solid particles from an aqueous suspension. It 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 [156]. Froth flotation has been successfully used to treat oily wastewater from refineries, and its utilization for oily sludge treatment has recently received research attentions [16]. Fig. 7 presents a schematic overview of this process. Oily sludge is firstly mixed with a given amount of water to form a sludge slurry. Air injection then generates fine air bubbles which approach oil droplets in the slurry mixture, and the water film between oil and air bubble can get thinning to reach a critical thickness, causing the rupture of water film and the spreading of oil to air bubbles. Lastly, 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 [157]. Ramaswamy et al. [16] applied froth flotation treatment for oil-water separation from oily sludge, and they observed an oil recovery of up to 55% at the optimal flotation conditions. Addition of surfactants and extraction solvent could enhance the oil recovery performance of flotation. Al-Otoom et al. [158] applied a modified fluidized flotation process for bitumen recovery from tar sand, and the maximum bitumen recovery could reach 86 wt.% when 0.35 wt.% light cycle oil was added as an extraction solvent at 80 °C. Stasiuk et al. [159] found that the addition of surfactants such as Tween 80 or Alcopol O during the froth flotation process significantly reduced water contents (i.e. 10 v/v%) in the recovered oil.

In general, oil recovery performance using froth flotation can be affected by many factors, such as oily sludge properties (i.e. viscosity, solid content, and density), pH, salinity, temperature, size of air bubble, presence of surfactant, and flotation duration [160–162]. Ramaswamy et al. [16] reported that the oil recovery rate increased with the duration of flotation but approached its maximum after 12 min of treatment, and they also found that

surfactant had significant influence on the oil recovery process. Higher temperature could also enhance the oil recovery via flotation since decreased sludge viscosity would facilitate oil separation and the subsequent flotation [158]. Froth flotation is a simple and less expensive approach for oily sludge treatment, but it is usually effective when treating sludge with relatively low viscosity. It has limited effect on the desorption of oil from solid matrix, and the oil constituents in skinned oil/solids mixture still need to be further purified. The recovered oil could also contain relatively high moisture. Consequently, a number of limitations still exist when applying it to field-scale oily sludge treatment. Oily sludge needs to be pretreated to reduce its viscosity and remove the coarse solid particles. Moreover, the froth flotation requires a large volume of water when treating oily sludge with low moisture and high viscosity, and thus oily wastewater treatment problem can be generated.

### 5. Oily sludge disposal methods

In addition to oil recovery, a number of technologies are available for the disposal of oily sludge, including incineration, stabilization/solidification, oxidation, and biodegradation.

#### 5.1. Incineration

Incineration is a process of complete combustion of oily wastes in the presence of excess air and auxiliary fuels, and it is widely adopted in large refineries for sludge treatment. Rotary kiln and fluidized bed incinerator are the most commonly used incinerators. In rotary kiln incinerator, the combustion temperature is in the range of 980–1200 °C and the residence time is around 30 min. In fluidized bed incinerator, the combustion temperature can be in the range of 730–760 °C, and the residence time can be in order of days [163]. Fluidized bed incinerator is especially effective when treating low-quality sludge due to its fuel flexibility, high mixing efficiency, high combustion efficiency and relatively low pollutant emissions [164]. The incineration performance can be affected by a variety of factors, including combustion condition, residence time, temperature, feedstock quality, presence of auxiliary fuels, and waste feed rates. Liu et al. [165] investigated the incineration of oily sludge by the addition of an auxiliary fuel consisting of coal–water slurry (CSW) in a fluidized bed boiler, and they found that the temperature of combustion could be stabilized by controlling the CSW feeding rate, with a combustion efficiency of 92.6% being reached. They also found that the gaseous emission from incineration and heavy metals in ash residues could meet the corresponding environmental regulations. Wang et al. [166] examined the incineration

of a petroleum coke–sludge slurry (PCSS) which was obtained by blending oily sludge with a petroleum coke–water slurry (PCWS), and they found that the PCSS fuel exhibited low viscosity and satisfactory stability for combustion process, but the combustion efficiency, gaseous emission, and heavy metals in ash residues were not investigated in their study. Sankaran et al. [167] investigated the direct combustion of three types of oily sludge in a fluidized bed incinerator without auxiliary fuels, and a high combustion efficiency of 98–99% was observed for sludge with low water content, but the combustion was difficult to occur for sludge with a relatively high water content (i.e. >51%). They also found that oily sludge was too viscous to flow as the feedstock, and a pre-treatment such as heating was required to reduce the viscosity before incineration [167].

Through combustion in an incinerator, oily sludge can provide a valuable source of energy, which can be used to drive steam turbines and as a heat source in a waste oil reclamation factory. Moreover, a significant reduction in the volume of waste can be achieved after incineration treatment. Although the oily sludge incineration has been practised in a few developed countries [168], it suffers from a number of limitations [22]. Oily sludge with high moisture needs to be pre-treated to improve its fuel efficiency by lowering the excessive water content [10]. Auxiliary fuel is usually required to maintain a constant combustion temperature [8]. In addition, fugitive emission of pollutants (e.g., low molecular PAHs) from incineration and incomplete combustion could cause atmospheric pollution problem [8]. Moreover, ash residue, scrubber water, and scrubber sludge generated during the incineration process are hazardous and need further treatment. In general, the oily sludge contains high concentration of hazardous constituents that are resistant to combustion, and the incineration requires high capital and operating costs, with a cost of more than \$800 per ton of oily sludge incineration was reported [169].

## 5.2. Stabilization/solidification

Stabilization/solidification (S/S) is a quick and inexpensive waste treatment technique aimed at immobilizing contaminants by converting them into a less soluble or a less toxic form (i.e. stabilization), and encapsulating them by the creation of a durable matrix with high structural integrity (i.e. solidification) [170]. The use of this disposal method for inorganic wastes has been widely reported [171]. However, S/S was considered less compatible with organic wastes since organic compounds may inhibit cement-based binder hydration and are generally not chemically bound in the binder hydration products [170]. As a result, immobilization of organic contaminants depends mainly on physical entrapment in the binder matrix and sorption onto the surface of binder hydration products. There is a possibility of releasing undesirably high concentration of pollutants when exposed to environmental leachants. Karamalidis and Voudrias [172] studied the leaching behavior of TPH, alkanes and PAHs from refinery oily sludge stabilized/solidified with Portland cement, and their results showed that the waste was confined in the cement matrix by macro-encapsulation, but they also reported that increased cement addition to oil refinery sludge led to higher concentrations in leachates from batch extraction. Other leaching test studies of oily sludge S/S treatment using Portland cement have shown relatively high release of PAHs [173] and methanol and 2-chloroaniline [174]. In general, a Portland cement only binder system is not effective for the immobilization of several common organic contaminants. A possible method for improving the effectiveness of S/S treatment for organic wastes is to use binders that increase sorption of organic compounds (e.g., combined use of cement and activated carbon), thereby improving their immobilization and preventing their

detrimental effects on binder hydration. Caldwell et al. [175] reported that activated carbon used with Portland cement was effective in the S/S treatment of a range of organic contaminants. Leonard and Stegemann [171] found that Portland cement with the addition of high-carbon power plant fly ash (HCFA) significantly reduced the leaching of PHCs.

In addition to the immobilization of organic contaminants, an advantage of applying S/S method is that some hazardous heavy metals in oily sludge can be immobilized into the cement matrix. Karamalidis and Voudrias [176] evaluated the leaching behavior of heavy metals from stabilized/solidified refinery oily sludge and ash produced from oily sludge incineration with Portland cement (OPC), and an immobilization of >98% was observed for metals of solidified ash at pH > 6 and of >93% of solidified oily sludge at pH > 7. They found that pH had the strongest influence on the immobilization of heavy metals during the S/S process, and an extremely high Ni immobilization (>98%) was observed for solidified oily sludge samples at pH > 8, but the immobilization was very low (47%) at pH of 2.5. Al-Futaisi et al. [10] solidified tank bottom sludge mixtures using three combinations of selected additives such as Portland cement (OPC), cement by-pass dust (CBPD) and quarry fines (QF), and the toxicity characteristic leaching procedure (TCLP) analyses results revealed that no extracts exceeded the regulated TCLP maximum limits of metals. Although S/S technique has shown effectiveness on immobilizing inorganic and organic contaminants in oily sludge, little is known from the current literatures regarding the physical strength of S/S treated oily sludge and its cost for handling a large volume of oily sludge. Further researches, including the use of other binders such as pozzolanic substances (e.g., fly ash) and other cement-like materials in the S/S of oily sludge, are also worth to be conducted.

## 5.3. Oxidation treatment

Oxidation treatment has been used to degrade a range of organic contaminants through chemical or other enhanced oxidation processes [177]. Chemical oxidation involves introducing reactive chemicals into oily wastes to oxidize organic compounds to carbon dioxide and water, or transform them to other non-hazardous substances such as inorganic salts [177]. The oxidation can be brought by Fenton's reagent, hypochlorite, ozone, ultrasonic irradiation, permanganate, and persulfate, by generating a sufficient amount of radicals such as hydroxyl radicals ( $\text{OH}^\bullet$ ) which can quickly react with most organic and many inorganic compounds [178]. Many studies have proven that chemical oxidation can effectively degrade PHCs and PAHs in soils, and this method has recently been applied to oily sludge treatment. Mater et al. [4] found that a Fenton type reagent (i.e. 12 wt.% of  $\text{H}_2\text{O}_2$  and 10 mM of  $\text{Fe}^{2+}$ ) at a low pH (i.e. pH 3.0) can significantly reduce the concentrations of PAHs, phenols and BTEXs in oily sludge contaminated soil. Ultrasonic irradiation has also recently been investigated for its efficiency on oily sludge oxidation process. The sonication of water can produce intermediate radicals such as hydrogen ( $\text{H}^\bullet$ ), hydroxyl ( $\text{OH}^\bullet$ ), hydroperoxyxl ( $\text{HO}_2^\bullet$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) with high oxidation power in and around the cavitation bubbles [179]. Through sonolysis reaction by these free radicals, long-chain or aromatic petroleum hydrocarbons with complex structure and large molecular weight can be broken into simple hydrocarbons which have higher solubility and bioavailability. Ultrasound can be used to degrade many PHCs, such as chlorinated aliphatic hydrocarbons (CAHs), aromatic compounds, polychlorinated biphenyls (PCBs), poly aromatic hydrocarbons (PAHs), and various phenols [180–184]. Zhang et al. [185] utilized a combined process of ultrasonic and Fenton oxidation for the oily sludge treatment, and it was found that ultrasonic

irradiation could enhance the Fenton oxidation effect on oily sludge degradation by improving the contact of hydroxyl radicals ( $\text{OH}^\bullet$ ) with PHCs compounds.

Other advanced oxidation methods such as supercritical water oxidation (SCWO), wet air oxidation (WAO), and photocatalytic oxidation (PO) have been reported in recent literatures of oily sludge treatment. SCWO method uses water above its critical point (375 °C, 22.1 MPa) as a reaction medium where gases, oil and aromatics form a single homogeneous phase, and the oxidation could proceed quickly and completely by converting most H-C-N compounds to water, carbon dioxide, and molecular nitrogen [186]. Cui et al. [187] applied the SCWO method for oily sludge treatment, and their results indicated that 92% of chemical oxygen demand (COD) in oily sludge was removed after only 10 min of treatment. The WAO technology uses oxygen as the oxidant under high temperature and high pressure to convert hazardous organic compounds to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and other innocuous end products. Jing et al. [188] found that the WAO process could remove 88.4% of COD in oily sludge within 9 min of reaction at temperature of 330 °C and an  $\text{O}_2$  excess of 0.8, and the COD removal can be increased to 99.7% with the addition of  $\text{Ni}^{2+}$  catalyst.  $\text{Fe}^{3+}$  catalyst can also improve the COD removal during oily sludge treatment using WAO process. It was reported that a very promising COD removal rate of 95.4% was achieved under the catalytic effect of Fe salt (i.e. 50 mg/L of  $\text{Fe}^{3+}$ ) compared to that of 84.12% in the treatment without the addition of  $\text{Fe}^{3+}$  catalyst [189].

Another enhanced oxidation treatment is the heterogeneous photocatalytic oxidation which is based on the activation of the surface of a photo-conductor (e.g., titanium dioxide in the Anatase form) by light (e.g., UV light or sunlight). The absorption of photons with energy higher than the band gap of the photo-conductor produces pairs of conduction band electrons ( $e^-$ ) and valence band vacancies ( $h^+$ ). After this first step, the charge carriers either recombine within the bulk of the material or migrate to the particle surface, where they can react with adsorbed electron donors (D) and acceptors (A) species [190]. The presence of oxygen and water is essential to the photocatalytic process. Oxygen serves as the  $e^-$ -acceptor which can form the superoxide radical anion  $\text{O}_2^{\bullet-}$ . The surface-bound water and the surface hydroxyl groups are oxidized by the vacancies to form  $\text{OH}^\bullet$  radicals which are supposed to be the most active oxidizing species. da Rocha et al. [5] applied the heterogeneous photocatalytic oxidation ( $\text{H}_2\text{O}_2/\text{UV}/\text{TiO}_2$ ) for oily sludge treatment, and they found that white light catalyzed oxidation was able to eliminate 100% of PAHs in sludge after 96 h of treatment. They also revealed that white light was more effective than black light in terms of catalyzing oxidation on PAHs. However, the effect of photocatalytic oxidation on other constituents such as asphaltenes and resins in oily sludge was not investigated in their study. In general, oxidation requires a relatively short treatment duration to degrade oily sludge, and it is relatively insensitive to external disturbances (e.g., pollutant loading, temperature change, and the presence of biotoxic substances, etc.). Its reaction products are usually more biodegradable than the raw waste materials [188]. However, when treating a large volume of oily sludge, the oxidation may require a large amount of chemical reagents. The advanced oxidation methods such as WAO, SCWO and PO also require special equipments and considerable energy inputs which could increase the treatment cost.

#### 5.4. Bioremediation

Bioremediation is defined as the process of using microorganisms to remove environmental pollutants, and is commonly employed for the restoration of oil-polluted environments through accelerating the microbial degradation of PHCs [191]. The most

intensively studied bioremediation approaches include land treatment, biopile/composting, and bio-slurry treatment [192].

##### 5.4.1. Land treatment

Land treatment involves the incorporation of wastes into soil and then the use of various processes to degrade contaminants in that soil [193]. Biological activity usually accounts for most of the degradation of organic pollutants, while physical and chemical removal mechanisms such as evaporation and photo-degradation may also be important for some compounds. Landfarming is a widely employed land treatment approach, and it spreads the well-mixed oily sludge and fresh soil on the ground surface of a treatment site. The treatment efficiency can be improved by maintaining appropriate sludge application rate, aeration, fertilization, moisture content, and pH to maintain microbial density and enhance their activity in the sludge/soil mixture. Marín et al. [194] applied landfarming method to clean up oil refinery sludge in a semi-arid climate, and their results showed that 80% of the PHCs were removed within 11 months of treatment, while half of this removal occurred during the first three months. Admon et al. [42] also observed similar degradation pattern through experiments on the landfarming of refinery oily sludge, and 70–90% of PHCs degradation occurred within 2 months, while a relatively high biodegradation activity was observed in the first 3 weeks of treatment. Hejazi and Husain [195] compared the influence of three operating parameters (i.e. tilling, addition of water, and addition of nutrients) on a 12-month oily sludge land treatment under arid conditions, and they found that tilling was the main parameter responsible for achieving the highest PHCs removal rate of 76%. Mishra et al. [196] combined bioaugmentation (i.e. introducing extraneous bacterial consortium) and biostimulation (i.e. addition of nutrients and water) for oily sludge decontamination, and their results indicated that up to 90.2% of TPH can be degraded in 120 days in the land block which had extraneous bacterial consortium inoculum and nutrients enhancement, while only 16.8% of TPH was eliminated in the control land block.

As compared to other oily sludge disposal technologies, landfarming holds many merits such as relatively low capital costs, simple operation, high potential for success, low energy consumption, and the capability of treating a large volume of oily sludge [197]. However, landfarming of oily sludge requires a large area of land, and is a very time-consuming process (e.g., usually 6 months to 2 years or even longer) since the soil/sludge conditions favoured by biodegradation are largely uncontrolled, particularly for recalcitrant and heavy PHC compounds. In addition, temperature can greatly affect the contaminant biodegradation efficiency, and the performance of oily sludge landfarming in cold regions can be compromised. Moreover, landfarming can bring various environmental issues, such as the emission of volatile organic compounds (VOCs) and the risk of groundwater pollution due to the migration of leachate that may contain PHCs, phenols and heavy metals [22]. For example, Hejazi et al. [198] reported that weathering (i.e. evaporation) and not biodegradation was the overall dominant degradation mechanism occurring in a landfarm under hot and arid climate conditions. Results from a 12-month field study showed that up to 76% of oil and grease in oily sludge has been evaporated as a result of weathering, while relatively long chain alkanes such as  $\text{C}_{17}$  and  $\text{C}_{18}$  were biodegraded in the landfarm [198]. Another advanced land treatment approach is secure landfill after oily sludge dewatering. This technology isolates sludge wastes from air and water through the use of thick layers of impermeable clay and synthetic liner, and it also employs a leachate collection system above the bottom liner [199,200]. Secure landfill is popular in developed countries such as the USA, UK, Canada, and Germany, and it can greatly address the environmental problems associated with landfarming, but its treatment cost is much higher [22].

#### 5.4.2. Biopile/composting

Biopile/composting of petroleum wastes has received increased attention as a substitute technology for landfarming which often requires a large land area. Biopile refers to the turning of waste materials into piles or windrows usually to a height of 2–4 m for degradation by indigenous or extraneous micro-organisms. The piles may be static with installed aeration piping, or turned and mixed by special devices. The bio-treatment efficiency can be improved with moisture adjustment, air blowing, and the addition of bulking agent and nutrients. Bulking agents usually include straw, saw dust, bark and wood chips, or some other organic materials. Addition of bulking agents results in increased porosity in soil-sludge piles, which leads to better air and moisture distribution in the matrix. This technology is termed as composting if organic material is added [41]. The biodegradation rate can be enhanced by manipulating a number of operating parameters such as controlling carbon:nitrogen:phosphorous (C:N:P) ratio, air blowing or tilling to improve aeration, and moisture and temperature maintenance to keep high microbial activity [201]. A number of studies have been reported to use biopile/composting for refinery oily sludge treatment. Wang et al. [18] found that during the composting process of aged oily sludge, microbial metabolic activity and diversity were significantly enhanced by the addition of bulking agent cotton stalk, with a TPH removal rate of 49.62% being observed in the middle layer of biopile after 220 days, but the application of large amounts of nutrient (i.e. urea) had a suppressing effect on the microbes. Liu et al. [29] found that the addition of manure (as nutrients) to oily sludge significantly increased the microbial activity and diversity, and the TPH in the treated sludge was decreased by 58.2% after about 1 year of bioremediation, but this number was only 15.6% in the control plot.

Ouyang et al. [202] investigated the effect of bioaugmentation on the composting of oily sludge, and they found that the TPH content decreased by 46–53% in the piles after 56 days of treatment, but only decreased by 31% in the control piles. Kriipsalu et al. [203] reported the aerobic biodegradation of oil refinery sludge in composting piles with four different amendments, and their results showed that after 373 days of treatment, the reduction of TPH was 62%, 51%, 74% and 49% in the piles with amendments of sand, matured oil compost, kitchen waste compost, and shredded waste wood, respectively. As compared to landfarming, biopile/composting is able to more efficiently remove PHCs in oily sludge and could treat more toxic compounds since it creates controlled conditions more favoured by biodegradation. Another noticeable characteristics of biopile/composting is that temperature in the piles could increase up to 70 °C or more due to the heat generated by intense microbial activity, and the application of this method for PHCs degradation under extreme climatic conditions such as sub Antarctica area has been proven successful [201,204]. In addition, it is more environmentally friendly since the composting can be conducted in treatment vessels and the VOCs emissions can be controlled by auxiliary collection units. It is also easy to design and implement, and can be engineered to fit different site conditions. However, the treatment capacity of biopile/composting is much smaller than that of land treatment and it still requires a relatively large area of land and long treatment duration for oily sludge degradation [197].

#### 5.4.3. Bio-slurry treatment

Slurry-phase bio-treatment was reported to have faster pollutant removal than solid-phase treatment (e.g., landfarming and composting), and has been successfully applied to the cleanup of oil contaminated soils [205]. This technology mixes sludge-associated solids with water (i.e. 5–50% w/v) and dissolves contaminants into aqueous phase to obtain a larger amount of solubilized pollutants. The microbial degradation can then transform the pollutants to

less toxic intermediates (e.g., organic acids and aldehydes) or end products of carbon dioxide and water. Slurry-phase biodegradation usually occurs in designed slurry bioreactors where the contact between microorganisms, PHCs, nutrients, and oxygen can be maximized [206]. A variety of bioreactor designs are available, such as the rotating drum equipped with lifters to provide internal mixing, and the vertical tank equipped with an impeller for mixing [207]. Bio-slurry treatment has been successfully applied to oily sludge decontamination [208]. Ayotamuno et al. [14] applied a bio-slurry remediation approach to treat oily sludge through the addition of extraneous microbes as well as regular mixing and watering, and they found that the TPH reduction in sludge was 40.7–53.2% and 63.7–84.5% within two weeks and six weeks of treatment, respectively. Machín-Ramírez et al. [209] reported that the addition of commercial fertilizer to the sludge slurry could greatly enhance the degradation of weathered oily sludge, with a TPH removal of 24% occurring within 25 days of treatment. Ward et al. [31] investigated the biodegradation of oily sludge in slurry phase with sludge concentration in the range of 1.55–12.8%, and they found that the TPH degradation was in the range of 80–99% within 10–12 days by using three different bio-surfactant-producing microbial consortiums.

Large-scale application of bio-slurry remediation on oily sludge also showed promising results. For example, Maga et al. [210] reported that a 10,000-gallon sequencing batch reactor (SBR) was used for the on-site biodegradation of oily sludge, and the micro-organisms degraded the PHCs in sludge from 20,000 ppm to less than 100 ppm within two weeks of treatment [210]. According to Ward and Singh [211], a large-scale bio-slurry reactor system with a  $4.55 \times 10^6$  L capacity was designed to treat oily sludge at the Gulf Coast refinery, while air sparging and mechanical agitation system were incorporated to improve the homogenization of oily sludge slurry, with 50% of oil and grease removal being achieved after 80–90 days of treatment. Bio-slurry degradation is a rapid and effective approach for oily sludge disposal which can greatly decontaminate oily sludge within a short treatment period. Unlike other biodegradation treatments, bio-slurry processing only requires a small area of land. A major concern with the application of this technology to field-scale oily sludge treatment is the relatively high treatment cost. The oily sludge slurry is non-homogeneous and clayey mixtures which can cause operation problems, and thus needs pretreatment. During the bio-slurry treatment process, volatile gaseous compounds can be generated and thus may require treatment. After bio-slurry treatment, the mixtures also need dewatering. All of these pre-treatments and/or post-treatments could significantly increase the overall cost. It was estimated that the operating cost of the bio-slurry treatment of refinery oily wastes was above \$625 per ton, while the operating cost of landfarming was around \$155 per ton [205].

#### 5.4.4. Factors affecting oily sludge biodegradation

The oily sludge biodegradation can be affected by a variety of factors, such as the type of microorganisms, treatment duration, temperature, nutrients, concentration and characteristics of oily sludge. Many microorganisms, mainly bacteria and fungi, are capable of degrading PHCs, but there is no single microbial strain which has the metabolic capacity to degrade all of the components found in oily sludge [212]. The degradation of PHCs in sludge may involve progressive or sequential reactions where a group of micro-organisms may initially degrade the petroleum constituents into intermediate compounds, and these intermediates are then utilized by a different group of microorganisms for further degradation [213]. As a result, the biodegradation of oily sludge typically needs a microbial consortium with a succession of species. It was reported that the employment of a mixed bacterial culture was more advantageous in comparison with pure cultures due to synergistic interactions among microbial species [214]. In addition,

the biodegradation can be affected by treatment duration. Generally, the degradation rate of PHCs decreases with time, reaching an apparent plateau associated with pollutant residues which are recalcitrant compounds and have very slow degradation. The PHCs characteristics can also affect the biodegradation efficiency. It was reported that the degradation was higher for saturates/alkanes, followed by light aromatics, high aromatics and polar compounds, and asphaltenes [215,216]. In addition, the initial PHCs concentration can affect the bioremediation performance. For example, Lazar et al. [217] observed that the best biodegradation occurred for the bio-treatment that received 10% of oily sludge (equivalent to 3.2% initial TPH). However, another study reported that the addition of oily sludge to soil (with equivalent TPH concentration of 9,000–61,000 mg/kg) resulted in a TPH reduction of 70–90% during two months of treatment regardless of the initial PHCs concentrations [42].

Nutrient is an important factor affecting the degradation of PHCs, and thus nutrient supplementation is the foremost strategy employed for biodegradation stimulation [35]. Admon et al. [42] and Yerushalmi et al. [215] found that the removal of PHCs was observed only after nutrients were amended to oily sludge contaminated soil at a C:N:P ratio of 50:10:1. Roldán-Carrillo et al. [6] investigated the biodegradation of oily sludge under different nutrient conditions, and they found that after 30 days of treatment, the highest TPH removal was 51% in the sludge which had a C:N:P ratio of 100:1.74:0.5. However, Tahhan et al. [21] observed that adding nutrients caused the inhibition of oily sludge biodegradation probably because of the high nutrient concentration already present in the original sludge, and such inhibitory effect increased with the addition of nitrogen and phosphorous. In addition to the nutrient effect, the degradation of PHCs are usually restricted by their high hydrophobicity or low solubility [218]. One effective way to improve this is the use of surfactants to enhance the desorption and solubilization of PHCs, thereby enhancing their bioavailability and facilitating their assimilation by microorganisms [219–221]. For example, Shuchi et al. [222] used *Bacillus* sp. SV9 to produce bio-surfactant, and approximately 59% of TPH was degraded within 5 days. Vanessa et al. [223] isolated five bacteria from petrochemical oily sludge with two of them being capable of producing bio-surfactants, and the mixed bacterial consortium degraded 90.7% of the aliphatic fraction and 51.8% of the aromatic fraction in oily sludge within 40 days of treatment. Rahman et al. [224] investigated the combined effect of rhamnolipid bio-surfactant and nutrients (phosphorus and potassium solution) on the biodegradation of refinery oily sludge, and they found that a maximum degradation was achieved after 56 days of treatment, with the degradation rate of n-alkanes being 100%, 83–98%, 80–85% and 57–73% for nC<sub>8</sub>–nC<sub>11</sub>, nC<sub>12</sub>–nC<sub>21</sub>, nC<sub>22</sub>–nC<sub>31</sub> and nC<sub>32</sub>–nC<sub>40</sub>, respectively. Cameotra and Singh [225] also investigated the effect of two additives (a nutrient mixture and a crude bio-surfactant) on oily sludge biodegradation process, and they found that the individual use of any one additive along with a microbial consortium brought about a TPH removal of 91–95% within 4 weeks of treatment, with the crude bio-surfactant being more effective, but more than 98% of TPH removal was obtained when both additives were used with the consortium. As a result, bio-surfactants and inorganic nutrients can significantly enhance the biodegradation process, and will have great potential to be used in the application of oily sludge bioremediation [226].

## 6. Concerns of heavy metals in oily sludge

Most of the current oily sludge treatment methods have been developed for the purpose of recovery and/or removal of PHCs, and they have no or limited effects on the removal of heavy metals in

oily sludge. It was reported that metals usually exist in the form of relatively thermally stable and oil-soluble organometallic complexes (e.g., metal porphyrins and derivatives) in oily sludge [227]. On one hand, existence of heavy metals is one of the problems preventing oily sludge from being recycled as fuel since heavy metal would cause poisoning and fouling of catalysts used for the thermal cracking of heavy PHCs fractions [228]. Some metals such as vanadium and nickel along with sodium in the recovered oil can also cause serious corrosion problems in the refining installations [229]. On the other hand, the incineration of oily sludge can destroy PHCs and turn them into energy which can be further reutilized, but the incineration products such as oily sludge ash and fly ash can be enriched with heavy metals which could result in further environmental problems [230]. During the land treatment process of oily sludge, heavy metals could affect soil microorganisms by changing their morphology, growth, and metabolism [231]. Since heavy metal species and concentrations in different oily sludge vary, the effect of sludge land treatment on soil microbial activities may also show great difference, but heavy metals at high concentration are more toxic [232].

Moreover, the co-existence of PHCs and heavy metals in oily sludge contaminated soils could lead to a much more complex pollution problem. In particular, the combined effects of PAHs (i.e. common constituents in oily sludge) and heavy metals have been reported to be more toxic than PAHs alone [233]. Barbara and Bożena [234] found that soils contaminated with both PAHs and heavy metals had a stronger inhibitory effect on microorganisms and plant growth than soils amended with only heavy metals or only PAHs, while the inhibitory effect was more significant during the early stage of microorganisms and plant growth. Shen et al. [235] found that the interaction effect between heavy metals (Zn and Cd) and PAHs were strongly dependent on the time of pollution. Palanisami et al. [236] observed that the co-existence of PAHs and heavy metals significantly inhibited soil enzyme activities, and the co-contamination not only reduced the microbial diversity but also exerted selective pressure on microorganisms, with a few distinctive species being observed with a higher microbial activity. The combined effects of heavy metals and other PHCs in oily sludge on soil microbial activity have rarely been reported. However, the studies of such impacts can have important implications to oily sludge treatment since a considerably large amount of oily sludge were disposed in landfills or landfarms [237].

Overall, few attention has been paid to handle various heavy metals in oily sludge and/or its disposal treatment by-products although many methods are available. For oily sludge incineration byproducts such as sludge ash and fly ash, the stabilization/solidification technology could be used to prevent heavy metals from leaching [238]. For oily sludge ash that contains relatively high levels of valuable heavy metals such as vanadium (V) and nickel (Ni), metal recovery technologies (e.g., solvent extraction) could be attractive [230,239]. For example, Nabavinia et al. [230] applied sulfuric acid to extract vanadium in the oily sludge burnt ash, and an emulsion liquid membrane (ELM) treatment was applied for the purification and enrichment of vanadium from leaching solution. Their results showed that more than 65% of vanadium in sludge ash can be recovered by sulfuric acid extraction, and more than 86% of vanadium was collected within 1 hour by using ELM process [230]. Abbas et al. [229] found that centrifugation could effectively remove water-soluble metal salts in petroleum residual oil, while using ethyl acetate could extract oil-soluble metals from heavy residual fractions. The metal removal rate achieved 82% for vanadium and 88% for nickel by using the combined extraction of ethyl acetate and sulfuric acid, but the addition of acid could cause further environmental issues such as acid sludge problems [229]. Elektorowicz and Muslat [228] combined solvent extraction with ion exchange textile process to remove

**Table 1**  
Summary and comparison of oil recovery methods.

Method	Status <sup>a</sup>	Efficiency <sup>b</sup>	Cost <sup>c</sup>	Duration <sup>d</sup>	By-products	Advantages	Limitations	References
Solvent extraction	F	C–B	B–A	A	VOCs, unrecoverable sludge slurry	Easy to apply, fast and efficient	Large amount of organic solvents is used, high cost and not environmentally sound, unable to treat heavy metals	[7,58–60]
Centrifugation	F	D–C	B–A	A	Wastewater, unrecoverable sludge slurry	Easy to apply, fast and efficient, high throughput, no need of chemical addition	High capital and maintenance cost, large energy consumption, noise problem, viscosity reducing pre-treatment requirement, unable to treat heavy metals	[19,67]
Surfactant EOR	F	B	B–A	A	Wastewater and unrecoverable sludge slurry	Easy to apply, fast and efficient, limited effect on treatment of heavy metals	High cost, chemical surfactants could be toxic, surfactants need to be removed from recovered oil	[9,93–95]
Freeze/thaw	L	C	–	A	Wastewater and unrecoverable slurry	Easy to apply, short treatment duration, suitable for cold regions	Lower efficiency, cost could be high due to high energy consumption for freezing, unable to treat heavy metals	[37,96,97,101]
Pyrolysis	F	C–B	B–A	A	VOCs and chars	Fast and efficient, recovered oil can be upgraded, large treatment capacity	High capital, maintenance, and operating cost, high consumption of energy, and not suitable for oily sludge with high moisture content	[3,110,111,113–117]
Microwave irradiation	F	A	–	A	VOCs, wastewater and unrecoverable solids	Very fast and efficient, no need of chemical addition	Special designed equipment, high capital and operating cost, high consumption of energy, small treatment capacity, unable to treat heavy metals	[126–129,132–136,241]
Electrokinetic	L	C	–	A	Wastewater and sludge slurry	Fast and efficient, no need of chemical addition, limited effect on treatment of heavy metals	Low treatment capacity and not easy to apply	[138,139,141,169]
Ultrasonic irradiation	L	C–B	–	A	Wastewater and unrecoverable solids	Fast and efficient, no need of chemical addition	High equipment cost, small treatment capacity, unable to treat heavy metals	[1,101,147,149,155,185,242]
Froth flotation	L	C	–	A	Large amount of wastewater	Easy to apply, no intensive energy requirement	Relatively low efficiency, large amount of water is used, not suitable for treating oily sludge with high viscosity, unable to treat heavy metals	[16,32,158–160,162]

<sup>a</sup> F, field scale; L, laboratory scale.

<sup>b</sup> Efficiency (oil recovery rate) A: >90%; B: 75–90%; C: 50–75%; D: <50%.

<sup>c</sup> Cost (US\$/m<sup>3</sup>) A: >200; B: 100–200; C: 50–100; D: <50; –: unknown.

<sup>d</sup> Treatment duration A: <1–2 days; B: 1–6 months; C: 6–12 months; D: 1–2 years.

**Table 2**  
Summary and comparison of oily sludge disposal methods.

Method	Status <sup>a</sup>	Efficiency <sup>b</sup>	Cost <sup>c</sup>	Duration <sup>d</sup>	By-products	Advantages	Limitations	References
Incineration	F	A	A	A	Hazardous gas emissions and fly ash	Rapid and complete removal of PHCs in oily sludge, heat value can be reused	High cost of equipment and auxiliary fuels, gas emissions and fly ash need further treatment, pre-treatment of moisture removal is required, unable to treat heavy metals	[8,165,167,168]
Stabilization/solidification	L	A	B	B	Stabilized/solidified products	Fast and efficient of encapsulating PHCs in stabilized/solidified products, low cost, able to encapsulate heavy metals in oily sludge	Moisture content in oily sludge need to be reduced first, PHCs cannot be completely removed, loss of recyclable energy, stabilized/solidified products require proper management	[171,172,176,238]
Oxidation	L	A	A	A	CO <sub>2</sub> , oxidation intermediates	Rapid and complete removal of PHCs in oily sludge, relatively insensitive to external disturbances	Large amount of chemical reagents is utilized, high cost and not environmentally sound, loss of recyclable energy, high cost if advanced oxidation process taken place, limited effect on heavy metals	[5,177,178,187]
Landfarming	F	B	D–C	D–C	VOCs, contaminated soils, hazardous leachate	Low cost and do not need much maintenance, large treatment capacity	Very slow process, pollutants may build up on repeated applications, VOCs emission problems, risk of underground water pollution, occupy a very large area of land	[193–195,197,198,201]
Landfill	F	B	C	D–C	Contaminated soils, relatively small amount of VOCs	Large treatment capacity, relatively low cost, VOCs emission is collected and groundwater pollution could be prevented	Higher cost than landfarming, very slow process, occupy a very large area of land	[22,197,199–201]
Biopile/composting	F	B	D–C	C–B	VOCs emissions if no VOCs collecting units exist	Relatively large treatment capacity, faster process than land treatment, less land area requirement than landfarming, suitable for cold regions and various terrain	Higher cost and smaller treatment capacity than land treatment, still requiring a large area of land	[18,41,197,201,202,243–245]
Bioslurry	F	A	C–B	C–B	Sludge slurry	Fastest biodegradation approach, great PHCs removal performance, small land area requirement	High cost, small treatment capacity, need skilled operation, maintenance and monitoring, slurry residues need proper management	[31,197,201,206,209]

<sup>a</sup> F, field scale; L, laboratory scale.

<sup>b</sup> Efficiency (PHCs removal rate) A: >90%; B: 75–90%; C: 50–75%; D: <50%.

<sup>c</sup> Cost (US\$/m<sup>3</sup>) A:>200; B: 100–200; C: 50–100; D: <50; -: unknown.

<sup>d</sup> Treatment duration A: <1–2 days; B: 1–6 months; C: 6–12 months; D: 1–2 years.

heavy metals in oily sludge, and their results indicated that the cadmium, zinc, nickel, iron and copper were removed by 99%, 96%, 94%, 92% and 89%, respectively, when the oily sludge was first extracted by acetone and then processed by an ion exchange textile. Further information of potential heavy metal removal technologies for oily sludge treatment can be found in Ali and Abbas [227].

## 7. Discussion and conclusions

Oily sludge generation is an inevitable problem during the operation of petroleum industry. Due to its toxicity and adverse environmental effect, oily sludge needs effective treatment. A variety of oil recovery and sludge disposal technologies have been developed, and some of them have been applied to field-scale treatment. Tables 1 and 2 summarizes the treatment methods introduced in this paper based on their development status, performance, treatment duration, costs, advantages and limitations. In general, a particular technology cannot satisfy all of the reuse and disposal requirements for different oily sludge wastes. Some treatments may be very promising in terms of fuel recovery and/or the decontamination of unrecyclable residues, but their capital and/or operating costs could be very high, or their implementation to large-scale treatment might be infeasible. Other treatments such as landfarming and composting may have great applicability and low operating costs for large-scale treatment, but their microbial degradation process can be very time-consuming. The selection of oily sludge treatment technologies should depend on sludge characteristics, treatment capacity, costs, disposal regulatory requirements, and time constraints. Some methods such as centrifugation, surfactant enhanced oil recovery, freeze/thaw, froth flotation, and bio-slurry treatment may be more suitable for treating oily sludge with high moisture content. However, other methods such as incineration, pyrolysis and stabilization/solidification require sludge pretreatment to reduce its moisture content. Since the technology selection involves a variety of criteria, it is difficult to evaluate the overall performance of the available technologies. Some multi-criteria decision analysis approaches may help develop an overall technology evaluation system and help practitioners to select the most suitable treatment methods.

As shown in Tables 1 and 2, each oily sludge treatment method is associated with some advantages and limitations. A more effective treatment performance might be achieved by integrating different methods into a process train. For example, the ultrasonic irradiation method can be combined with freeze/thaw treatment of oily sludge to obtain a promising oil recovery performance [101]. The Fenton's oxidation can be combined with solidification/stabilization method to offer a safer way of oily sludge disposal [4]. The addition of bio-surfactants during froth flotation and/or bioremediation of oily sludge can also enhance the overall efficiency [16,224]. Other combination of oily sludge treatment technologies such as emulsion liquid membrane process and microwave irradiation, microwave and freeze/thaw, and oxidation and pyrolysis can be found in recent literatures [24,103,128,240]. Moreover, most studies were either focusing on oil recovery from oily sludge or aiming at the maximum removal of PHCs from oily sludge. The oil recovery may significantly reduce the volume of sludge wastes for further disposal, but the unrecyclable residues may contain more recalcitrant and toxic components which could increase the difficulty of disposal. It is expected that the oil recovery technologies and sludge disposal treatments introduced in this paper have the potential to be used in conjunction to reduce the overall adverse environmental impacts, but their combinations have still rarely been reported. Thus, the economic and environmental performance of combined oil recovery and sludge disposal is worthy of further investigation. In addition, most reported studies of oily sludge treatment were

focusing on the removal of PHCs from oily sludge, and only a few of them investigated the variation of heavy metals in oily sludge during the treatment processes. Heavy metals in oily sludge may accumulate to a hazardous concentration level during sludge treatments such as incineration and biodegradation, leading to perilous effects on environment and human health. As a result, the change of heavy metal concentrations during different oily sludge treatment processes is worthy of investigation in future research, and the integration of available heavy metal control technologies into oily sludge treatment is recommended.

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