Journal of Environmental Management 285 (2021) 112124

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: http://www.elsevier.com/locate/jenvman

Comprehensive characterization of an oily sludge from a petrol refinery: A step forward for its valorization within the circular economy strategy

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ARTICLE INFO

Keywords:
Oily sludge
Valorization
Physicochemical characteristics
Fractional characterization

ABSTRACT

Refinery treatment plants produce large quantities of oily sludge during the petroleum refining processes. The hazardousness associated with the disposal of these wastes, make necessary the development of innovative technologies to handle it adequately, linked to the concepts of circular economy and environmental sustainability. This work provides for the first time a methodology for the deep characterization of this kind of wastes and consequently new insights regarding its valorization. A review of works dealing with the characterization of this type of wastes has been addressed evidencing the complexity and variability of these effluents. The oily sludge under study contains a high concentration of Chemical Oxygen Demand of 196 g COD/L, a Total Kjeldahl Nitrogen of 2.8 g TKN/kg, a phosphorous content as PO_4^{3-} of 7 g/kg, as well as a great presence of heavy metals in a different range of concentrations. This sludge is composed of three different phases: oily, aqueous and solid. The oily and the solid phases present high percentages of carbon content (84 and 26%, respectively), related to the presence of alkanes ranged from n-C_9 to n-C_{44}. Therefore, it could be possible their valorization by the synthesis of catalyst and/or adsorbents. A dark fermentation process could be also proposed for the oily phase to obtain H_2 as an alternative energy source. Finally, the aqueous phase contains low carbon and nutrients concentration. A previous thermal pre-treatment applied to the oily sludge might increase nutrient and organic loading in the aqueous phase due to solid destruction, making this aqueous effluent suitable for a further conventional biological treatment.

1. Introduction

The petroleum industry generates huge amounts of oily sludge waste during different steps of oil treatment such as mining, transportation, storage and refine treatments (Hu et al., 2015; Zhao et al., 2020). Focusing on the refinery, the oily sludge waste generated depends on the processing scheme, oil storage system, and crude properties, but it is assumed that 1 ton of oily sludge is produced for every 500 tons of crude processed in the refinery (Hu et al., 2013).

The oily wastewater generated during the refining of the oil crude is directly related to the plant operations such as oil emulsion, solids washing or heat exchange cleaning. As can be seen in Fig. 1S, a variety of oily sludge residues can be found during the treatment of that oily wastewater: oil/water separators, flocculation–flotation, and excess activated sludge from on-site wastewater treatment plants (Hu et al., 2013). The oily sludge generated during these operations is a recalcitrant residue characterized by being a stable water-oil emulsion of water, solids, petroleum hydrocarbons and metals (Mazlova and Meshcheryakov, 1999). As being recognized as hazardous waste, improper disposal or insufficient treatment of oily sludge can produce serious threats to the environment and human health (Liu et al., 2009; Zhao et al., 2020). Likewise, oil refineries have already a strong commitment to the reduction and valorization of wastes linked with the EU Circular Economy Action Plan.

The chemical composition of the oily sludge varies in a wide range, depending on crude oil source, processing scheme, as well as equipment and reagents used in the refining process. For example, the total petroleum hydrocarbon (TPH) contents in oily sludge frequently range from 15% to 50% w/w, whereas the contents of water and solids are in the range of 30–85% and 5–46%, respectively (Liu et al., 2012; Mohan and Chandrasekhar, 2011; Tahhan et al., 2011). Due to the heterogeneity of the chemical compositions in oily sludge, its physical properties such as density, viscosity, and heating value can vary significantly. Moreover, the properties obtained from one oily sludge source cannot be extended to that from a different source or to those from the same source collected on a different day or different location (Hu et al., 2013). Thus, deep

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https://doi.org/10.1016/j.jenvman.2021.112124
Received 9 September 2020; Received in revised form 29 December 2020; Accepted 2 February 2021
Available online 14 February 2021

characterization of the sludge is compulsory as a preliminary step before proposing a treatment and/or valorization approach.

Strategies described in the literature to treat oily sludge from the petroleum industry are the recovery of the valuable oily phase to back to the refining scheme and disposal methods of the remaining fraction without any valorization. To recover the oily phase, solvent extraction (Qin et al., 2016) and centrifugation (Hu et al., 2013) have been used. Before the final disposal, other methods are usually employed such as incineration or stabilization/solidification (Hu et al., 2013). Nevertheless, novel approaches to introduce more commercially achievable options and/or products to reduce socio-economic and environmental problems associated with its current treatment must be studied. Oily sludge may be processed to produce useful products or as a feedstock for energy generation. Different valorization technologies, such as recovering the oily phase (Taiwo and Otolorin, 2009) or the production of a char or activated carbon (Lin et al., 2019), can be found in the literature. However, all these treatments are only focused on one of the phases of the sludge (solid or oily), which means that only 15–50% of the oily sludge is valorized, the remnant (50–85%) is disposed without taking advantage of the potential resources contained in it.

The complex composition and variability of oily sludge make it necessary to develop a methodology for its comprehensive characterization and to achieve an efficient valorization. A step forward has been carried out in this work with the fractional characterization of the different phases involved in the oily sludge (oily, aqueous, and solid phases) coming from an API separator (Fig. 1S). The characterization of the sludge (and the different phases) is discussed in terms of physical and chemical composition and, consequently, different strategies have been proposed for the potential valorization of the oily sludge under study in this work.

2. Materials and methods

2.1. Source of oily sludge

The oily sludge used in this study was collected from an API separator placed in a petroleum refinery wastewater treatment plant, located in Spain. Samples were collected and immediately stored at 4 °C to keep in unchanged conditions.

2.2. Analytical methods

2.2.1. Extraction and isolation of different phases

Oily sludge is mainly composed of three different phases: oily, solid and aqueous phases. For the separation of each phase, physical techniques were used. Firstly, the aqueous phase was separated by centrifugation with a speed of 30,000 rpm for 15 min, extracted with a syringe, and filtered using a nylon filter of 0.45 μm, to remove suspended solids. The remaining sludge containing oil and solids was treated with diethyl ether (2:1 mass ratio) to extract the oily phase. After stirring during 120 min the solution was filtered to collect the solid and the oily-rich organic phase was subjected to an evaporation step to separate the solvent and recovery the oily phase. Resultant solid was washed twice with 15 mL of diethyl ether to remove some oily phase remained in the solid phase after extraction step.

2.2.2. Oily sludge and fractional characterization of the different phases

pH was measured using a GLP-22 digital pH meter (HACH LANGE SPAIN, S.L.U). Higher Heating Value (HHV) was evaluated using a Plain Jacket Bomb Calorimeter (model PARR 1341). Total Chemical Oxygen Demand (TCOD) was measured following an optimized method for samples with a high content of solids published elsewhere (Raposo et al., 2008). Soluble Chemical Oxygen Demand (SCOD), Total Solids (TS), and Volatile Total Solids (VTS) were measured following APHA-AWWA Standard Methods 5220.D, 2540.B and 2540.E, respectively. Total Kjeldahl Nitrogen (TKN) was measured using a Vapodest 450 (Gerhardt, Analytical Systems) for the digestion of the samples, following APHA-AWWA Standard Method 4500-Norg C. The content of metal elements was measured with an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) using a Varian Vista AX spectrometer. Thermogravimetric Analysis (TGA) was performed on a simultaneous TGA-DSC thermobalance (TGA-DCS1, Mettler-Toledo, S.A.E.) using a flow rate of 100 mL/min of nitrogen and a heating rate of 10 °C/min. For Total Petroleum Hydrocarbon (TPH) determination, 1g of oily sludge sample was dissolved into 20 mL of cyclohexane and was added into the glass column to remove solid particles and undesired polar organic compounds. The glass column was previously packed with silica gel and anhydrous sodium sulphate and wash out with cyclohexane and dichloromethane in proportion 1:1. TPHs were eluted with 100 mL of cyclohexane and dichloromethane (1:1 vol:vol). The elution volume were collected and the solvents were allowed to volatilize in a rotary evaporator (Zhang et al., 2012).

Ammonia (NH_4^+) and phosphate (PO_4^{3-}) concentration dissolved in the aqueous phase were determined using Smartchem 140 (AMS Alliance), following APHA-AWWA Standard Method 4500-NO2 B and 4500-P E, respectively (APHA-AWWA-WEF, 2005). Total Organic Carbon (TOC) in the aqueous phase was measured using a combustion/nondispersive infrared gas analyzer model TOC-V CSH (Shimadzu).

The elemental composition in the solid and oily phases was determined using a CHNS analyzer Flash 2000 (Thermo Fisher Scientific, Massachusetts, USA), equipped with a thermal conductivity detector (TCD). The contents of carbon (C), hydrogen (H), sulfur (S), and nitrogen (N) were determined by an oxidation/reduction reactor kept at a temperature of 900 °C. The oxygen (O) determination was achieved through an Oxygen-specific pyrolysis reactor heated at 1060 °C.

The solid phase was also analyzed by XRF (X-Ray Fluorescence), XRD (X-Ray Diffraction) and FTIR (Fourier-Transform Infrared) spectroscopy. XRF spectrometer Philips MagiX was used to determine the presence of metals. XRD pattern of the solid phase was obtained with a Philips X-Pert diffractometer using Cu Kα radiation. The data were recorded in the 2θ range from 5 to 90°. The FTIR spectra were recorded in the region 4000-400 cm^{-1} in a Varian 3100 FTIR Excalibur Series registering 64 scans.

The oily phase was analyzed by GC-MS (Gas Chromatography coupled to Mass Spectrometry), NMR (Nuclear Magnetic Resonance) and HPLC (High-Performance Liquid Chromatography). The main organic compounds contained in the oily phase were analyzed by direct aqueous-injection gas-chromatography coupled to a mass detector (320 GC-MS) using a Bruker column Stalbiwax-MS (30 m × 0.25 mm, 0.25 μm). This specific column for aqueous samples was initially maintained at 50 °C for 3 min, then heated to 180 °C at 12 °C/min, and finally maintained for 5 min at 250 °C (7 °C/min). The injector was held at 320 °C, and He (1 mL/min) was used as the carrier gas. ^{13}C and ^{1}H-NMR were performed on a VARIAN INFINITY 400 spectrometer operating at 79.4 MHz under the following conditions: MAS at 6 kHz; π/2 pulse, 4.5 μs; repetition delay, 15 s; 3000 scans. The total aromatics content was analyzed following UNE: EN 12916:2019, using an Agilent HP 1100 HPLC equipped with a refractive index detector (RI) Varian star with internal temperature of 35 °C. Zorbax-NH2 packed column (25 cm length and 4.6 mm × 5 μm internal diameter) maintained at 40 °C was used with a mobile phase of 100% HPLC grade heptane at a flow rate of 1 mL/min. The result was analyzed by means of external calibration curves generated for all of the suitable products, or model compounds, separately using standard solutions with known concentrations.

3. Results and discussion

3.1. Physical and chemical characterization of oily sludge

Oily sludge shows a dark colour (as seen in the graphical abstract) with a density slightly higher than water, and similar in aspect and texture to that of crude oil. The oily sludge under study in this work

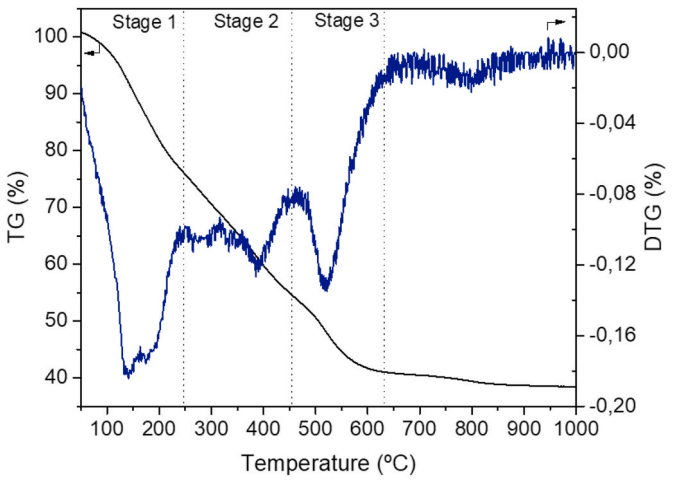

Fig. 1. TGA-DTG profile of the oily sludge.

consists of three different phases: oily phase, aqueous phase and solid phase, which were analyzed separately.

Oily sludge was preliminary characterized by different physical and chemical analytical techniques, in order to reach a basic knowledge of its composition. Table 1 shows all the measured parameters and their comparison with those found in the literature. Although some of them are in the same range, others are far from those measured in this work, which confirms the variable composition of this kind of wastes as above mentioned. It should be highlighted, that some of these parameters, such as TKN or P-PO_4^{3-} concentration, are still not reported, being this work the first reference of these parameters.

Oily sludge pH was in the neutral range with practically no variation. The higher heating value of the dry-oily sludge was 3765 kcal/kg, similar to that found for a refinery oily sludge reported by Nazem and Tavakoli (2017), and closed to that of peat or brown coal (Regulation UE nº 431/2014). The oily sludge has a high concentration of organic matter in the form of TCOD, TPHs, and TKN, which is mainly driven for the solid and/or oily phase. In contrast, SCOD, TOC, and N–NH_4^+ concentration measured in the aqueous phase was very low. The percentage of volatile total solids corresponds with approximately 50% of the total solids, confirming the high inorganic content of the sludge (ca. 50% of the solids in the sludge have inorganic nature).

Metal content was determined by ICP-AES analyses and classified by their concentration into low (<0.1 g/kg), intermediate (<1 g/kg) and high (>1 g/kg) concentration (Figure S2). As can be seen, Fe is the predominant metal with a concentration of 77 g/kg. Ca and Al were also found with high concentrations (27 and 26 g/kg respectively). Other metals that exceed 1 g/kg were Mg, Na, P, Zn, Ba, K, and Sn with values below 10 g/kg. At intermediate concentration, some metals appeared principally Mn (0.7 g/kg) or V (0.5 g/kg) among many others below 0.3 g/kg.

Specifically, the concentration of metals had been widely studied in the literature, and an extensive review of these concentrations is shown in Supporting Material, Table S1. The reported concentrations matching with this work are highlighted in colour green. The information shown in Table S1 demonstrates a tendency towards the concentration of some of these metals. Metal concentration is quite variable, showing the already mentioned heterogeneity of this kind of waste. According to a report from the American Petroleum Institute (Hu et al., 2015), metal concentration in oily sludge is generally lower than those reported in this study. However, this type of sludge, coming from oil-water separators, is characterized by having higher concentrations of some of the metals compared with other types of slurries such as oil drilling or waste engine oil sludge (Ramirez et al., 2019). In this oily sludge, there are metals typically presented in high concentrations (>1 g/kg), such as Ca, Fe or Zn, while others such as Cr, Mn, or Ni are commonly reported at intermediate range (<1 g/kg). As, Cd or Co are usually found at low range (<0.1 g/kg) (Admon et al., 2001; da Rocha et al., 2010; Marín et al., 2006; Roldán-Carrillo et al., 2012; Zhang et al., 2014).

The pyrolysis characteristic of the oily sludge was studied by thermogravimetric analysis in the range of temperatures from 30 to 1000 °C. Fig. 1 shows the weight loss profile as well as the differential thermogravimetric data (DTG) of the residue with the temperature. Fig. 1 clearly shows three main weight losses during pyrolysis, marked as stage 1, 2 and 3. The first weight loss, (25.2%; T ˂ 260 °C) was attributed to the removal of the light component of the mixture, including water and low boiling hydrocarbons. The second stage (20.8%; 280 °C < T ˂ 460 °C) was ascribed to the organic compounds and hydrocarbons of the oily fraction (Lin et al., 2019). The composition will be correlated in the proper section of this article using GC-MS analysis of the oily fraction. Finally, the third weight loss (12.8%; 460 °C < T ˂ 620 °C) was attributed to the decomposition of heavy components with higher boiling points, but also, it might be due to the reduction of metals in the presence of char at high temperatures (Wang et al., 2017a). Finally, there is a remaining inorganic solid, which accounts for 39.4% of the total oily sludge. The composition of this solid fraction will be further analyzed and discussed in the next sections of this work. Compared with other refinery wastes (Jasmine and Mukherji, 2015; Singh and Kumar, 2020) it is worth to highlight the large amount of inorganic residue present in the oily sludge under study.

Table 1
Characterization of the oily sludge of this study compared with literature.

Parameter	This work	Studies with similar results	Range found in the literature	References
pH	7.4 ± 0.1	(Jasmine and Mukherji, 2015; Kriipsalu et al., 2008; Yan et al., 2012; Zhao et al., 2018)	6–8	(Kriipsalu et al., 2007; Mounteer and Bioremed Biodegrad, 2011)
Density (kg/L)	1.2 ± 0.1	Nezhdbahadori et al. (2018)	0.92–1.28	(Mounteer and Bioremed Biodegrad, 2011; Nezhdbahadori et al., 2018)
TCOD (g/kg)	196 ± 18	Haak et al. (2016)	228–406	Mrayyan and Battikhi (2005)
TPHs (%)	26.2	Ke et al. (2021)	5–86	(Da Silva et al., 2012; Hu et al., 2013)
TS (g/kg)	213 ± 16	Zhen et al. (2019)	100–200	Haak et al. (2016)
VTS (g/kg)	102 ± 8	Jasmine and Mukherji (2015)	120–850	Haak et al. (2016)
TKN (gN/kg)	2.8 ± 0.3	NR	–	NR
SCOD (g/L)*	1.0 ± 0.7	Yan et al. (2012)	0.36–3.7	Haak et al. (2016)
N– NH_4^+ (mg/L)*	41 ± 4	NR	1829	Zhen et al. (2019)
P-PO_4^{3-} (mg/L)*	1.0 ± 0.1	NR	–	NR
TOC (g/L)*	0.2 ± 0.1	NR	180–830	(Mrayyan and Battikhi, 2005; Zhang et al., 2017)

* = determined for aqueous phase; NR = not reported.

3.2. Fractional characterization of the oily sludge

To carry out a more efficient valorization of the oily-sludge, this work, for the first time, proposes a fractional characterization of the different phases. Hence, the chemical composition of each phase will be discussed in this section.

3.2.1. Analysis of the oily phase

The chemical composition of the oily phase has been preliminarily addressed by GC-MS and ^{1}H, ^{13}C-NMR to obtain more information about the nature of the organic compounds present in this phase. GC-MS was employed for the identification of specific components in different fractions of oil. Fig. 2 shows the chromatogram corresponding to this oily phase comparing the peaks with the NIST library.

As can be seen, the oily sludge is predominantly formed by alkanes ranging from n-C_9 to n-C_{44}. Other aliphatic compounds are resolved and listed in Table S2 of Supporting Material. Some of the detected organic compounds of the oily sludge were corroborated in other works such as decane, tetratetracontane or pentadecane (Nazem and Tavakoli, 2017).

The mass loss observed in the TG-DTG analysis showing in Fig. 1 could be associated with the mass percentage of the group of compounds found in the analysis of the GC-MS (Table S2), by their boiling temperature range. Table 2 summarizes the results of this analysis. As can be seen, the major compounds presented in this oily sludge are light organics, that taking into account the hydrocarbons detected in the GC-MS could correspond mainly to C_9–C_{13}. The minor fraction is the heavier organics (probably asphaltenes > C_{30}) that could be associated with the solid fraction. The knowledge of the chemical composition of the mixture is essential to propose a wise valorization strategy, choosing between a biological or chemical treatment, although a combination of both technologies could be a possible option.

Biomarkers, such as pristane and phytane, frequently found in petroleum sludge (Gallego et al., 2007; Jasmine and Mukherji, 2015) were also present. The peak height ratio of pristane/n-C_{17}, phytane/n-C_{18} and pristane/phytane were determined as 1.48, 0.22, and 1.32, respectively. The isoprenoids, pristane, and phytane degrade at a significantly slower rate than n-C_{17} and n-C_{18} (straight-chain n-alkanes). Hence, the height ratios, pristane/n- C_{17}, and phytane/n- C_{18} are commonly used as biodegradation indicators during the formation of crude oil (Lee et al., 2006; Mcintyre et al., 2007). Pristane/n-C_{17} ratio 0.63, 0.97, 1.29, 3.89, 4.97, and infinity (n-C_{17} not present) were used to classify the oil as non-biodegraded, very slightly biodegraded, slightly biodegraded, slight-moderately biodegraded, moderately biodegraded, and heavily biodegraded, respectively. The pristane ratio found in this study shows that the oil extracted from the oily sludge has undergone from slightly to slight-moderately bio-degraded (Peters et al., 2005). This biodegradation indicator will be useful to study a potential bio-treatment of this fraction.

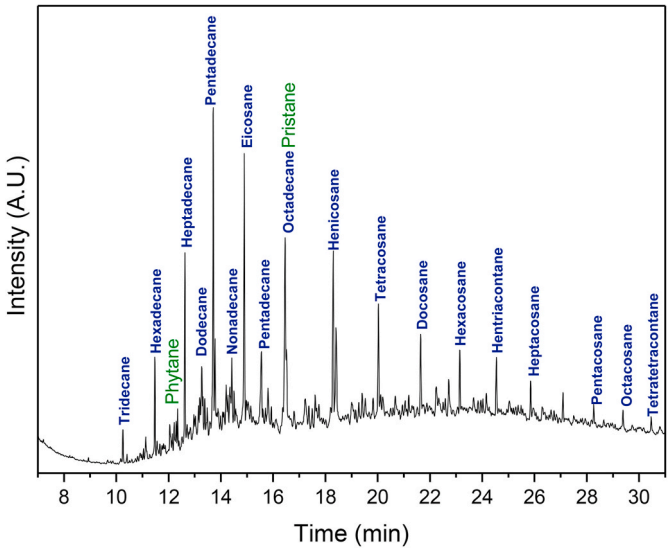

Fig. 2. GC-MS profile of oily sludge phase.

Table 2
Analysis of the oily phase composition associated with the TGA analysis.

Stage	T range (°C)	% weight loss	Group of compounds
1	120–244	19.0	C_9–C_{13}; $C_{26}H_{54}O$; $C_9H_{10}O_4$
2	300–346	4.8	C_{17} – C_{20}
	368–446	8.2	C_{24}–C_{30}
3	486–633	11.0	> C_{30}

Generally, the oil from a refinery sludge has higher aliphatic hydrocarbon percentages (40–60%) than the aromatic ones (25–40%) (Speight, 2006). However, our analysis of GC-MS showed the absence of aromatics in this phase, an uncommon fact considering the origin of this residue (Jasmine and Mukherji, 2015). To confirm the absence of aromatics, ^{1}H, and ^{13}CNMR analyses were performed (Ramirez et al., 2019). If aromatics were presented in this mixture some peaks would be observed in the proper region of the spectrum (Castro, 2006). Fig. 3a and b shows the ^{1}H-NMR and ^{13}C-NMR spectra, respectively. The peaks observed in the ^{1}H spectra (Fig. 3a) correspond to the aliphatic carbon fraction from 0.5 to 4 ppm and the aromatic carbon fraction from the 6–9 ppm region. In the case of the ^{13}C spectra (Fig. 3b), the 10–60 ppm region corresponds to the aliphatic, whereas signals at 110–160 ppm regions regard the aromatic carbon fraction (Ramirez et al., 2019). As can be inferred from Fig. 3, signals associated with aromatics compounds are hardly detected and the low quantity makes it impossible to settle which kind of aromatics compounds are in the sample. Both ^{1}H and ^{13}C are in fair agreement with those extracted from the GC-MS and those published with some other authors (Ramirez et al., 2019) who also observed the low presence of aromatic fraction in a similar oily sludge.

HPLC-RI analysis has been demonstrated to be a robust and precise technique for the determination of mono-, di- and polyaromatics within a complex mixture (Pasadakis et al., 2001). Hence, HPLC-RI analysis of the oily phase was carried out to precisely measure the percentage and type of aromatics present in the mixture. A low content of aromatic compounds was detected by HPLC-RI (ca. 4.7 wt %) corroborating the analysis by ^{13}C and ^{1}H NMR and GC-MS. In the mixture, monoaromatics represented the major content (ca. 3.0 wt%), following by di- and polyaromatics (ca.0.9 and 0.8 wt%, respectively).

Elemental analysis of the oily phase showed 84.4 wt% carbon, 12.2 wt% hydrogen, 1.7 wt% sulfur, 1.6 wt% nitrogen and 1% oxygen. As was expected, these results correspond to a fraction composed mostly of alkanes (C/H mass ratio of 0.57) with some impurities of S, N and O. These results are consistent with the above chemical analysis for the oily phase.

Due to the nature of this residue, it is usual to find heavy metals dissolved into the different phases. Metal content is a key factor to take into account for the valorization strategy of this oil-phase. Figure S3 shows the metals detected divided by their concentration. A wide variety of metals were detected in the oily phase, but most of them in a low concentration (less than 1 mg/kg) which will not affect the alternatives proposed later for its valorization. However, Si was detected with a significant concentration of 110 mg/kg, a fact that will have to be carefully considered in its valorization. Other authors have reported a high concentration of iron, nickel, and vanadium, indicating that further treatment for these metals was required to use the oil as fuel (Zubaidy and Abouelnasr, 2010).

3.2.2. Analysis of the solid phase

In the previous analysis by TGA-DTG (section 3.1; Fig. 1) was found that the weight loss associated with the solid fraction accounts for a 39.4 wt%. This corresponds to the matter that did not decompose at the

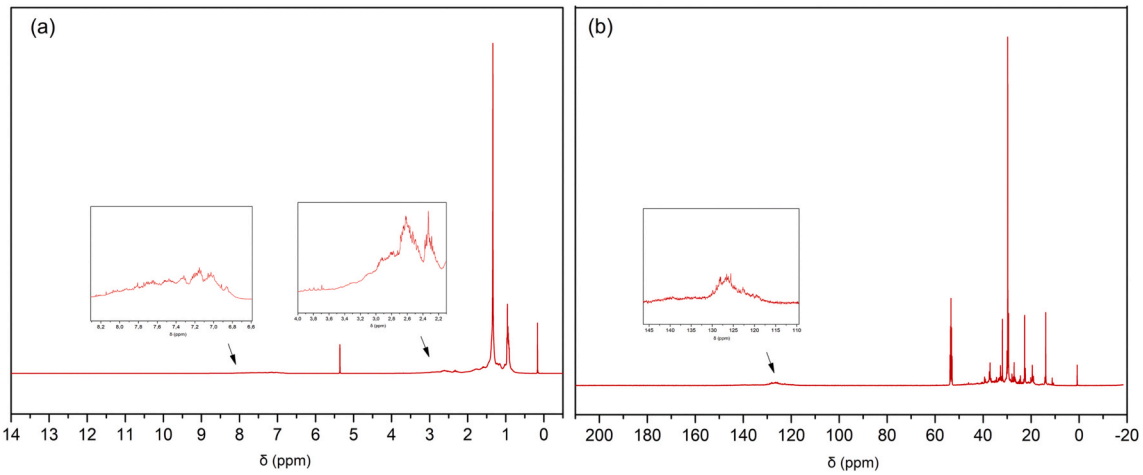

Fig. 3. (a) ^{1}HNMR; (b) ^{13}CNMR of oily phase. CD_2Cl_2 was used as a deuterated solvent. Aromatics regions are magnified in both spectrums.

working temperature of the TG analysis and will be fully characterized in this section. As it was mentioned in other sections of this article, this fraction represents a significant contribution to the whole residue, and it has to be carefully taken into account when planning the integral valorization of this sludge. Thus, solid sludge isolated by oil extraction with diethyl ether and drying at 100 °C for 24 h was thoroughly characterized by different techniques.

Fig. 4 shows the XRD analysis of the solid phase to investigate the presence of some crystalline solids. Despite the heterogeneity of the sample, some peaks corresponding to silica and calcium carbonate are identified, which agrees with other authors (Hu et al., 2017), who concluded that sludge mainly contains species of Si, Al, and Ca. Some broad peaks associated with CaO could be also detected. These results contrast with our results of ICP and XRF, which confirms the presence of not only Si and Ca but also other metals such as Fe (see next section). However, their identification by XRD was not possible because of their low crystallinity. Moreover, Fig. 4 shows a peak around 26.74° that could correspond to standard graphite material, while that observed at 42.38° is associated with the diffraction of the graphite layer.

Metal content in the solid phase (Figure S4) was estimated from the metal content of the whole residue for each metal studied (Figure S2), and subtracting the sum from oil (Figure S3) and aqueous metal content

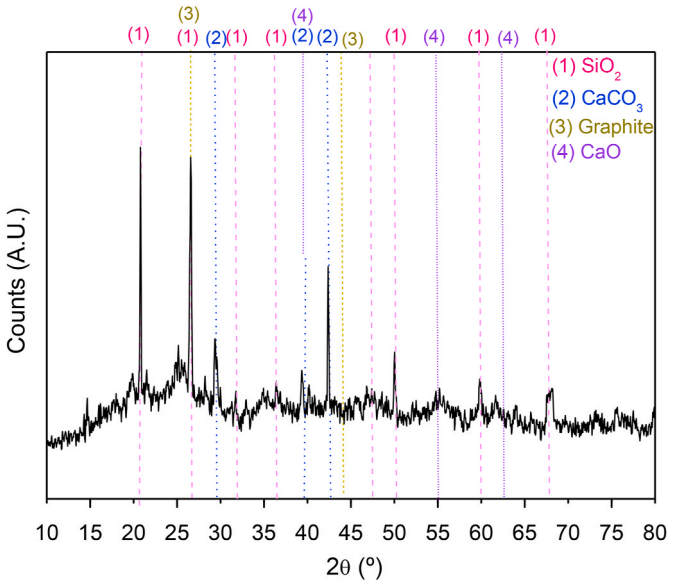

Fig. 4. XRD pattern of the solid phase.

(Figure S5). To verify these results, a semi-quantitative analysis by XRF was also performed. The results were not far from those estimated by metal balance and thus confirming the validity of the employed method. Fe by far is the major component of this mixture achieving 17% of the total solid, following by Ca, Al, S, Zn, Si, Cr and P. All these metals were probably part of amorphous phases since no peaks were observed in the XRD pattern, except Si in form of quartz and Ca in form of $CaCO_3$. A high concentration of Ca in the sludge solids indicates the presence of calcite mineral ($CaCO_3$) as reported by other authors (Jasmine and Mukherji, 2015). The high concentration of Fe could be related to the tank and pipes walls, as also suggested by other researchers (Duan et al., 2018; Jasmine and Mukherji, 2015). Other metals such as Al or S were also detected in <0.5%.

The metal content represents a 39 wt% of the solid fraction. Elemental analysis of the extracted solid allows us to find out the components of the remnant 61 wt%. C and O are the major components in the mixture (25.6 and 19.5 wt%, respectively), giving a ratio C/O of 1.31. There was also a low proportion of H (2 wt%), S (5.5 wt%), and N (0.8 wt%), and a 7.6 wt% of non-detected compounds. Summarizing, the solid phase contains an inorganic fraction and a carbonaceous phase, which represent a 15.2 wt% and 23.8 wt%, respectively, of the whole waste.

These results also led us to think that all of the inorganic compounds are in the form of single or mixed oxides because of the high percentage of oxygen. On the other hand, the high amount of C shows that there must be some kind of amorphous or crystalline C in the mixture, as previously commented in the XRD pattern from Fig. 4.

To go deeper about the phases presented in the solid mixture, FTIR of the dried solid was carried out. The peaks in the solid fraction were identified in the wavenumber range of 3600–3100, 2900–2700, 1750–1600, 1500–1300, and 1150-800 cm^{-1} (Fig. 5). The waveband at 3300 cm^{-1} was attributed to hydroxyl groups, which refer to water molecules entrapped in the solid fraction of the sludge. The $–CH_2$- and $–CH_3$ stretching vibrations of the alkyl chain are very well established at 2923 cm^{-1}, 2853 cm^{-1} and 1450 cm^{-1}. The band at 1641 cm^{-1} is usually associated with the C═C bonds of aromatic rings (Duan et al., 2018). Waveband observed in the regions of 1000–650 cm^{-1} could be attributed to = C–H bond. These findings led us to underscore the conclusions extracted from the XRD and ICP/XRF analysis, a complex mixture of inorganic solids, mixed oxides, and amorphous carbonaceous species are present in this solid residue with some heavy components of the crude oil adsorbed on the solid surface, such as long-chain alkanes or asphaltenes (Duan et al., 2018).

Duan et al. showed the characterization of the solid phase of an oily sludge coming from an oilfield. In that case, this oily sludge was characterized by a high concentration of inorganic material, principally

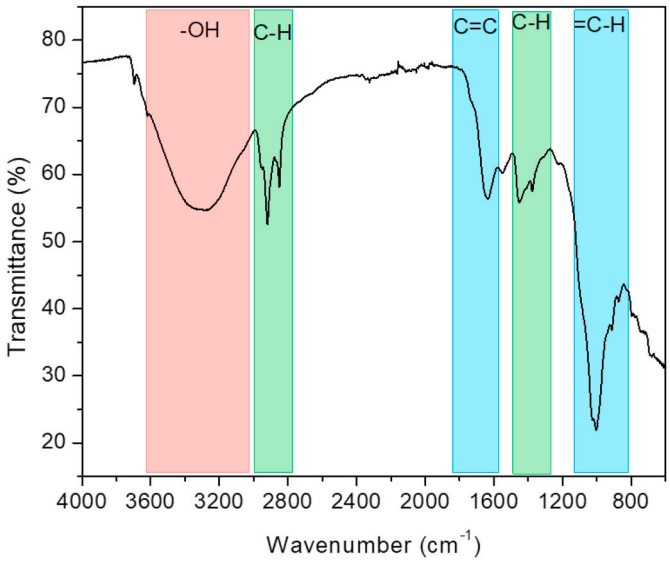

Fig. 5. FTIR spectrum of the solid fraction of the oily sludge.

clinoptilolite, and a low concentration of C. As the sludge studied in this work comes from the refinery process, the concentration of carbon is much higher, although the presence of inorganic compounds is still maintained (Duan et al., 2018).

3.2.3. Analysis of the aqueous phase

As it was shown in section 3.1, this fraction is characterized by a low organic content and the almost absence of nutrients. Nevertheless, to design a wise strategy to valorize this aqueous phase, analysis of metals, even in a trace concentration, must be performed. Figure S5 shows the distribution of the metals analyzed by ICP. They are divided into three main fractions according to their concentration: higher than 1 mg/L (Figure S5 a), between 1 and 0.1 mg/L (Figure S5 b), and less than 0.1 mg/L (Figure S5 c). Ca is the major element detected in the residue following by Mg and K, although a huge variety of metals were detected with a low concentration.

3.3. Insight into the valorization process

Management strategy of this kind of waste is normally focused on recovering and reclaiming valuable fuel or disposing of the unrecoverable residues (Hu et al., 2013). Because of increasingly stringent environmental regulations, disposal is becoming less accepted and more expensive, making problematic this management method. Hu et al. have recently investigated a comparative life cycle assessment of traditional and emerging treatment approaches for hazardous refinery oily sludge handling (incineration, landfilling, solvent extraction and pyrolysis) (Hu et al., 2020). The results showed that traditional oily sludge treatment approaches are generally associated with relatively high global warming potential, ecotoxicity, and adverse human health effects. Solvent extraction has the lowest total effect on the environment, but the main adverse effects related to ecotoxicity and fossil fuel depletion. Thus, new technologies must be proposed to handle this sludge, decreasing adverse impacts. The fractional characterization of the oily sludge presented above offers insights into innovative and alternative approaches for its valorization. Fig. 6 shows a possible road map for the valorization of the oil sludge under study and taking into consideration the characterization results.

Strategy 1: As can be seen in Table 1 and Figure S2, the concentration of COD (196 g/kg), N (TKN = 2800 mg/kg) and P (7000 mg/kg) in the sludge is very high. However, the main amount of these compounds are in the solid/oily phase, being only the SCOD, N–NH_4^+, and the P-PO_4^{3-} available in the aqueous phase of 1 g/L, 41 mg/L and 0.8 mg/L, respectively. Sludge thermal hydrolysis or Wet Air Oxidation (WAO) result in the reduction of the solids contained in the oily sludge (Tyagi and Lo, 2013) producing at the same time the accumulation of a high concentration of dissolved organic compounds in the aqueous phase. Thermal hydrolysis has been widely applied for waste-activated sludge (Wang et al., 2016), and never for an oily sludge, because of its heterogeneity and complexity, therefore this strategy will be a new approach that would be implemented to reduce the high solid concentration of the initial residue. Moreover, the WAO process is useful to break down biologically refractory compounds into simpler ones, increasing the biodegradability of the sludge (Zhao et al., 2018). Thus, a strategy to reduce the content of solids of the initial sludge, to enhance its biodegradability and to promote the solubilization of organic matter within the aqueous phase is proposed using thermal hydrolysis and

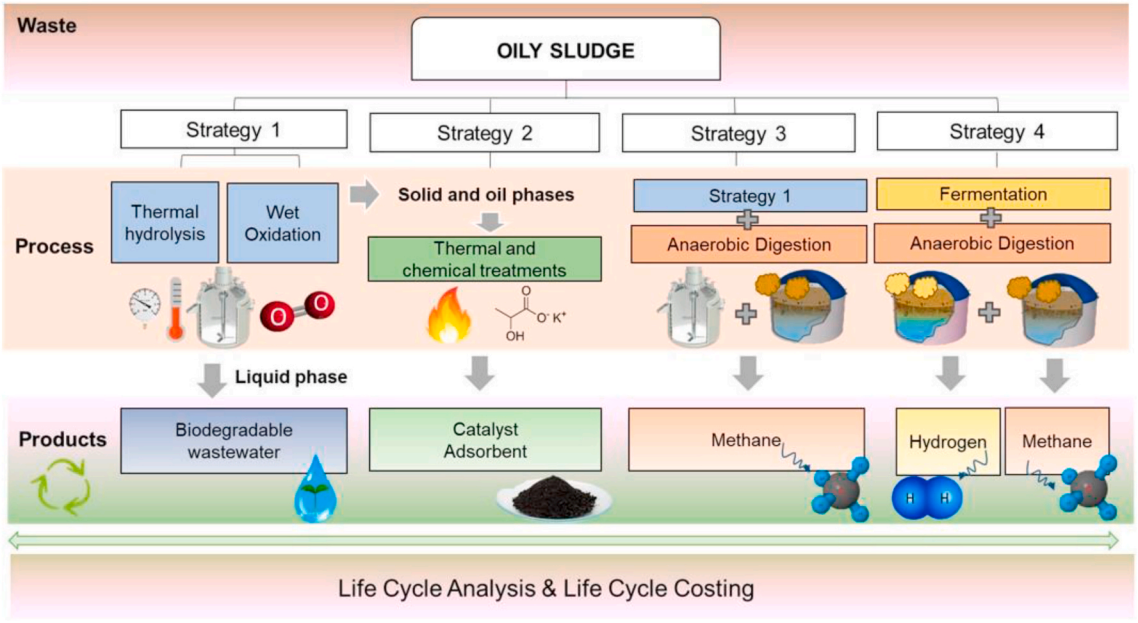

Fig. 6. Proposed road map for the valorization of the oily sludge characterized in this work.

WAO processes. These thermal treatments would yield a sludge with enhanced biodegradability and/or a high concentrated organic aqueous effluent, which could be further treated in a biological process in the refinery.

Strategy 2: The use and valorization of the solid and oily fraction are proposed in this strategy. After pre-treatment described in strategy 1, a potential biodegradable aqueous effluent would be obtained, but two streams remain without further treatment or even valorization: the oily phase, which could be recycled to the refinery after its purification, and the solid fraction. A possible way to valorize this mixture could be its transformation into an activated carbon due to its high concentration of carbon (Wang et al., 2017b). Adsorbent materials from sludge were normally produced by chemical activation using different reagents such as KOH, H_2SO_4, or $ZnCl_2$ followed by pyrolysis. These adsorbent solids possess high porosity and surface area (Tyagi and Lo, 2013) suitable for different applications. Due to the high metal content detected in the solid phase, the same treatment for this solid phase (thermal or chemical) can be proposed, but with a different objective, the preparation of catalysts with active metals such as iron. Lin et al. used an oily sludge to produce a Fe-char taking advantage of the iron content in the sludge (Lin et al., 2019). Moreover, due to the high hydrocarbon content of the oily phase achieved in the present work, this oily fraction could be suitable to convert into a high-quality activated carbon by using chemical or thermal treatments (Wang et al., 2017b). Thus, the two streams that have not been valorized in the abovementioned strategy 1, can be used in the form of activated carbon or catalysts with different suitable applications in the refining scheme.

Strategies 3 and 4 are focused on energy valorization, an important key due to the constant and continuous depletion of fossil fuel reserves and exponential rise in energy demand.

Strategy 3: It is well known that thermal treatments such as hydrolysis and WAO (Strategy 1) can produce several volatile acids (acetic, formic and propionic), which can be recovered using anaerobic biodigestion (Tyagi and Lo, 2013). Digestion of organic material is a useful and widely used strategy to valorize biosolids, livestock manure, or wet organic materials (Angelidaki et al., 2019). Anaerobic treatments have been explored within the petrochemical industry, however, applications have been limited to clean up operations for contaminated land/water (Coates et al., 1996; Haritash and Kaushik, 2009). In section 3.2 the potential biodegradation of the oily phase by the use of the biomarkers pristane and phytane was discussed, giving a classification of biodegradability of the oily phase. It was classified from slightly to slight-moderately bio-degraded, consequently, a bio-valorization of this pre-treated oily sludge could be proposed. The main product of this valorization will be methane, together with a remained solid which could be used as biochar (Adhikari et al., 2018). This strategy would allow fulfilling part of the energetic requirements of the refinery.

Strategy 4: Co-production of bio-hydrogen and bio-methane, via fermentation. Anaerobic digestion stages connected in series, is a potential high-value solution for the valorization of different types of wastes (Khan et al., 2018). This approach would start with a dark fermentation treatment to break the medium and large-chain molecules found in the oily phase dropping the concentration of solids and toxic materials following by an anaerobic digestion, as a promising way for renewable hydrogen and methane production. Some works applied this strategy to a sewage refinery sludge (Yang and Wang, 2017) combined with other residues such as forestry wastes. The main problem to perform a dark fermentation with refinery waste is the low C/N ratio normally found in this type of wastes, usually lower to 9, whereas it should be higher than 20 to achieve, at least, moderates H_2 volumes. In our study, a very high C/N ratio is observed ≈70 for the whole residue and ≈52.7 for the oily fraction, therefore it could be a very promising way for renewable hydrogen production. After fermentation, the resultant sludge can be anaerobically treated following strategy 3 to produce methane.

Finally, it is important to point out that there is currently a seeming disconnect between the academic literature and commercial adoption of technologies for oily sludge waste valorization. Thus, it is essential to performed LCA studies to determine and compare the potential resources, as well as the environmental impacts of each technology to consider opportunities and limitations to their implementation. Moreover, information regarding the cost of these technologies is scarce, hence cost assessment methods should also take into account in future studies of oily waste valorization technology alternatives (Hu et al., 2020).

4. Conclusions

This contribution reports the use of a wide range of different and complementary analytical techniques for the fractional characterization of an oily sludge coming from an API separator and comparison with other works described in the literature. The oily phase is formed by aliphatic hydrocarbons between C_9 and C_{44}. The solid phase is a complex mixture of inorganic solids, mixed oxides, and amorphous carbonaceous species. The aqueous phase is low concentrated in organic matter and nutrients and with the presence of some dissolved metals. According to the characterization results, four different potential strategies have been proposed for the integral valorization of oily sludge to produce valuable by-products such as biodegradable wastewater, activated carbons, methane and/or hydrogen. This work evidences that the characterization of such complex samples is a key factor as their valorization strongly depends on their composition. Characterization methodology before treatment must be standardized for refinery sludge coming from different sources. The success of these valorization strategies might allow a positive economic impact in the refining scheme and in line with the principles of the circular economy.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The financial support of the Ministry of Research and Innovation of Spain through the project [CTM2017-82865-R] and of the Regional Goverment of Madrid through the project REMTAVARES-CM [52018 / EMT-4341] is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.112124.

CRediT author statement

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References

Adhikari, S., Nam, H., Chakraborty, J.P., 2018. Conversion of solid wastes to fuels and chemicals through pyrolysis. In: Bhaskar, T., Pandey, A., Mohan, S.V., Lee, D.J., Khanal, S.K. (Eds.), Waste Biorefinery. Potenctial and Perspectives. Elsevier, pp. 239–263.

Admon, S., Green, M., Avnimelech, Y., 2001. Biodegradation kinetics of hydrocarbons in soil during land treatment of oily sludge. Bioremediat. J. 5 (3), 193–209. https://doi.org/10.1080/20018891079285.

Angelidaki, I., Xie, L., Luo, G., Zhang, Y., Oechsner, H., Lemmer, A., Munoz, R., Kougias, P.G., 2019. Chapter 33 - biogas upgrading: current and emerging technologies. In: Pandey, A., Larroche, C., Dussap, C.-G., Gnansounou, E., Khanal, S. K., Ricke, S.B.T., B A F, C.P. for the P. of L., G.B., Second E. (Eds.), Biomass, Biofuels, Biochemicals. Academic Press, pp. 817–843. https://doi.org/10.1016/B978-0-12-816856-1.00033-6.

APHA-AWWA-WEF, 2005. Standard methods for the examination of water and wastewater, twenty-first ed. APHA Am. Public Heal. Assoc.

Castro, A.T., 2006. NMR and FTIR characterization of petroleum residues: structural parameters and correlations. J. Braz. Chem. Soc. 17, 1181–1185.

Coates, J.D., Anderson, R.T., Woodward, J.C., Phillips, E.J.P., Lovley, D.R., 1996. Anaerobic hydrocarbon degradation in petroleum-contaminated harbor sediments under sulfate-reducing and artificially imposed iron-reducing conditions. Environ. Sci. Technol. 30, 2784–2789. https://doi.org/10.1021/es9600441.

da Rocha, O.R.S., Dantas, R.F., Duarte, M.M.M.B., Duarte, M.M.L., da Silva, V.L., 2010. Oil sludge treatment by photocatalysis applying black and white light. Chem. Eng. J. 157 (1), 80–85. https://doi.org/10.1016/j.cej.2009.10.050.

Da Silva, L.J., Alves, F.C., De França, F.P., 2012. A review of the technological solutions for the treatment of oily sludges from petroleum refineries. Waste Manag. Res. 30 (10), 1016–1030. https://doi.org/10.1177/0734242X12448517.

Duan, M., Wang, X., Fang, S., Zhao, B., Li, C., Xiong, Y., 2018. Treatment of Daqing oily sludge by thermochemical cleaning method. Colloids Surfaces A Physicochem. Eng. Asp. 554, 272–278. https://doi.org/10.1016/j.colsurfa.2018.06.046.

Gallego, J.L.R., García-Martínez, M.J., Llamas, J.F., Belloch, C., Peláez, A.I., Sánchez, J., 2007. Biodegradation of oil tank bottom sludge using microbial consortia. Biodegradation 18, 269–281. https://doi.org/10.1007/s10532-006-9061-y.

Haak, L., Roy, R., Pagilla, K., 2016. Toxicity and biogas production potential of refinery waste sludge for anaerobic digestion. Chemosphere 144, 1170–1176. https://doi.org/10.1016/j.chemosphere.2015.09.099.

Haritash, A.K., Kaushik, C.P., 2009. Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. J. Hazard Mater. 169, 1–15. https://doi.org/10.1016/j.jhazmat.2009.03.137.

Hu, G., Li, J., Zeng, G., 2013. Recent development in the treatment of oily sludge from petroleum industry: a review. J. Hazard Mater. 261, 470–490. https://doi.org/10.1016/j.jhazmat.2013.07.069.

Hu, G., Li, J., Hou, H., 2015. A combination of solvent extraction and freeze thaw for oil recovery from petroleum refinery wastewater treatment pond sludge. J. Hazard Mater. 283, 832–840. https://doi.org/10.1016/j.jhazmat.2014.10.028.

Hu, J., Gan, J., Li, J., Luo, Y., Wang, G., Wu, L., Gong, Y., 2017. Extraction of crude oil from petrochemical sludge: characterization of products using thermogravimetric analysis. Fuel 188, 166–172. https://doi.org/10.1016/j.fuel.2016.09.068.

Hu, G., Feng, H., He, P., Li, J., Hewage, K., Sadiq, R., 2020. Comparative life-cycle assessment of traditional and emerging oily sludge treatment approaches. J. Clean. Prod. 251, 119594. https://doi.org/10.1016/j.jclepro.2019.119594.

Jasmine, J., Mukherji, S., 2015. Characterization of oily sludge from a refinery and biodegradability assessment using various hydrocarbon degrading strains and reconstituted consortia. J. Environ. Manag. 149, 118–125. https://doi.org/10.1016/j.jenvman.2014.10.007.

Ke, C.Y., Qin, F.L., Yang, Z.G., Sha, J., Sun, W.J., Hui, J.F., Zhang, Q.Z., Zhang, X.L., 2021. Bioremediation of oily sludge by solid complex bacterial agent with a combined two-step process. Ecotoxicol. Environ. Saf. 208, 111673. https://doi.org/10.1016/j.ecoenv.2020.111673.

Khan, M.A., Ngo, H.H., Guo, W., Liu, Y., Zhang, X., Guo, J., Chang, S.W., Nguyen, D.D., Wang, J., 2018. Biohydrogen production from anaerobic digestion and its potential as renewable energy. Renew. Energy 129, 754–768. https://doi.org/10.1016/j.renene.2017.04.029.

Kriipsalu, M., Marques, M., Nammari, D.R., Hogland, W., 2007. Bio-treatment of oily sludge: the contribution of amendment material to the content of target contaminants, and the biodegradation dynamics. J. Hazard Mater. 148, 616–622. https://doi.org/10.1016/j.jhazmat.2007.03.017.

Kriipsalu, M., Marques, M., Maastik, A., 2008. Characterization of oily sludge from a wastewater treatment plant flocculation-flotation unit in a petroleum refinery and its treatment implications. J. Mater. Cycles Waste Manag. 10, 79–86. https://doi.org/10.1007/s10163-007-0188-7.

Lee, T.H., Byun, I.G., Kim, Y.O., Hwang, I.S., Park, T.J., 2006. Monitoring biodegradation of diesel fuel in bioventing processes using in situ respiration rate. Water Sci. Technol. 53, 263–272. https://doi.org/10.2166/wst.2006.131.

Lin, B., Huang, Q., Yang, Y., Chi, Y., 2019. Preparation of Fe-char catalyst from tank cleaning oily sludge for the catalytic cracking of oily sludge. J. Anal. Appl. Pyrolysis 139, 308–318. https://doi.org/10.1016/j.jaap.2019.03.006.

Liu, J., Jiang, X., Zhou, L., Han, X., Cui, Z., 2009. Pyrolysis treatment of oil sludge and model-free kinetics analysis. J. Hazard Mater. 161 (2–3), 1208–1215. https://doi.org/10.1016/j.jhazmat.2008.04.072.

Liu, W., Wang, X., Wu, L., Chen, M., Tu, C., Luo, Y., Christie, P., 2012. Isolation, identification and characterization of Bacillus amyloliquefaciens BZ-6, a bacterial isolate for enhancing oil recovery from oily sludge. Chemosphere 87 (10), 1105–1110. https://doi.org/10.1016/j.chemosphere.2012.01.059.

Marín, J.A., Moreno, J.L., Hernández, T., García, C., 2006. Bioremediation by composting of heavy oil refinery sludge in semiarid conditions. Biodegradation 17, 251–261. https://doi.org/10.1007/s10532-005-5020-2.

Mazlova, E.A., Meshcheryakov, S.V., 1999. Ecological characteristics of oil sludges. Chem. Technol. Fuels Oils 35, 49–53. https://doi.org/10.1007/BF02694263.

Mcintyre, C.P., Harvey, P.M.A., Ferguson, S.H., Wressnig, A.M., Volk, H., George, S.C., Snape, I., 2007. Determining the extent of biodegradation of fuels using the diastereomers of acyclic isoprenoids. Environ. Sci. Technol. 41, 2452–2458. https://doi.org/10.1021/es0621288.

Mohan, S.V., Chandrasekhar, K., 2011. Self-induced bio-potential and graphite electron accepting conditions enhances petroleum sludge degradation in bio-electrochemical system with simultaneous power generation. Bioresour. Technol. 102 (20), 9532–9541. https://doi.org/10.1016/j.biortech.2011.07.038.

Mounteer, A., Bioremed Biodegrad, J., 2011. Oil recovery from fuel oil storage tank sludge. Using Biosurfactants 2, 1000125. https://doi.org/10.4172/2155-6199.1000125.

Mrayyan, B., Battikhi, M.N., 2005. Biodegradation of total organic carbons (TOC) in Jordanian petroleum sludge. J. Hazard Mater. 120 (1–3), 127–134. https://doi.org/10.1016/j.jhazmat.2004.12.033.

Nazem, M.A., Tavakoli, O., 2017. Bio-oil production from refinery oily sludge using hydrothermal liquefaction technology. J. Supercrit. Fluids 127, 33–40. https://doi.org/10.1016/j.supflu.2017.03.020.

Nezhdbahadori, F., Abdoli, M.A., Baghdadi, M., Ghazban, F., 2018. A comparative study on the efficiency of polar and non-polar solvents in oil sludge recovery using solvent extraction. Environ. Monit. Assess. 190 https://doi.org/10.1007/s10661-018-6748-6.

Pasadakis, N., Gaganis, V., Varotsis, N., 2001. Accurate determination of aromatic groups in heavy petroleum fractions using HPLC-UV-DAD. Fuel 80, 147–153. https://doi.org/10.1016/S0016-2361(00)00082-X.

Peters, K.E., W, C.C., M, J.M., 2005. The Biomarker Guide II. Biomarkers and Isotopes in Petroleum Systems and Earth History, second ed.

Qin, H., Ma, J., Wang, Q., Li, J., Chi, M., Zhang, L., Liu, H., 2016. Treatment of oil shale sludge using solvent extraction and thermo-chemistry. Chinese J. Environ. Eng. 10, 851–857.

Ramirez, D., Kowalczyk, R.M., Collins, C.D., 2019. Characterisation of oil sludges from different sources before treatment: high-field nuclear magnetic resonance (NMR) in the determination of oil and water content. J. Petrol. Sci. Eng. 174, 729–737. https://doi.org/10.1016/j.petrol.2018.11.078.

Raposo, F., de la Rubia, M.A., Borja, R., Alaiz, M., 2008. Assessment of a modified and optimised method for determining chemical oxygen demand of solid substrates and solutions with high suspended solid content. Talanta 76, 448–453. https://doi.org/10.1016/j.talanta.2008.03.030.

Roldán-Carrillo, T., Castorena-Cortés, G., Zapata-Peñasco, I., Reyes-Avila, J., Olguín-Lora, P., 2012. Aerobic biodegradation of sludge with high hydrocarbon content generated by a Mexican natural gas processing facility. J. Environ. Manag. 95, S93–S98. https://doi.org/10.1016/j.jenvman.2011.04.014.

Singh, B., Kumar, P., 2020. Physicochemical characteristics of hazardous sludge from effluent treatment plant of petroleum refinery as feedstock for thermochemical processes. J. Environ. Chem. Eng. 8, 103817. https://doi.org/10.1016/j.jece.2020.103817.

Speight, J.G., 2006. The Chemistry and Technology of Petroleum, fourth ed. Chemical Industries, Wyoming, USA.

Tahhan, R.A., Ammari, T.G., Goussous, S.J., Al-Shdaifat, H.I., 2011. Enhancing the biodegradation of total petroleum hydrocarbons in oily sludge by a modified bioaugmentation strategy. Int. Biodeterior. Biodegrad. 65 (1), 130–134. https://doi.org/10.1016/j.ibiod.2010.09.007.

Taiwo, E.A., Otolorin, J.A., 2009. Oil recovery from petroleum sludge by solvent extraction. Petrol. Sci. Technol. 27, 836–844. https://doi.org/10.1080/10916460802455582.

Tyagi, V.K., Lo, S.L., 2013. Sludge: a waste or renewable source for energy and resources recovery? Renew. Sustain. Energy Rev. 25, 708–728. https://doi.org/10.1016/j.rser.2013.05.029.

Wang, Q., Liang, Y., Zhao, P., Li, Q.X., Guo, S., Chen, C., 2016. Potential and optimization of two-phase anaerobic digestion of oil refinery waste activated sludge and microbial community study. Sci. Rep. 6, 38245. https://doi.org/10.1038/srep38245.

Wang, Jiaofei, Jin, L., Li, Y., Hu, H., 2017a. Preparation of fe-doped carbon catalyst for methane decomposition to hydrogen. Ind. Eng. Chem. Res. 56 (39), 11021–11027. https://doi.org/10.1021/acs.iecr.7b02394.

Wang, Jun, Liu, T.L., Huang, Q.X., Ma, Z.Y., Chi, Y., Yan, J.H., 2017b. Production and characterization of high quality activated carbon from oily sludge. Fuel Process. Technol. 162, 13–19. https://doi.org/10.1016/j.fuproc.2017.03.017.

Yan, P., Lu, M., Yang, Q., Zhang, H.L., Zhang, Z.Z., Chen, R., 2012. Oil recovery from refinery oily sludge using a rhamnolipid biosurfactant-producing Pseudomonas. Bioresour. Technol. 116, 24–28. https://doi.org/10.1016/j.biortech.2012.04.024.

Yang, G., Wang, J., 2017. Enhanced hydrogen production from sewage sludge by Co-fermentation with forestry wastes. Energy Fuels 31, 9633–9641. https://doi.org/10.1021/acs.energyfuels.7b02135.

Zhang, J., Li, J., Thring, R.W., Hu, X., Song, X., 2012. Oil recovery from refinery oily sludge via ultrasound and freeze/thaw. J. Hazard Mater. 203–204, 195–203. https://doi.org/10.1016/j.jhazmat.2011.12.016.

Zhang, J., Li, J., Thring, R.W., Hu, G., Liu, L., 2014. Investigation of impact factors on the treatment of oily sludge using a hybrid ultrasonic and fenton's reaction process. Int. J. Environ. Pollut Remed. 2, 37–44. https://doi.org/10.11159/ijepr.2014.006.

Zhang, Y., Zhao, Q., Jiang, J., Wang, K., Wei, L., Ding, J., Yu, H., 2017. Acceleration of organic removal and electricity generation from dewatered oily sludge in a bioelectrochemical system by rhamnolipid addition. Bioresour. Technol. 243, 820–827. https://doi.org/10.1016/j.biortech.2017.07.038.

Zhao, M., Wang, X., Liu, D., Li, Z., Guo, S., Zhu, W., Shi, N., Wen, F., Dong, J., 2020. Insight into essential channel effect of pore structures and hydrogen bonds on the solvent extraction of oily sludge. J. Hazard Mater. 389, 121826. https://doi.org/10.1016/j.jhazmat.2019.121826.

Zhao, Y., Yan, X., Zhou, J., Li, R., Yang, S., Wang, B., Deng, R., 2018. Treatment of oily sludge by two-stage wet air oxidation. J. Energy Inst. 92 (5), 1451–1457. https://doi.org/10.1016/j.joei.2018.08.006.

Zhen, G., Tan, Y., Wu, T., Wang, J., Lu, X., Zhao, Y., Zhu, X., Niu, J., Xiong, J., 2019. Strengthened dewaterability of coke-oven plant oily sludge by altering extracellular organics using Fe(II)-activated persulfate oxidation. Sci. Total Environ. 688, 1155–1161. https://doi.org/10.1016/j.scitotenv.2019.06.308.

Zubaidy, E.A.H., Abouelnasr, D.M., 2010. Fuel recovery from waste oily sludge using solvent extraction. Process Saf. Environ. Protect. 88, 318–326. https://doi.org/10.1016/j.psep.2010.04.001.