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New strategies for the management of a primary refinery oily sludge: A techno-economical assessment of thermal hydrolysis, Fenton, and wet air oxidation treatments

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ABSTRACT

Petroleum refinery wastewater treatment plants produce a significant amount of oily sludge, a hazardous waste that requires proper disposal. It is necessary to develop technologies to treat and valorise it, avoiding the current environmental problems associated with its landfill disposal. This work explores the application of different advanced technologies for the pre-treatment and further valorisation of this oily sludge, which includes thermal hydrolysis, Fenton oxidation, and wet air oxidation. These treatments reduce the solid content by 51–78%. Moreover, the increasing dewaterability and settleability facilitate phase separation, thus enabling further valorisation, obtaining an aqueous effluent more biodegradable (ca. 63%). A conceptual design based on experimental data obtained at bench scale has been developed for the three pre-treatment systems under study. Techno-economic analysis of the three advanced treatments gave unitary costs ranging from 78 €/m^3 for thermal hydrolysis to 192 €/m^3 for the Fenton treatment, which are all in the low range of the current management cost (70–350 €/m^3). Thus, the techno-economic analysis developed in this study demonstrates its feasibility compared to the current management of oily sludge from API separators. Thermal hydrolysis can be a low-cost and suitable strategy for producing biodegradable effluent that can be directly treated in the conventional biological treatment plant of the refinery. However, WAO might be a more appropriate option to recover carbon and nutrients for further valorisation in advanced biological processes.

1. Introduction

Oily sludge is generated in large quantities in petroleum refinery wastewater treatment plants (WWTP). In these plants, wastewater is initially treated in conventional oil /water API (American Petroleum Institute) separators to recover oil content generating a primary oily sludge [1]. The resultant aqueous effluent is fed to a dissolved air flotation (DAF) unit to remove solids, producing additional primary sludge with low oil content. Finally, the aqueous stream after this primary process is further treated by conventional biological treatments obtaining an aqueous effluent and a secondary biological sludge [2]. Due to their composition, the primary oily sludge from the API separators is considered a hazardous residue by the European List of Wastes (Directive 2008/98/CE). The generation of hazardous refinery industry sludges is estimated at 310,000 tons in the EU annually [3]. Usually, oily sludge is composed of three different phases: oil (15–50 wt%), water (30–85 wt%) and solid (5–46 wt%) [4]. However, its composition fluctuates significantly depending on the quality of crude oils, the processes applied during petroleum refining and the use of different chemicals. Likewise, this waste contains hydrocarbons (5–86 wt%) coming from petroleum refining [5], heavy metals such as Fe, Cu or Ni, nitrogen, sulphur, oxygen compounds, and solid particles [6,7]. The most common organic compounds are alkenes, benzene, toluene, ethylbenzene, phenols and polycyclic aromatic hydrocarbons (PAHs) [2], which can be toxic, mutagenic and carcinogenic compounds. Therefore, the inappropriate disposal of oily sludge supposes severe environmental hazards causing water, soil, and air pollution.

Thus, adequate waste management of oily sludge is vital to meet current EU legislation. The conventional treatments are mainly focused on reducing sludge volume and recovering oil content through centrifugation, solvent extraction, or surfactant recovery processes [6]. Although these traditional treatments allow the recovery of the hydrocarbon content of the oily sludge, this only represents a small part of the overall waste. Therefore, the remaining sludge needs additional

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management, being incineration and further ash disposal in landfills one of the most used alternatives [8,9]. Hence, the current strategy implies substantial management costs for the refinery treatment plant without any recovery and further valorisation.

In previous works, our group has investigated new potential strategies for treating and valorising this oily sludge [4]. These strategies are focused on well-established technologies used for conventional sewage sludge to enhance its biodegradability, such as thermal hydrolysis [10,11], Fenton oxidation [12,13] and wet air oxidation [14,15]. The selected technologies are divided into two groups: non-oxidative and oxidative techniques. On the one hand, thermal hydrolysis (TH) is a mature non-oxidative treatment, working at temperatures between 100 and 200 °C. This technology allows solid destruction, so residue reduction [16]. On the other hand, the most popular oxidative technologies are wet air oxidation (WAO) and advanced oxidation processes (AOPs). WAO is applied with air or oxygen at high pressure (20–150 bar) and high temperature (150–320 °C) to oxidase and solubilise the organic compounds. In contrast, AOPs use moderate temperatures (25–120 °C) and atmospheric pressure but with different oxidants (hydrogen peroxide or ozone) to produce highly reactive ·OH radicals, oxidising organic compounds and reducing the solid content [17,18].

The goal of those previous works was the removal of solids and organic compounds to minimize waste, as shown in other works in the literature [19–23]. Additionally, these treatments improved the dewatering and settling properties of the sludge, easing selective phase separation and further individual valorisation of the different phases present in the oily sludge (oil, water, and solid). Consequently, the oily phase, which contains high levels of petroleum hydrocarbons, can be recycled back to the refinery. Due to its composition, the aqueous effluent with enhanced biodegradability can be treated by a conventional biological process or used to recover value-added products [16]. Finally, the solid phase with high carbon content can be thermochemically treated under controlled conditions to yield porous materials with potential properties as adsorbent and catalyst support [4]. As a result, these new strategies enable the complete valorisation of the refinery's oily sludge. Fig. 1 summarises the proposed WWTP refinery scheme (b) and the comparison with the conventional one implemented at the refinery (a), where a high-cost centrifugation step is currently used.

To our knowledge, these technologies have not yet been applied to valorise refinery oily sludge. Additionally, the use of different types of sludges in each study makes benchmarking the proposed technologies difficult with the data found in the literature. Therefore, in this work, we have used the same sludge and installation setup to provide better benchmarks for the three proposed technologies. Hence, the main objective of this study is the comparison of the three different pretreatments in terms of solubilisation of the oily phase, release biodegradable organic matter into the aqueous phase, and enhance the solid-liquid separation. Moreover, a preliminary techno-economic analysis of each approach is carried out and compared with the current management method. Thus, a unitary treatment cost has been estimated to assess the economic feasibility of the proposed strategies. The results of this study will allow a step forward in transitioning these processes from research to the industrial stage and identify potential bottlenecks.

2. Materials and methods

2.1. Oily sludge characterisation

Oily sludge was supplied from an API separator unit in a petroleum refinery wastewater treatment plant located in Spain. This oily sludge was initially characterised. The phases of the oily sludge were extracted and isolated following the procedure published elsewhere [4].

pH was determined using a GLP-22 digital pH meter (Hach Lange Spain, S.L.U). Total solids (TS) were measured following APHA-AWWA standard methods 2540. B [24]. Total Kjeldahl Nitrogen (TKN) was measured using a Vapodest 450 (Gerhardt, Analytical Systems), following APHA-AWWA Standard Method 4500-Norg C. Soluble chemical oxygen demand (SCOD) was determined for the aqueous phase following APHA-AWWA standard methods 5220. D [24]. Ammonia ($N\text{-}NH_4^+$) and phosphate ($P\text{-}PO_4^{3-}$) concentrations 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 [24]. Total Organic Carbon (TOC) in the aqueous phase was measured using a combustion/nondispersive infrared gas analyser model TOC-V CSH (Shimadzu), and acetic acid concentration was determined by GC (Gas chromatography) using a CP-Wax 52B column (30 m × 0.25 mm, 0.25 μm). The oily and aqueous phases were analysed by GC/MS (Gas Chromatography coupled to Mass Spectrometry) using a Restek column, Rxi 5Sil MS (30 m × 0.25 mm, 0.25 μm) and Stalbiwax-MS (30 m × 0.25 mm, 0.25 μm), respectively. The Total

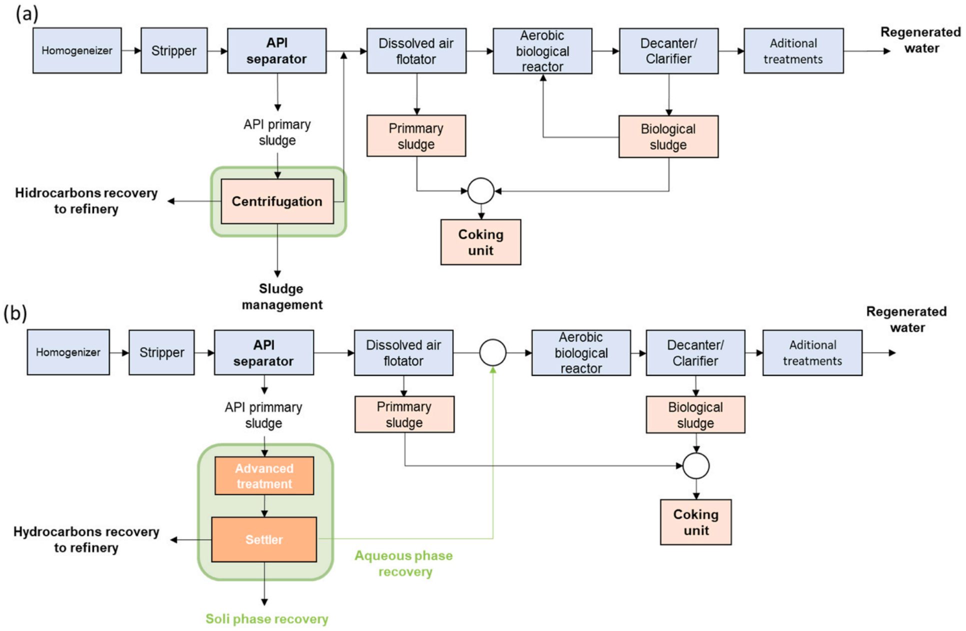

Fig. 1. Schematic representation of a conventional WWTP of a petrol refinery (a) and the new approach proposed in this work (b).

Petroleum Hydrocarbons (TPHs) of the oily sludge were measured following the procedure described elsewhere [4]. Capillary suction time (CST) was measured using OFI Testing Equipment to determine the oily sludge dewaterability.

Biodegradability assays were also carried out for the aqueous phase of the oily sludge [18,25]. These analyses were performed at 25 °C in an LFS (liquid-flow-static) respirometer based on a 1 L vessel inoculated with biomass (2.4 ± 0.5 g VSS/L) from an urban WWTP located in Móstoles (Madrid). pH and dissolved oxygen (DO) were constantly monitored during the assays. All the analysis were carried out by triplicate to settle the deviation error.

Table 1 shows the initial characterisation of the oily sludge. This waste shows a pH in the neutral range, as reported in other works [6]. It is composed of three different phases: oily (34 wt%), aqueous (41 wt%) and solid (25 wt%). The oily phase contains total petroleum hydrocarbons (TPH) from the refining processes, mainly alkanes ranging from n-C_9 to n-C_{44} [4]. The solid phase is a complex mixture of inorganic solids (34%) and amorphous carbonaceous species (45%). The inorganic part is mainly formed by Fe with a 15 wt%, followed by Ca, Al or Si. The aqueous phase presents a low organic content in terms of SCOD and TOC and almost the absence of nutrients in terms of TKN, N-$NH_4^+$and P-PO_4^{3-}, with the presence of some dissolved metals. The biodegradability test of the aqueous phase showed a low biodegradability with only 18%, which indicates the presence of toxic compounds such as organics or metals [6, 9].

2.2. Pretreatments of refinery oily sludge

Thermal hydrolysis (TH), wet air oxidation (WAO), and Fenton (FT) treatments have been carried out in a stainless-steel reactor with a total volume of 500 mL with the raw oily sludge without dilution (Parr model 4575 A). The reactor had an electrically heated jacket, a turbine stirrer, and a variable-speed magnetic drive. The temperature was controlled using a thermocouple immersed in the liquid phase. The stirring rate was controlled using a Parr 4842 controller, the pressure by the gas inlet, and a gas release valve located on the top of the reaction vessel. Typically, 250 mL of the oily sludge was placed in the reactor and heating up to the desire temperature with a heating rate of 10 °C/min and continuous stirring at 400 rpm. TH experiment was performed at 200 °C for 1 h of reaction time with an initial nitrogen pressure of 5 bar [16]. FT experiment was carried out at 80 °C and 2 h of reaction time, adding 90 g H_2O_2 per L of oily sludge and using the content of Fe in this waste as a catalyst [18]. Finally, WAO experiment was performed at 200 °C and 1 h with 50 bar of initial air pressure. The reaction conditions for TH and FT experiments were based on previous results published in our research group [16,18]. However, as far as authors knowledge, there are not published results of a wet air oxidation process for an oily sludge. So, WAO conditions were the same as TH to compare with the experiment without air.

Table 1

Characterisation of the initial oily sludge of this study and after the pretreatments.

	Initial	TH	FT	WAO
Sludge				
TS reduction (%)	-	51	78	77
CST (s)	181 ± 20	29 ± 3	21 ± 2	17 ± 2
TPHs (wt%)	30 ± 5	23 ± 2	10 ± 1	6 ± 1
Aqueous phase				
pH*	7.6 ± 0.1	7.4 ± 0.3	4.0 ± 0.1	2.1 ± 0.1
SCOD (g/L)*	1.5 ± 0.2	1.8 ± 0.3	2.4 ± 0.3	16.7 ± 0.8
TOC (g/L)*	0.4 ± 0.5	1.2 ± 0.1	1.4 ± 0.1	4.9 ± 0.1
TKN (mg/L)*	69 ± 7	198 ± 20	279 ± 30	1221 ± 50
NH_4^+ (mg/L)*	46 ± 7	51 ± 5	88 ± 10	447 ± 56
PO_4^{3-} (mg/L)*	0.7 ± 0.2	2.0 ± 0.5	8.0 ± 1	96 ± 2
Acetic acid (mg/L)*	22 ± 2	134 ± 10	501 ± 45	1517 ± 58
Biodegradability (%)*	18 ± 10	60 ± 10	60 ± 19	63 ± 27

[*] Determined for the aqueous phase

This work studied the efficiency of TH, FT and WAO processes for treating the oily sludge by applying the best conditions previously determined for each technology [16,18]. Carbon content and nutrients' solubilisation were monitored by measuring SCOD, TOC, TKN, N-$NH_4^+$and P-PO_4^{3-} concentration in the aqueous phase before and after the different treatments (Table 1).

2.3. Techno-economic analysis

The methodology followed for the techno-economic study comprises several steps:

2.3.1. Process definition

Process flow diagrams were proposed for each treatment and considering the current volumetric flow rate of this primary sludge in the API section of the WWTP of the petrol refinery under study, which account for 2.8 m^3/d (Q) (see details in Figs. S1, S2, and S3 of the Supporting Information).

2.3.2. Process design and cost estimation

Mass and energy balances were used for sizing the different equipment (design parameters are included in Tables S1, S2 and S3 in Supporting Information) through bibliographic methods and heuristic correlations [26] described in Supporting Information. The resultant equipment costs were updated using the annualized Industrial Price Index (IPRI) to the current year, provided by the Spanish National Institute of Statistics [27].

2.3.3. Economic analysis

An economic analysis was performed for the different approaches based on the previous design and equipment sizing. Total capital investment (TCI) was estimated using the mass and energy balances and the equipment design parameters. The inside battery limits (ISBL) and outside battery limits (OSBL) were calculated following the Peters and Timmerhaus factor method [28], which is based on a relative percentage of the equipment purchase costs (see Table S4 for details). ISBL include the equipments, materials, engineering, construction and supervision costs, while OSBL were considered as a 10% of the ISBL, auxiliary services and interconnections. Amortisation costs (AC) were estimated from TCI for 20 years (n) and a 7% interest rate (i), following Eq. 1.

$$AC(€\Big/y) = \frac{TCI\cdot i}{1-\left(\frac{1}{1+i}\right)^{n}} \tag{1}$$

Operation costs (OC) included energy requirements (heating and electricity), staff, maintenance, and insurance. Steam water heating costs were obtained from the consumption of natural gas with a price of 8.99 €/GJ (high-pressure steam) and 7.07 €/GJ (low-pressure steam) [29]. Electric expenses were calculated considering a price of 0.257 €/kWh [30]. The staff cost is estimated to be 40,000 €/year (including only an additional expense for a new contract to supervise the pretreatment plant). Finally, maintenance and insurance were considered 3% of the total investment. FT treatment also considers the H_2O_2 (30% purity) expenses with a cost of 0.23 €/L [31,32]. Hence, the total annualised costs (TAC) can be calculated as the sum of AC and OC.

2.3.4. Assessment of current management strategy and proposed alternatives

The unitary costs of treatment per m^3 of sludge were calculated following Eq. 2, considering the actual flow rate of oily sludge (Q) in the refinery treatment plant and assuming that the plant is running 8000 h per year. A comparison of each cost for the proposed treatments in this work and the current cost of the management as a residue in landfill [18] was analysed to settle the feasibility of each technology.

$$\text{Unitary costs}\left(\frac{€}{m^3\text{sludge}}\right)=\frac{OC+AC}{Q\cdot h} \tag{2}$$

3. Results and discussion

3.1. Pre-treatment technologies

Thermal hydrolysis, Fenton oxidation, and wet air oxidation pretreatments can oxidize and solubilize the organic particulate components of the sludge during the disruption of the sludge floc. SCOD concentration increases after TH, FT and WAO, being higher for the oxidative treatments, especially for the WAO process, which increases the SCOD concentration tenfold (Table 1). Other authors also reported a significant SCOD solubilisation by applying a WAO treatment to sewage sludge, reaching a maximum concentration at 200 °C [33]. The same trend was observed for TOC and nutrients content, that are higher for the oxidative treatments. As expected, the WAO process applied at the same temperature as the TH process is more effective in reducing total solids, solubilising organic content, and forming nutrients and volatile fatty acids [34].

The acetic acid concentration accounts for approximately 3%, 31%, and 31% of the total TOC in the aqueous phase after the TH, FT, and WAO experiments, respectively. The formation of acetic acid is significantly higher for the oxidative treatments, particularly for the WAO process, giving a concentration of 1517 mg/L. This high concentration of acetic acid and other low-chain carboxylic acids leads to an acid pH for the effluent after the WAO treatment. Other authors have published similar results, applying thermal treatment to sewage sludge, reaching an acetic acid concentration of around 500 mg/L at 180 °C [35]. Also, an acetic acid concentration of 1230 mg/L after WAO treatment at 200 °C for sewage sludge was reported [36].

The solubilisation of organic content and nutrients into the aqueous phase is produced due to the breakdown of complex molecules present in the oily phase of the sludge into simple ones that can solubilise into the aqueous phase. Fig. 2 shows the hydrocarbon distribution analysed by GC/MS for the oily and aqueous phase. The initial oily phase contains long-chain hydrocarbons ($> C_{17}$-C_{23}), as other authors also reported [6] (Fig. 2a). However, this composition changes after the treatments, decomposing long-chain hydrocarbons into short-chain hydrocarbons (from C_{17}-C_{23} to C_1-C_{16}). At the same time, the aqueous phase also changes its composition showing higher C_1-C_{16} hydrocarbons (practically 100%) after the treatments (Fig. 2b). Moreover, the short-chain hydrocarbons present in the aqueous phase after the applied treatments are mostly oxygenated hydrocarbons (C-H-O) (Fig. 2c), transforming the C-H hydrocarbons. Thus, evidencing the oxidation and subsequent solubilization promoted by the studied treatments, reducing the oily phase and increasing the content of oxidized compounds in the aqueous phase. Also, Fig. 2c shows the presence of "C, H, N, S" long chain hydrocarbons ($C_6H_{12}OS$) in the initial aqueous phase. However, this compound disappears after the pretreatments, probably due to oxidated S compounds are formed.

The oily sludge initially contains a 30% wt. of TPH in a non-soluble form or adsorbed onto the surface of the solid particles of the oily sludge [22,37], decreasing to 23–10% after the proposed treatments (Table 1). As can be seen, the oxidative treatments (FT and WAO) promote a higher TPH reduction due to the oxidative radicals generated, which breakdown the bindings between TPH and the solid particles of the oily sludge, oxidating the hydrocarbons and promoting its solubilisation into the aqueous phase. Zhao et al. studied a two-step WAO process at different temperatures and using also H_2O_2 as oxidant to reduce the oil content of the oily sludge, achieving a maximum reduction of ca. 2% wt. It is important to note that they used H_2O_2 (270 g/L) as additional oxidant and higher temperature (240 °C), even applying second step of treatment, at the same temperature but reducing slightly the oxidant dosage and the reaction time from 90 to 60 min [23]. Also, Farzadkia et al. studied a Fenton process for reduce TPH of oily sludge with 33% initial content. The highest reduction reported was 35 wt% using a mass ratio of 15:1 H_2O_2 to sludge and an additional source of iron catalyst in the form of $FeSO_4$ [19]. Thus, the oxidative treatments proposed in this work (FT and WAO) reach similar and even higher TPH reduction, requiring lower temperatures and H_2O_2 dosages than other works found in the literature.

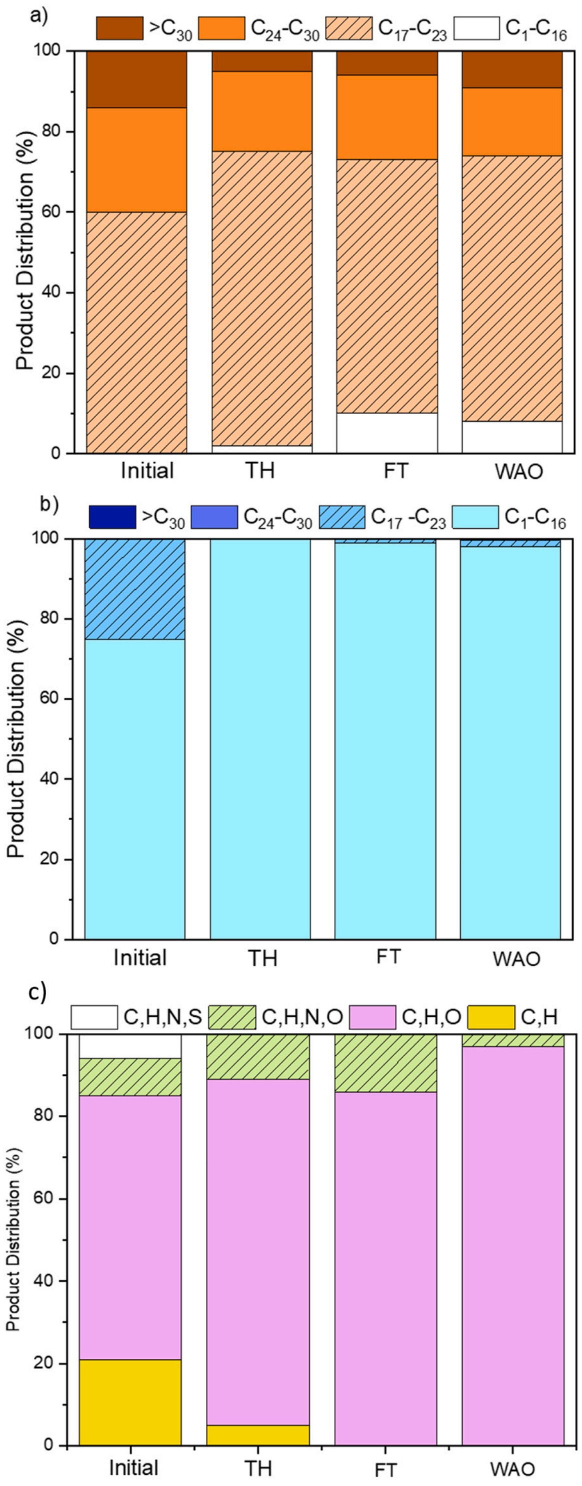

Fig. 2. Product distribution for the oily phase (a) and aqueous phase (b, c) before and after TH, FT and WAO treatments.

Furthermore, a C balance has been performed to show the evolution of the carbon content in each phase. The carbon balance obtained for the initial oily sludge was 356 gC/kg. This content corresponds to 125, 231 and 0.2 gC/kg of the solid, oily, and aqueous phases, respectively. In the case of solid and oily phases, the C content was determined by elemental analysis and for the aqueous phase based on TOC results. The increase of the carbon content in the aqueous phase from 0.2 to 0.8–3.5 gC/kg comes principally from the oily phase, as it is reduced from 231 gC/kg to 156–41 gC/kg, as previously commented and shown in Fig. 2. The oily phase is reduced by means of the cracking and oxidising of the long-chain hydrocarbons to short-chain and oxidised hydrocarbons, being more soluble in the aqueous phase and increasing the carbon concentration. It is also important to note that during these processes, CO_2 is formed due to complete mineralization reactions. These values have been calculated considering the overall carbon balance (data shown in Fig. S1), and obtaining 81, 118 and 199 g C per kg of sludge for the TH, FT and WAO treatments, respectively.

The proposed treatments substantially reduce total solids (TS) in oily sludge, ranging from 51% to 78%. Moreover, they enable the gravitational separation of the previously not separable phases, requiring centrifugation methods, as shown in Fig. S2. The improved settleability was also confirmed by capillarity suction time (CST) measurements. The CST results of TH, FT, and WAO experiments (as presented in Table 1) indicate the enhancement of the dewaterability of the oily sludge. A reduction of this parameter ranging from 84% to 90% was achieved due to the structural changes in the oily sludge [18]. CST reduction for oily sludge was much lower than in previous studies using a Fenton process [21].

Biodegradability assays of the aqueous phase before and after the different treatments were carried out, the results are depicted in Table 1. The initial aqueous phase of the oily sludge presents poor biodegradability (18%). In contrast, the pretreated aqueous phases by TH, FT and WAO containing a large amount of biodegradable organic acids and nutrients evidence a notable increase of biodegradability up to 63%. It should be noted that although the presence of these organic acids and nutrients is more significant for the oxidative treatments, specifically for WAO, this effect is not evidenced for the biodegradability assays, obtaining similar results for all the treatments. This fact might be attributed to the high acid character of the WAO effluent ($pH = 2.1$), high metals concentration or toxic product formation. Fig. S3a shows the concentration of the principal metals in the aqueous phase of the oily sludge before and after each treatment. It is essential to note the solubilisation of some metals into the aqueous phase, principally for WAO treatment. This oxidative treatment produced Al, Ca, and Fe solubilisation at nearly 400 mg/L and Si and Mg at around 200 mg/L. FT treatment also generates solubilisation of Ca, Al and Mg, reducing biodegradability. However, TH treatment practically does not show the release of metals in the aqueous phase. The concentration of these metals in the initial oily sludge was significantly high, with 3.9 g/kg of Fe, 2.1 g/kg of Ca, and 1 g/kg of Al, while Mg and Si present concentrations lower than 0.5 g/kg. So, the solubilisation rate into the aqueous phase after the studied pretreatments represents 9% for the Fe content, 41% of Ca, 38% of Mg, 36% of Si and 44% of Al after the oxidative treatments (FT or WAO), which generates the higher metals solubilisation into the aqueous phase. Furthermore, the recovery rate of valuable inorganics (es: Mg) could add value to the proposed processes and will be further investigated in future works. Also, XRF analysis was determined for the solid phase after the pretreatments, showing a decrease in the total metal content from 34 to 26 wt% after the oxidative treatments (Fig. S3b).

All in all, it has been demonstrated the viability of the processes for the management of a refinery oily sludge as the TPHs, and thus, the oily phase is reduced, increasing the biodegradable compounds in the aqueous phase, breaking down the stable oil-water emulsion, and avoiding the use of centrifugation methods used as actual treatment in the refinery.

3.2. Processes definition and design

The oily sludge generated in the refinery WWTP is currently managed following the scheme shown in Fig. 1(a). The primary oily sludge from the API separator is treated by high-speed centrifugation to recover the hydrocarbon fraction from petroleum refining. The primary sludge from the DAF unit and the biological sludge with a high carbon content is fed to the coking unit. This centrifugation process for the API oily sludge treatment can recover 40–50% of the oil content, and part of the water phase is mixed with the refinery wastewater [29]. However, the remaining residue (solid phase and low-biodegradable water) still needs further treatment due to its toxic composition. The remaining waste is externally managed and commonly disposed of in landfills, with environmental consequences and high economic costs.

Thus, the present work proposes a new refinery scheme depicted in Fig. 1(b) to achieve an integral valorisation of the primary oily sludge from the API separator. For this purpose, the non-oxidative (TH) and oxidative (FT and WAO) treatments studied are now included in this new scheme replacing conventional centrifugation. This approach reduces waste and improves the oily sludge's properties and subsequent valorisation. A gravity settler is incorporated after the proposed pretreatments to isolate the oily sludge phases, which can be valorised and reintegrated into the refinery scheme. The aqueous effluent with higher biodegradability could be recirculated to the biological treatment obtaining regenerated water to use as process water in the refinery. The oily fraction with high hydrocarbon content can be recycled to the refinery plant, as in the current treatment. And lastly, the solid phase can be valorised into added-value porous materials with potential applications as adsorbents and catalysts [4].

Once this new refinery process definition is raised, flow diagrams are established for each treatment, including main and auxiliary equipment and mass and energy balances. Fig. S4 shows the TH flow diagram with an initial storage tank for the oily sludge (C-101), a reactor at 200 °C and 16 bar (R-101), and a gravity settler (C-102) for the phase's separation as the main equipment. Also, pumps and heat exchangers were included, as well as a CO_2 capture system. Similar flow diagrams were depicted for the oxidative treatments. Fig. S5 shows the FT treatment flow diagram, including an H_2O_2 storage tank (C-103) and an auxiliary pump connected to the reactor. Finally, Fig. S6 shows the flow diagram for WAO treatment which needs higher pressure conditions and includes an air compressor (G-101) connected to the reactor inlet stream.

3.3. Economic analysis

This section shows the results corresponding to the Total Capital Investment (TCI), the Total Annualized Costs (TAC), and the unitary cost estimated for the processes under study. Economic analysis was carried

Table 2
Total Capital Investment (TCI), Operation Costs (OC), Amortization Costs (AC), and Total Annualized Cost (TAC).

	TH	FT	WAO
Equipment (€)	51,436	82,385	91,261
Materials (€)	33,433	53,550	59,320
Engineering (€)	38,191	61,171	67,761
Construction (€)	50,921	81,561	90,348
Supervision (€)	8487	13,594	15,058
ISBL (€)	182,468	292,262	323,748
Auxiliary services (€)	7299	11,690	12,950
Interconections (€)	14,597	23,381	25,900
Start-up expenses (€)	6386	10,229	11,331
OSBL (€)	20,436	32,733	36,620
TCI (€)	231,187	370,295	410,189
OC (€/y)	50,871	143,315	60,761
AC (€/y)	21,822	34,953	38,719
TAC (€/y)	72,694	178,268	99,480

out to settle the economic feasibility of each treatment and its potential weaknesses. Table 2 summarises the main items required for the estimation of the TCI, as well as the results of the techno-economic analysis for each advanced treatment. ISBL and OSBL expenses are shown, including their breakdown. The TCIs required were in the range of 232–410 k€ depending on the technology. Considering the installed equipment and associated components, the ISBL investment ranged from ca. 182–324 k€. The OSBL, with 20–37 k€, regards to equipment pieces and associated components supporting the whole ISBL. Data clearly indicated that TH treatment has the lowest capital costs and is the more economic technology for the required investment. The oxidative treatments increase equipment costs because of the additional equipment and higher energy requirements for FT and WAO, respectively.

Techno-economic assessment for a TH process to treat sewage sludge has been reported by other authors [38]. These authors described significant savings (35,000–60,000 €/year), comparing TH with conventional sludge disposal. Other authors reported similar costs for a Fenton process applied to pharmaceutical wastewater, in which the annual operation costs were slightly higher (542,000 €/year), and the annual amortisation costs were stablished in 42,000 €/year, reporting, the significant expenses of the hydrogen peroxide required [39]. Also, techno-economic assessment of a WAO process has been reported [40], applied to sewage sludge. These results show that this technology saves on sludge disposal and has lower material and reagent consumption, demonstrating that WAO are more profitable.

The installed equipment in the ISBL concept included the elements necessary to treat and valorise the oily sludge from the API separator. As shown in Fig. 3(a), the reactor (21.6 k€) and heat exchanger (20.6 k€), costs were the highest for the TH, with 42% and 40% of the total equipment, respectively. FT treatment needed a high volume of H_2O_2 and, therefore, a large storage tank which supposes 38% of total costs (31.3 k€), followed by the reactor (30%, 24.7 k€). WAO treatment required the highest equipment costs due to the high-pressure requirements, significantly increasing the reactor costs, representing more than half of the total equipment costs (64%; 58,535 €). The rest of the equipment (settler, pumps, air compressor, and sludge storage tank) represented a minimum expense of the total costs for all the cases.

Fig. 3(b) includes each treatment's operating costs (OC) breakdown, showing the electricity, staff, maintenance, and reagent expenses. The staff costs represented 79% and 66% of the total costs for the TH and WAO treatments, being the electricity and maintenance a minor cost. In the case of FT treatment, the use of reagents supposed to be a significant cost (81.6 k€/year; 57%) due to the high costs of H_2O_2 [31,32], followed by the staff costs (28%). Therefore, the FT oxidation treatment implied the highest OC (143.3 k€/year) due to the use of expensive H_2O_2, which is almost three times lower for TH and WAO (50.8 and 60.8 k€/year, respectively).

Amortisation costs were in line with TCI. Hence, calculated TAC indicated that the most expensive treatment was FT, followed by WAO, and finally TH (Table 2), with unitary cost of 78 €/m^3, 107 €/m^3 and 192 €/m^3 for TH, WAO and FT, respectively. These results must be compared with the unitary costs of the current management of the oily sludge to prove its feasibility.

The current treatment scheme for API oily sludge is based on high-speed centrifugation pretreatment for the oil recovery, followed by the external management of the remanent sludge, which can suppose around 50% of the total operating cost of a WWTP [41]. Despite its environmental consequences, landfilling is the most common way to dispose of sludge. Spanish estimations for sewage sludge disposal determine a cost ranging from 70 to 350 €/ton, depending on its composition, moisture, and distance to the landfill [42]. Moreover, it is important to note that the centrifugation pretreatment costs must also be considered. Other authors indicate that the overall thermal dewatering, transportation, and landfill costs for sewage sludge suppose 250 $/ton of dry solids, excluding the electricity and natural gas costs [41]. Thus, the techno-economic analysis developed in this work for the TH, FT and WAO treatments evidenced its economic feasibility compared with the

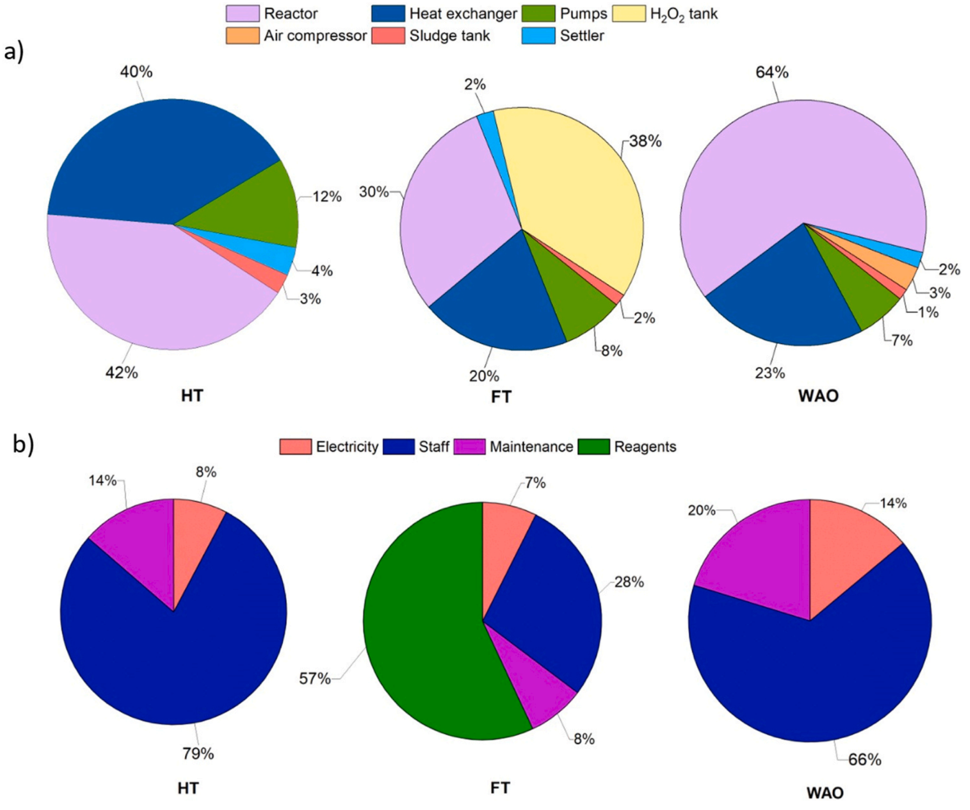

Fig. 3. Distribution of equipment (a) and operation (b) costs for TH, FT and WAO treatments.

current management for the oily sludge from API separators, being these costs, at least, 4.5 (TH), 3.3 (FT) and 1.8 (WAO) times cheaper than current technologies.

However, the comparison among the different technologies must be based not only on economic issues but also on the effectiveness of these treatments. The oxidative treatments reached higher solid and TPH reductions in the oily sludge, maximising carbon, and nutrient solubilisation within the aqueous phase. In contrast, the non-oxidative treatment (TH) implied lower unitary cost but also, lower TS and TPH reduction and an aqueous phase with limited loading of carbon and nutrients. Thus, the recovery strategy for each phase after treatment must be carefully studied to propose a treatment that considers the efficiency and cost of each process. Moreover, although solids removal is high, the costs of management or valorization of the solid fraction must be taken into account. Considering the TS reduction, the management by landfill of this fraction could suppose additional OC of 14% for TH, 2.5% and 6% for FT and WAO treatments, respectively. In any case, these costs are still lower than the current ones.

Hence, the TH can be a suitable low-cost treatment yielding a biodegradable effluent which can be treated directly in the conventional activated sludge of the refinery. In contrast, if we are thinking of recovering carbon and nutrients in advanced biological processes, WAO could be a more suitable alternative.

4. Conclusions

The TH, FT, and WAO treatments proposed in this study for oily sludge valorisation effectively degraded total petroleum hydrocarbons into simpler molecules, resulting in the oxidation and solubilisation of more biodegradable compounds in the aqueous phase, as evidenced by the increase in TOC, SCOD, nutrients, and biodegradability up to 63%. These treatments also significantly reduced TS and TPH content, reducing waste volume. Additionally, the treatments broke down the emulsion of phases, enabling gravitational separation and avoiding the costly centrifugation operation. In this way, the pre-treated sludge can be easily valorised by: i) recycling the oil fraction into the refinery, ii) treating the biodegradable aqueous phase in the refinery WWTP iii) using the solid phase for the synthesis of porous carbonaceous materials. A conceptual design based on experimental data obtained at the bench scale experiments has been developed for the three processes under study. Techno-economic analysis of the three advanced treatments reveals that their unitary costs range from 78 €/m^3 for TH to 192 €/m^3 for FT. These treatments have operational costs in the low range of the current management cost (70–350 €/ m^3), proving their feasibility. However, the bottlenecks of oxidative treatments are the high pressure and temperature required for WAO and the high cost of hydrogen peroxide in FT. However, WAO achieves higher solid (71%) and TPH reduction (80%) in the oily sludge, with more concentration of carbon and nutrients solubilised in the aqueous phase (TOC= 5 g/L; SCOD = 17 g/L) which might be of interest for their recovery in advanced biological processes.

CRediT authorship contribution statement

Sara Jerez: Writing – original draft, Validation, Investigation, Formal analysis, Writing – review & editing. **Maria Ventura:** Validation, Investigation, Formal analysis, Writing – review & editing. **Fernando Martínez:** Writing – review & editing, Project administration, Funding acquisition. **Juan Antonio Melero:** Conceptualization, Methodology, Formal analysis, Writing – review & editing, Funding acquisition, Supervision. **M. Isabel Pariente**: Conceptualization, Validation, Investigation, Formal analysis, Data curation, Supervision, Validation, Writing – review & editing.

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.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.110730.

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