APPLICATION OF AN AUTOCATALYTIC FENTON PROCESS FOR THE PRE-TREATMENT OF AN OILY SLUDGE: A SUSTAINABLE MANAGEMENT FOR REFINERY WASTES

S. Jerez, M. Ventura, R. Molina, F. Martínez, M.I. Pariente*, J.A. Melero

Department of Chemical and Environmental Technology, Rey Juan Carlos University, Mostoles, 28933, Madrid, Spain.

Abstract

The feasibility of a Fenton-type process for the pre-treatment of an oily refinery sludge has been explored to reduce total petroleum hydrocarbons (TPHs) with the enhancement of the organic solubilisation in the liquid phase. The maximum solubilisation of the oily sludge reached 1624 mg/L of TOC and 1253 mg/L of acetic acid at the higher temperature (80 ºC) and with a hydrogen peroxide initial concentration of 90 g/L. High concentrations of nitrogen and phosphorous species (250 and 11 mg/L, respectively) were also released in the aqueous phase after oxidation. Respirometry assays of the aqueous phase have evidenced an increase in its biodegradability with the Fenton pre-treatment. Moreover, ca. 58 wt.% of TPHs reduction was also obtained after Fenton pre-treatment yielding a sludge with a better settleability. This study provides an interesting approach to treat oily sludge improving its dewaterability, decreasing TPHs contents, and increasing the concentration of biodegradable carbon and nutrients in the aqueous phase for further biological treatment.

Keywords: oily sludge disintegration, Fenton, TPH reduction, biodegradability, organic solubilisation, settleability.
INTRODUCTION

Nowadays, the refinery industry generates huge amounts of hazardous wastes during the petroleum refining processes [1,2]. Oily sludge is produced at crude oil tank bottoms, slop oil emulsions, oil/water separators, and on-site wastewater treatment plants [3,4]. Due to its hazardous composition, the improper disposal of oily sludge leads to serious environmental risks, such as soil, groundwater and air pollution [5]. Therefore, the development of technologies to treat and valorise it properly within the framework of circular economy and sustainability is currently highly required [2].

Oily sludge is a stable emulsion, usually composed of three different phases: oily, aqueous, and solid. The stable oil-water-mud emulsion of oily sludge makes it difficult to demulsify and limits the efficiency of solid-liquid separation [6]. The oily phase presents a high percentage of carbon content, due to the presence of petroleum hydrocarbons, such as n-alkanes, cycloalkanes, aromatics, asphaltenes, or resins, among others [5]. The solid phase contains carbonaceous and inorganic material, with a high concentration of heavy metals (principally iron), and the aqueous phase usually shows a low presence of nutrients and carbon concentration [7].

Currently, several technologies have been developed with the aim of recover and reuse the valuable oily phase such as solvent extraction [8] or freeze-thaw [3]. Moreover, some disposal methods -incineration or stabilization/solidification [1]- have been also proposed to manage the oily sludge. Nevertheless, these technologies do not avoid the environmental risk associated with oily sludge, so the development of new novel strategies is still required. Accordingly, different valorisation strategies have been proposed taking into account its composition [7].

High sludge reduction effectiveness may be obtained through chemical oxidation treatments [6] such as advanced oxidation processes (AOP). Fenton oxidation is a well-known AOP for the removal of harnessing pollutants with the simultaneous presence of hydrogen peroxide and ferrous salt [9]. The process consists in the decomposition of H₂O₂ into •OH radicals, in the presence of an iron catalyst, performing the non-selective oxidation of organic compounds. The Fenton process has inherent advantages since it is easy to operate, needs low energy requirements, reaction time and operational costs, as compared to other oxidation processes [2]. However, a major drawback arises when treating a large volume of oily sludge, as the oxidation may require a large number of chemical reagents. Nevertheless, the oily sludge contains a high concentration of iron, which makes unnecessary the addition of a catalyst to promote Fenton reactions, and consequently reducing the operational costs. It was reported that many metal components could act as a catalyst to trigger the chain oxidation reactions associated with the Fenton process [10]. Many metals, such as Fe, Al, Ca, Cu, Zn, have been found in oily sludge and might act as a source of catalyst for Fenton-like reactions [11]. However, up now, this autocatalytic treatment for oily refinery sludge has not been reported in the literature.

There are a lot of benefits to using a Fenton pre-treatment for oily sludge. First of all, it has been demonstrated that dewaterability is improved [12]. Dewatering is necessary to decrease the high volume of oily sludge, but conventional physical treatments are limited in their efficiency and required further mechanical equipment, resulting in poor applicability in the industry. Moreover, use chemical conditioners in the dewatering chemical process could significantly increase the final sludge volume, producing uneconomical properties in industrial applications [13]. Secondly, Fenton oxidation treatment can remove harnessing pollutants, especially those who are difficult to degrade by microorganisms, such as the removal of organic compounds from oily sludge [14]. Farzaddock et al. reported that the Fenton process allows a Total Petroleum Hydrocarbon (TPH) reduction degree of 36 wt.% [15]. Typical final products in the uncompleted mineralization of organic pollutants (short-chain carboxylic acids like oxalic, acetic or malonic) are oxidation products of larger molecules after fragmentation, yielding biodegradable products, together with the destruction of the initial toxic or inhibitory species [16]. Consequently, the Fenton process is an alternative as pre-treatment to degrade organic compounds and increase biodegradability, followed by a biological process, making a combined treatment sustainable and economically attractive [17]. Finally, the hydroxyl radicals can disrupt sludge flocculation and lead to a massive release of compounds to the aqueous phase, including carbohydrates and volatile fatty acids (VFA) [6]. In this way, the organic matter in sludge can be applied as a rich carbon source for subsequent biological processes.

Up to now, the Fenton process has been evaluated for the treatment of an oily sludge but only focused on its capacity to increase dewatering [12,18] or TPH reduction [2], but without the evaluation of the treatment on the whole phases. Thus, the novelty of this work is the evaluation of an autocatalytic Fenton oxidation
process for the treatment of an oily sludge to 1) break down the stable oil-water-mud emulsion and improve the solid-liquid separation, 2) solubilise the oily sludge, decreasing its hydrocarbon content, and 3) release of biodegradable organic matter into the aqueous phase. To evaluate the effectiveness of the process, different hydrogen peroxide concentrations and operation temperatures were considered.

MATERIALS AND METHODS

Source of oily sludge

The oily sludge used in this work was collected from an API separator placed in a petroleum refinery wastewater treatment plant, located in Spain. Oily sludge was stored at cold temperature (4 °C) to keep it at adequate conditions. Oily sludge was formed by three phases, and the relative content of each was 34, 41 and 25 % for oily, aqueous and solid, respectively.

The main sludge characteristics used in the experiments are presented in Table 1. The oily sludge had a high concentration of organic matter in the form of Total Carbon, Total Petroleum Hydrocarbons (TPHs), and Total Kjeldahl Nitrogen (TKN). Although, Soluble COD, Total Organic Carbon (TOC), TKN, and P concentration measured in the aqueous phase was very low. Fe (4 g/kg), Ca (2 g/kg) and Al (1 g/kg) were the predominant metals with others in much less concentration.

Table 1. Macroscopic characterization of the oily sludge.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Carbon (g/kg)</td>
<td>357 ± 35</td>
</tr>
<tr>
<td>Total Solids (g/kg)</td>
<td>94 ± 15</td>
</tr>
<tr>
<td>TPHs (%)</td>
<td>26 ± 2</td>
</tr>
<tr>
<td>TKN (gN/kg)</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>Soluble COD (g/L)*</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>TOC (g/L)*</td>
<td>0.40 ± 0.05</td>
</tr>
<tr>
<td>TKN (mgN/kg)*</td>
<td>69 ± 41</td>
</tr>
<tr>
<td>P (mg/L)*</td>
<td>0.7 ± 0.2</td>
</tr>
</tbody>
</table>

*in the aqueous phase

Fenton experiments

Fenton experiments were carried out under magnetic stirring (500 rpm) in a non-pressurised glass reactor with a refrigerant pipe to condensate the by-products. Typically, a glass flask was filled with 50 mL of the studied oily sludge, then a certain amount of hydrogen peroxide (H2O2) was added, and thereafter the flask was introduced into an oil bath at the desired temperature, monitoring the inner temperature. The reaction time, for all experiments, was two hours without the addition of an iron catalyst. The initial pH was set at natural (ca. 7.5) and a value of 3. Reactions were carried out using different hydrogen peroxide concentrations (90, 45 and 20 g/L) and temperatures (25, 40, 60 and 80 °C).

Analytical methods

After the Fenton reaction, Total Petroleum Hydrocarbons (TPHs) of the pre-treated oily sludge were measured following the procedure described elsewhere [7]. Moreover, phases were separated and individually analysed. These phases were extracted and isolated following the protocol described in previous work [7]. The oily and aqueous phases were analyzed by GC/MS (Gas Chromatography coupled
Total Organic Carbon (TOC) in the aqueous phase was measured using a combustion/nondispersive infrared gas analyser model TOC-V CSH (Shimadzu). Soluble Chemical Oxygen Demand (SCOD) was measured following AWWA-APHA Standard Methods 2540E. 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 metals was measured with an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) using a Varian Vista AX spectrometer. The biodegradability tests were performed, at room temperature, in a LFS (liquid-flow-static) respirometer based on a magnetically stirred vessel of 1 L inoculated with biomass taken from an urban wastewater treatment plant located at Mostoles (Madrid). The biomass concentration for all the batch respirometric experiments was 927 ± 1 mg VSS/L. A detailed description of the procedure can be found elsewhere [19].

RESULTS AND DISCUSSION

Oily sludge solubilisation by Fenton pre-treatment

Fenton oxidation can solubilize the particulate component of the sludge, as the organic matter is released and solubilized during the disruption of the sludge floc [20] and oily phase. In our work, the oily sludge solubilisation experiments were conducted in the range of 25-80 °C for 2 hours and different initial H$_2$O$_2$ concentrations (20-90 g/L) using a Fenton-like process. Moreover, the oxidation treatment was carried out under natural pH (ca. 7.4) and taking advantage of the iron content in the oily sludge and hence without an acidification step and the addition of iron catalysts.

Carbon solubilisation in the aqueous phase was monitored through the measuring of TOC concentration before and after the different Fenton experiments (Figure 1a). TOC concentration increased with the increase of the H$_2$O$_2$ concentration, from 400 mg/L (aqueous phase in the untreated sludge) to 600 and 1100 mg/L (at 25 °C), and from 910 to 1624 mg/L (at 80 °C). Blank experiments in absence of oxidant at 80 °C yielded negligible carbon solubilization. Increased dose of hydrogen peroxide resulted in higher production of hydroxyl radicals to attack the floc structures and promote the release of organic matter resulting in a raised TOC concentration. A similar trend has been reported for the dewatering of oily sludge using Fe(II)-activated persulfate oxidation [21]. However, a more pronounced upward trend of solubilisation was reported in our study using a Fenton-like process instead of persulfate oxidation. Higher H$_2$O$_2$ concentrations (180 g/L) were evaluated and discarded as the high hydrogen peroxide concentration promotes the generation of scavenging reactions between H$_2$O$_2$ and hydroxyl radicals leading to water and less active perhydroxyl radicals (and a negligible effect over the TOC concentration).

The effect of the temperature on TOC solubilisation was also investigated at 25, 40, 60 and 80 °C. It is generally believed that the Fenton reaction is accelerated by the increase of the temperature [22] but the effectiveness of the Fenton-driven degradation of organic molecules may be affected due to the decomposition of H$_2$O$_2$ under high-temperature conditions. Qin et al. found potential loss of H$_2$O$_2$ due to elevated temperature applying Fenton-like processes for the treatment of long-chain petroleum hydrocarbons [23]. Hence, the right choice of temperature is crucial to enhance the effectiveness of the oxidation. Data in Figure 1a evidence that the increase in the working temperature had a positive effect on the TOC solubilisation for all the oxidant tested concentrations within the studied temperature range.
Approximately, 1624 mg/L of TOC was solubilized for the highest temperature (80 °C) and oxidant loading (90 g/L) with an H₂O₂ conversion higher than 98 %. The production of soluble TOC from partial oxidation of an oily sludge has the potential to provide a carbon source for further biological treatment and it might lead to substantial cost savings [20]. Many researchers have studied the solubilization of sewage sludge by Fenton reagent [24] but it is not so common for oily refinery sludge, and what is even more significant, without the addition of iron and acidification.

The organic composition of the aqueous phase was also explored by analysing the presence of carboxylic acids as final organic compounds in Fenton degradation processes [25]. Fig. 1b shows the concentration of acetic acid in the aqueous effluent after Fenton pre-treatment for the different conditions. It is worth noting that acetic acid concentration enhanced with the increase of temperature and H₂O₂ loading, accounting approximately for 30 % of the total TOC in the liquid phase [26]. Other VFAs (e.g., acetic, butanoic, formic and propionic acids) were also detected in the GC/MS chromatogram, although some of them such as butanoic and formic were not detected for the highest temperatures. As the main amount of VFAs, the concentration of acetic acid increased from 77 to 1253 mg/L at 80 °C and using 90 g/L of hydrogen peroxide. Sun et al. reported a concentration of acetic acid of 590 mg/L (from an initial concentration of 99 mg/L) applying an ozonation process to oily sludge [6]. Thus, comparing both treatments, the Fenton process proposed in this work doubles the concentration of acetic acid in the aqueous effluent, producing a higher biodegradable effluent for a further combination with biological treatment, as acetic acid is considered a readily biodegradable carbon source.

According to those results, the variable that mainly influences on sludge solubilisation was the concentration of the initial H₂O₂. Thus, the rest of the characterization of the oily sludge through Fenton pre-treatment was determined only for those reactions carried out with 90 g/L of H₂O₂ under the range of temperatures from 25 to 80 °C.

Additional experiments were performed at a pH value of 3 as it was reported that low pH conditions favoured the oxidation of organic hydrocarbons [27]. However, the effect of the pH on the TOC solubilisation was negligible, yielding the same results to those obtained in the absence of the acidification step regardless of the temperature (ca. 1720 mg/L). Our results are in line with those reported by Watts et al. where the oxidation of the aliphatic compounds proceeded more effectively at near-neutral pH [27].

Pre-treatment has also led to an increase in the concentration of dissolved nutrient species as shown in Table 2. After Fenton pre-treatment, higher nitrogen and phosphorous concentrations were measured in the liquid phase as compared to that presented in the raw sludge. Total P and TKN concentrations almost increased by an order of magnitude independently of the working temperature. Nitrogen release due to the
oxidation with Fenton reagent of a diesel contaminated soil has been documented previously reaching concentrations of 175-202 mg/kg [28]. The ratio between dissolved C and N of approximately 6.5:1 fits well into the results of previous studies on the degradation of contaminated soils by Fenton reagent [28]. Thus, Fenton oxidation resulted in the release of carbon, nitrogen, and phosphorous species into the aqueous phase, with possible effects for its subsequent biological treatment.

Table 2 Nutrients release and biodegradability of the aqueous effluent, and reduction of TPH in oily sludge through Fenton process using 90 g/L of H2O2 at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>25 °C</th>
<th>40 °C</th>
<th>60 °C</th>
<th>80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TKN (mg/L)</td>
<td>69 ± 41</td>
<td>248 ± 39</td>
<td>240 ± 58</td>
<td>250 ± 51</td>
<td>297 ± 55</td>
</tr>
<tr>
<td>P (mg/L)</td>
<td>0.7 ± 0.2</td>
<td>11 ± 1</td>
<td>11 ± 1</td>
<td>7 ± 1</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>Biodegradability (%)</td>
<td>18 ± 10</td>
<td>30 ± 9</td>
<td>31 ± 12</td>
<td>49 ± 1</td>
<td>33 ± 2</td>
</tr>
<tr>
<td>TPHs (wt. %)</td>
<td>26 ± 3</td>
<td>11 ± 1</td>
<td>10 ± 1</td>
<td>10 ± 1</td>
<td>11 ± 1</td>
</tr>
</tbody>
</table>

Biodegradability assays of the aqueous effluent under the different reaction conditions were carried out being the results depicted in Table 2. It is expected that the Fenton process can effectively improve the biodegradability of the aqueous phase of the oily sludge because of the increasing of short-chain carboxylic acids (mainly acetic), coming from the oxidative degradation of aliphatic hydrocarbons [20]. The low concentration of organic acid intermediates in the aqueous phase of the un-treated oily sludge resulted in poor biodegradability (18 %). In contrast, the pre-treated samples containing a larger amount of biodegradable organic acids in the aqueous phase evidenced a gradual increase of biodegradability with the increase of temperature (from 18 % to 49 %). Some authors proposed this hypothesis [6], but up to now, it has not been demonstrated with biodegradability assays. Surprisingly, for the highest temperature (80 °C) a decrease of the biodegradability was evidenced which could be attributed to the presence of recalcitrant components, detected by GC/MS analyses, such as amides, some pyrrol, and benzene compounds, which were not detected, or in less concentration, at lower reaction temperatures. In addition, the concentration of Al and Fe were higher (increment of 11 and 80 % respectively), in the aqueous effluent at 80 °C than for lower temperatures, which could inhibit the microorganism growing. These both facts could contribute to the decrease in the biodegradability observed for higher temperatures.

Fig. 2 illustrates the distribution of the compounds detected by GC/MS in the aqueous phase. Data in Fig. 2a shows the evolution of hydrocarbons distribution with the temperature. As can be seen, the aqueous phase of the initial un-treated sludge was formed exclusively by hydrocarbons of a low number of carbons (< C24), being predominately < C17 (70 %). Moreover, as can be seen in Fig. 2b, most of them (75 %) were oxygenated hydrocarbons, but some were aliphatic (15 %), and the rest (10 %) corresponded to other types of hydrocarbons with S or halogens in their structure. During the Fenton pre-treatment, the degradation of hydrocarbons with high molecular weight (> C17) to hydrocarbons of lower molecular weight (C1-C18) was evidenced (Fig. 2a) even at the lower temperature. At the same time, hydrocarbons were transformed into oxidised compounds after chemical oxidation (Fig. 2b). The percentage of oxidized compounds increased progressively with the reaction temperature up to be almost the whole fraction at 80 °C. Hydroxyl radicals could convert macromolecular organics in the oily sludge into biodegradable and hydrophilic organic compounds by promoting the insertion of O groups into the components [6]. This is also confirmed due to a higher ratio between TOC and COD (from 0.3 to 0.6-0.7), indicative of more oxidized compounds containing less COD per gram of carbon [28].
Hence, the Fenton pre-treated aqueous effluent contained a large amount of biodegradable organic acids, which could serve as a useful source of carbon for the microorganism in the biological treatment. Acetic acid concentration increased rapidly with the temperature and hydrogen peroxide concentration, whereas the higher biodegradability was obtained at a temperature of 60 ºC. In consideration of the above results, hydrogen peroxide concentration of 90 g/L and a temperature of 60 ºC were suitable conditions for sludge solubilisation yielding a biodegradable aqueous effluent.

**TPHs reduction by Fenton pre-treatment**

Table 2 presents the TPH concentration using the Fenton pre-treatment under different temperatures and high oxidant concentration (90 g/L). The initial TPH mass percentage in the untreated oily sludge was 26 wt. %. After the Fenton process, the remaining TPH was ca. 10 wt. %. However, the temperature did not improve TPH reduction in the range of the studied temperatures. TPHs are adsorbed on soluble and colloidal matters in oily sludge, hydroxyl radicals might unlock the tight binding between TPH and sludge organic, which results in the release of the oxidized TPH to the aqueous phase as evidenced by the TOC increase (Figure 1). Zhang et al. studied three advanced oxidation processes to reduce petroleum hydrocarbons in oily sludge achieving a reduction of ca. 14 % [25]. It is important to note that they used higher hydrogen peroxide concentrations ranging from 80 to 320 g/L and an extra source of iron catalyst in form of FeSO₄. The lower TPHs reduction observed could be explained by the higher initial TPHs concentration (61 %) which could hinder the interaction of hydroxyl radicals with the TPHs of the sludge [25]. On the other hand, Zhang et al. obtained a TPHs reduction of 88 wt. % using a hybrid ultrasound and Fenton process, but with a high dilution of the raw oily sludge (1/50) [11]. When the initial sludge content is high, the viscosity of the bulk liquid also increases, making more difficult the diffusion of the hydroxyl radicals. However, this high dilution degree makes the process not feasible for scale-up from an economical and technical point of view. The autocatalytic Fenton process proposed in this work taking advantage of the high iron content in the sludge seems to be beneficial for the reduction of the TPHs compared to other works found in the literature.

Figure 3 shows the distribution of the petroleum hydrocarbon fractions in oily samples after the Fenton pre-treatment at different operating temperatures detected by GC/MS analysis. Results indicated that the oily phase consisted of a variety of components with different molecular weights (Figure 3a) and structures (Figure 3b). The oily phase of the un-treated oily sludge was formed by aliphatic hydrocarbons (100 %) of high molecular weight (> C₁₇). It can be found that different distribution of TPHs fractions was obtained after Fenton treatment at different temperatures. Lower molecular weight hydrocarbons (C₁-C₁₆ fraction) were not presented in the untreated oily sludge and they increased gradually with the temperature up to 40 ºC. After this temperature, the C₁-C₁₆ fraction was gradually decreasing due to the degradation towards
lower molecular weight molecules (mainly carboxylic acids) which were solubilized in the aqueous phase (Figures 1) [28]. A similar trend was shown for the C_{17}-C_{24} fraction having a low presence of those samples treated at 60 and 80 °C. However, long-chain alkanes (> C_{24}) had strong chemical resistance, which has been reported in the previous literature [11,23]. Thus, this fraction was predominant at higher temperatures as the low molecular weight hydrocarbons were partially degraded and released to the aqueous phase. Moreover, as can be seen in Figure 3b, 30% of the aliphatic compounds were oxidized at 25 °C, and the rest (70%) were still dissolved into the oily phase. However, higher Fenton pre-treatment temperatures could result in the thermal scission of C-C bonds of the oxygenated molecules, as product distribution shows (Fig. 3a), which was dissolved into the aqueous phase, remaining in the oily phase only aliphatic hydrocarbons (89-99%) of high molecular weight.

![Figure 3](image)

**Fig. 3** Hydrocarbon product distribution based on the number of carbon atom (a) and components (b) in the oily phase of the oily sludge after Fenton pre-treatment.

Thus, it can be concluded that the Fenton pre-treatment could convert the remaining hydrocarbons into compounds with lower molecular weights and greater water solubility by oxidising the alkanes, being preferentially dissolved into the aqueous phase, and reducing the TPHs content by 58 wt. %.

**Solid transformation by Fenton pre-treatment: Carbon balance**

To further confirm the changes in the solid during the treatment of the oily sludge, FTIR was employed to study the structure of certain components in the solid phase of the sludge before and after the process. Fig. 4 shows that the solid was almost the same before and after the Fenton pre-treatment although some slight differences could be observed. The wavebands at 3300 cm\(^{-1}\) were maintained, indicating the presence of -OH sites. The wavebands at 2900, 2850, and ca. 1450 cm\(^{-1}\), corresponding to alkanes were preserved before the pre-treatment. However, the waveband at 1315 cm\(^{-1}\) disappeared, which could indicate that some alkanes have been removed from the oily sludge after the process. The stretching vibration of the C=O group (1736 cm\(^{-1}\)) was slightly detected after the pre-treatment, whereas it was not observed in the raw sludge. This could evidence that the oxidation was occurring during Fenton pre-treatment [29]. The waveband of C=C near 1620 cm\(^{-1}\) decreased during the Fenton process. This illustrates that hydroxyl radicals attacked the unsaturated structures. In the range of 1200 to 800 cm\(^{-1}\), attributed normally to C-C, C-O, and C-N bonds, although the composition was complex and difficult to identify, were similar. The absorption wavebands at 460–780 cm\(^{-1}\) correspond to the stretching vibration of O–Si–O in SiO\(_2\) previously detected by DRX [7]. Similar results were found by other authors applying an ultrasound process [30]. However, Sun et al., found more differences applying an ozonation process as the IR analysis was performed of the whole residue, implying more signals reduction by the TPHs on the oily phase than by the solid [29].
The carbon content of the solid phase was determined by elemental analysis of the extracted solid before and after the Fenton pre-treatment at 60 °C and 90 g/L of hydrogen peroxide initial concentration. The initial solid phase was formed by an organic phase corresponding to 50 wt. % in C. After the Fenton pre-treatment, the C content was maintained in the same value of ca. 53 wt. %. Though more differences were found in the oily phase, as the C content was reduced from 68 to 50 wt. %. Thus, Fenton pre-treatment caused the release of carbon from the oily to the aqueous phase at the same time that produced a loss of TOC converted to CO$_2$ (ca. 27 % of the initial carbon concentration). These results further supported the hypothesis that Fenton can oxidize the TPHs into biodegradable components, and part of the released organic matter was mineralized to CO$_2$ [6].

**Oily sludge disintegration and settleability**

The physical appearance of the sludge changed before and after the pre-treatment as shown in Fig. 5. The raw oily sludge sample was very viscous and black, similar to crude oil. Whereas after being treated by the autocatalytic Fenton process at the optimum conditions obtained in this study (60 °C and 90 g/L), the oily sludge was easily settleable and the three phases were perfectly differenced. Therefore, hydroxyl radicals generated facilitated the decomposition of the oily sludge destructing the emulsification structure [6]. As can be seen after the pre-treatment a conventional sedimentation process could be applied for dewatering the sludge and further treatment of the oily and solid phases.
CONCLUSIONS

This paper has studied the effects of the Fenton oxidation in the degradation of TPHs contained in an oily sludge, and its solubilisation in the aqueous phase and with further settleability of the sludge. The conclusions drawn from this study can be summarized as follows:

1) The Fenton pre-treatment was able to break down the stable oil-water emulsion and improve the solid-liquid separation. The enhancement in the settleability was visually evidenced after the pre-treatment.

2) Under the conditions of natural pH, 90 g/L of H$_2$O$_2$ dose, and 80 °C, 58 wt. % of the TPHs content of initial untreated sludge were decreased. At the same time, the TOC solubilisation in the aqueous increased up to 1600 mg/L, where ca. 31 % corresponds to acetic acid, which can be served as a carbon source for microorganisms.

3) Respirometry assays demonstrated the enhancement of the biodegradability of the aqueous phase when the oily sludge was pre-treated with the autocatalytic Fenton system under optimized conditions (90 g/L of H$_2$O$_2$ dose and 60 °C).

Overall, the present study demonstrates the technical feasibility of the Fenton oxidation for the treatment of and oily sludge, thereby providing an alternative option for sustainable management of this hazardous waste.


Funding This work was supported by the Ministry of Research and Innovation of Spain through the project (CTM2017-82865- R) and the Regional Government of Madrid through the project REMTAVARES-CM (52018 / EMT-4341).

Data Availability The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations Ethical approval and consent to participate
Ethics approval and consent to participate Not applicable
Consent to publish Not applicable
Conflict of interest The authors declare no competing interests.

REFERENCES

[3] G. Hu, J. Li, H. Hou, A combination of solvent extraction and freeze thaw for oil recovery from


