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Treatment of petroleum oil spill sludge using the combined ultrasound and Fenton oxidation process

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ABSTRACT

In this paper, advanced oxidation process (AOP) combining ultrasound (US) and Fenton's process was proposed for the treatment of total petroleum hydrocarbons present in oil spill sludge. The effect of several parameters like pH, ultrasonic power, weight ratio of hydrogen peroxide to iron [H_2O_2/Fe^{2+}], Fenton reagent dosage, addition of salts and contact time were analyzed for the reduction of Petroleum Hydrocarbons (PHCs) in terms of hydrocarbon fractions (nC7–C10, nC11-C20). Chemical characterization of oil spill sludge was analysed by gas chromatography- mass spectrum (GC–MS) Elemental analyser, Fourier Transform Infra Red (FT-IR) Analyser and particle size analyser. Experiments were conducted for identifying the wide range of hydrocarbons fractions (nC7–C10, nC11–C20 and nC21–C30). Results shown that maximum solubilisation and PHC removal rate of up to 84.25% could be achieved at a pH of 3.0, sludge/water ratio of 1:100, ultrasonic power of 100 W with 40–50% ultrasonic amplitude, a H_2O_2/Fe^{2+} weight ratio of 10:1, and an ultrasonic treatment time of 10 min. The lower and medium fractions (nC7–C10, nC11–C20) were amenable to degradation due to ultrasound treatment compared to the heavier carbon fraction (nC21–C30). The study concludes that the combined sono-Fenton (SF) process significantly enhanced the degradation of oil spill sludge as compared to ultrasound treatment and Fenton oxidation alone. The enhanced solubilisation achieved by US alone is highly beneficial when we couple this with biodegradation which will be greatly facilitated by the enhanced solubility.

1. Introduction

Petroleum sludge possesses a complex composition of various toxic hydrocarbons legally classified as hazardous waste [16]. These petroleum hydrocarbons include long-chained alkanes and alkenes, polycyclic aromatic hydrocarbons (PAHs), resins and asphaltenes [47]. Due to its complex nature and high concentrations of heavy oil fractions, disposal of oil sludge without adequate treatment can cause serious threat to human health and environment [8]. Bioremediation is the most commonly used method to treat oil sludge and oil-contaminated soil. However, it necessitates a sequential treatment process to handle recalcitrant compounds that may take months or years to attain the permitted clean up level [33,13]. Hence it is mandatory to employ another potential treatment process for rapid and efficient remediation of petroleum hydrocarbons. Advanced Oxidation Processes (AOP) had proved to be highly effective for the destruction of a wide range of recalcitrant compounds. AOP treatment methods generate a large amount of hydroxyl radicals (•OH) and subsequently oxidize the organic pollutants. Different AOPs like Fenton, Photo Fenton, Electro Fenton, Photo catalysis and Ozonation were employed to treat wide range of pollutants. But treatment of petroleum sludge with above processes were limited due to the amount of solids present in the sludge. The percentage of solids limit the mass transfer rate and rate of reaction. Ultrasound processes are limited by high energy and low mineralization rate [14,19]. But, it shows higher performance in heterogeneous catalytic systems by decreasing mass transfer resistances and provide higher surface area by means of fragmentation of catalyst. Hydrophobic chemicals like petroleum sludge with high vapour pressure have been exposed to thermal decomposition inside the cavitation bubbles. Higher amount of OH radicals are ejected in the bulk phase due to collapse of cavities. To increase the OH radical concentration in the bulk solution, Fenton and sonolysis can be combined together to utilize the advantages of each technique [18,10]. Individual AOP may not result in high degradation efficiency but a combination of these individual AOPs might complement one another. Introduction of Ultrasound during treatment enhances the Fenton process, that is, continuous reduction of Fe^{3+} to Fe^{2+} is observed, thereby enabling the reaction to start again using the regenerated Fe^{2+} [4].

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Fenton's process is one of the AOP technologies that uses Fe^{2+} catalyst and hydrogen peroxide (H_2O_2) for the formation of ·OH radicals.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (2)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \quad (3)$$

Fenton's process is favoured since it is easy to operate, has short reaction time and it works at room temperature and pressure which makes it less expensive [3]. Fenton based studies have been carried out for the removal of hydrocarbons from refinery wastewater [7], diesel contaminated soil [40]and refinery oil sludge [12]. They also reported that the remediation of refinery oil sludge by Fenton process requires the integration of complementary treatment methods to achieve regulatory limits. Main factors which influence the Fenton process efficacy are free radicals production and extent of contact between generated radicals and contaminants [9]. Sonolysis causes acoustic cavitation which involves the formation and expansion of high-energy microbubbles under the influence of periodic pressure. When these bubbles collapse, an increase in pressure (~500 bar) and temperature (~5000 K) facilitate the cleavage of toxic compounds [24]. Several studies have investigated the scope of ultrasound treatment for the degradation of organic compounds [47,37,32,2]. However complete mineralization was difficult to achieve by sonolysis alone.

$$H_2O \rightarrow H + HO^{\bullet} \quad (3)$$

$$O_2 \rightarrow 2O \quad (4)$$

$$O + H_2O \rightarrow 2HO^{\bullet} \quad (5)$$

$$H + O_2 \rightarrow HO^{\bullet} + O \quad (6)$$

Ultrasonication (US) process induces severe micromixing in the reaction mixture by the microturbulence and microstreaming mechanisms. In addition to micromixing, the sludge particles also get disrupted effectively [24]. This phenomenon could enhance the interaction between the ·OH radicals and contaminant molecules which results in the better utilization of Fenton reagents for the purpose of oxidation [5]. Hence, the combined US and Fenton treatment is a promising technology for the oxidation of recalcitrant organic pollutants. Lin et al. [24] investigated the degradation of PAHs in textile dying sludge. Virkutyte et al. [39] tested sono-Fenton oxidation for the degradation of naphthalene in soil. Liang et al. [23,22] studied the oxidation of 4-chlorophenol. Li and Song [34] reported the degradation of acid dye aqueous solution by combined US and Fenton process. Very limited studies have been carried out using the combined US and Fenton treatment process for remediation of oil sludge. Zhang et al. [47] demonstrated the potential of combined US and Fenton's reaction process for treating refinery oil sludge. However, detailed probing of individual hydrocarbons, degradation products identification through GC–MS analysis and their proposed degradation mechanisms have not been clearly stated so far.

This study mainly focuses on the combined application of US and Fenton on the degradation of oil spill sludge. The effect of pH, ultrasonic power, change in H_2O_2/Fe^{2+} ratio, variation in the concentration of Fenton regents, addition of different salts and contact time were studied for the reduction of PHC in terms of three fractions (nC7–C10, nC11–C20 and nC21–C30). The degradation intermediates were identified using GC–MS analysis and the possible degradation pathway was proposed.

2. Materials and methods

2.1. Chemicals

Hydrogen Peroxide (H_2O_2–30%,Merck) and Ferrous Sulphate Hepta hydrate ($FeSO_4{\cdot}7H_2O$–99%, Rankem, India) were used as reagents for the Fenton Process. High Performance Liquid Chromatography (HPLC) grade n-Hexane (> 99% Rankem, India) was used as solvent for extraction and analysis. Sulphuric acid (H_2SO_4)- 98.8% purity, sodium hydroxide (NaOH– 97%) and other chemicals were supplied by Merck, India

2.2. Source of oil spill sludge

A oil spill occurred on 31st January 2017 in Ennore port near Chennai due to the collision of two cargo ships namely BW Maple and MT Dawn Kanchipuram, Tamilnadu, India. The accident released more than 100 tonnes of heavy fuel oil along the Chennai coast. Oily Sludge sample was collected from oil spill at Ramakrishna Nagar Beach, Chennai, India and stored at −4 °C temperature.

2.3. Characterization of oil spill sludge

Physical characterization of the oily sludge and associated solids involved determination of pH, moisture content, organic matter content and particle size distribution which were determined using standard procedures [49]. Viscosity of fresh oil sample from slop tank in ship and spilled-oil samples from day 1 and day 10 were measured using a Rheometer (Anton Paar, USA). The basic elemental composition such as carbon (C), hydrogen (H), oxygen (O), sulphur (S) and nitrogen (N) in the sludge solids after oil extraction was determined using a CHNS analyzer (Elementar, Germany). The IR spectra of initial pretreated sludge and treated sludge were analysed using a FT-IR Spectrophotometer (Perkin Elmer) over the frequency range 4500–600 cm^{-1}. (HORIBA nano-particle analyzer SZ-100, Japan) was used to find the particle size distribution of the sludge before and after treatment.

2.4. Pre-treatment and degradation of fuel oil sludge

Petroleum sludge (2 g) was weighed, mixed with different ratio (1:25, 1:50, 1:75 and 1:100) of distilled water, 200 µl of Tween 80, a nonionic surfactant and placed in a digital ultrasonic cleaner (Labman scientific instruments, India) for two hour to aid dissolution of viscous sludge into thin sludge. 100 ml of the pre-treated oily sludge samples were taken into 150 ml glass beaker for further treatment processes like Fenton, US and hybrid sono-Fenton processes. pH of sample was adjusted to 3.1 ± 0.1 with sulphuric acid and measured using EUTECH pH meter (Cyber Scan pH1100). $FeSO_4{\cdot}7H_2O$ and H_2O_2 concentration were varied and the probe was introduced into the beaker (Labman scientific instruments, PRO-250) equipped with titanium probe tip. The power intensity (%) and treatment time were varied from 30–75% and 10–30 min.

2.5. Hydrocarbon extraction procedure for GC–MS analysis

25 ml of the pre-treated and treated sample in beaker were transferred into 50 ml tubes and 5 ml n-hexane was added for solvent extraction. The tubes were vortexed for 2 min each. They were then centrifuged for 10 min at 8500 rpm which separated the liquid layers from the solid for further analysis of PHCs. After centrifugation, the

Table 1
Physico-chemical characteristics of the oil spill sludge.

S. No.	Characteristics	Values
1	pH	6.7–7.2
2	Moisture and VH content (g/kg)	222.4–496.5
3	Elemental composition (%)	
	Carbon	9.9–13.33
	Hydrogen	0.162–1.76
	Nitrogen	1.0–1.88
	Sulphur	0.09–0.29
4	Chemical composition of heavy fuel oil (%)	
	(i) nC7–C10 compounds Heptane, octane, nonane and Decane	10–20
	(ii) nC11–C20 compounds Undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane	45–80
	(iii) nC21–C30 compounds Eicosane, heneicosane, docosane, tricosane, tertracosane, pentacosane, hexacosane, heptacosane, octacosane and nonacosane	10–20
	(iv) Aromatics Benzene, Naphthalene, Indene, Acetylphenanthrene, p-Benzylphenol, Furan dione	25–39.7
	(v) Non hydro carbon	1–2

supernatant was passed through a separating funnel which formed two layers, an aqueous (water) layer and hydrophobic (oil) layer. Volume of each layer was determined after which 2 ml of the oil layer was collected in 2 ml centrifuge tubes. The tubes were then centrifuged for 10 min at 8500 RPM. 1 ml of this extracted solution was pipetted into 2 ml vials for GC–MS Analysis (Agilent Technologies 7820A).

3. Results and discussion

3.1. Physico-chemical characterization of oil spill sludge

The physico-chemical characteristics like pH, moisture and VH content, viscosity of oil spill sludge, elemental composition and GC–MS analysis of PHC finger printing were given in Table 1. pH of oil spill sludge varied from 6.7 to 7.2. Elemental composition C, H, N and S analysis of the oil spill sludge were varied from 10–13.3, 0.2–1.8, 1.0–1.88 and 0.1–0.3 percentages. These results are comparable with the results of Cheng et al. [6] where petroleum sludge composition of C, H, N, S were 16.89, 2.32, 0.16 and 0.53 percentage. Oil spill sludge was extracted with hexane and the chemical compounds present were identified using GC–MS system. Analysis of the sludge extract showed different functional groups like saturated alkanes, branched alkanes, alkenes, esters and aromatic compounds.

The major compounds of oil spill sludge were identified and tabulated in terms of peak intensities. Percentage match of the mass spectra of various organic compounds with complex functional groups was poor with respect to NIST database. Main organic compounds present in oily sludge were displayed in Table 1. Fig. 1 gives the GC–MS chromatogram of oil spill sludge.

3.2. Degradation of petroleum hydrocarbons (PHCs) by different advanced oxidation processes

Oil spill sludge was treated with different advanced oxidation processes like ultrasound, Fenton and Fenton assisted ultrasound were studied. Studies were conducted at a pH of 3.1 for a contact time of 10 min. The reduction in area of petroleum hydrocarbon peaks ranging from (nC7–C10, nC11–C20 and nC21–C30) were measured using Agilent Chem Station software. The results of PHC reduction in oily sludge were shown in Fig. 2. The ultrasonic degradation of PHCs was mainly due to collapse of cavitation bubbles and initiation of free radical mechanism by hydroxyl radicals in the interface and in bulk liquid. Cracking of PHCs and upgrading into heavy gas oil and vacuum residue using ultrasound was reported by Kaushik et al. [25]. Desorption of PHCs from the sludge to the bulk liquid phase is very important in order to be react with hydroxyl radicals generated in the reaction mixture. Watts et al. [41,42] reported that the presence of iron minerals in the sludge could improve the Fenton oxidation and enable the degradation of PHCs in presence of hydrogen peroxide.

The effect of different advanced oxidation process on oily sludge treatment were shown in Fig. 2. Oily sludge treatment with ultrasound alone shows the solubilisation of nC7–C10 and nC11–C20 PHCs fraction in the liquid phase due to collapse of cavitation bubbles. The rate of solubilisation of nC11–C20 fraction in the bulk liquid phase was found to be less. Fenton treatment was executed at pH 3, with 10:1 ratio of H_2O_2 to Fe^{2+}, ultrasonic power intensity of 40% and treatment time of 10 min. As observed in Fig. 2, ultrasonic treatment enhanced the solubility of the oily sludge and Fenton effectively removed the soluble PHC. Sono-Fenton process involves the combined effect of both ultrasonic and Fenton process where the subsequent solubilisation of sludge and oxidation of PHC takes place. GC–MS results proved that ultrasound treatment alone was not capable of effective degradation of PHCs. This was due to absence of sufficient contact between ·OH radicals and hydrocarbons present in the sludge [48].

A combination of both oxidants and ultrasound was necessary to achieve higher removal efficiency. Degradation of contaminants was attributed to thermo-chemical decomposition processes within the generated acoustic bubble and due to hydro mechanical shear forces [38]. Degradation of organic molecules using ultrasound can be attributed to the production of free radicals ·OH, ·O and $HO_2^{\cdot}$ from water molecules in extreme environments of high temperature and pressure. GC–MS overlay chromatogram of pretreated oil spill sludge, ultrasound treated sludge and Fenton-assisted ultrasound treated sludge were shown in Fig. 3. In Fenton process, Fe^{3+} is formed which reacts with H_2O_2 to produce Fe-$(OH)_2$ intermediate. This intermediate spontaneously decomposes to Fe^{2+} and ·OOH, but at an extremely slow rate. This decomposition rate is greatly enhanced in the presence of ultrasound. Thus hydroxyl radicals are formed more rapidly in the combined process [35]. The mechanism controlling sono chemical degradation is the production of free radicals and their attack on contaminant species [44]. Hydrogen Peroxide also dissociates under the influence of ultrasound producing hydroxyl radicals. Siddique et al. [50] reported that the ultrasound coupled Fenton treatment produced 10 times more hydroxyl radicals than that of ultrasonic treatment alone. Hence a combination of ultrasound and Fenton was proposed as a feasible treatment strategy. The percentage reduction in peak area of Sono-Fenton treated sample proves the enhanced efficiency of the treatment. Similar results were reported by Ma et al. [26] for the degradation of carbofuran and Sun et al. [35] for the reduction of Azo dye Acid Black 1 dye under US/Fenton process as compared to US alone or Fenton alone.

3.2.1. Effect of sludge/water ratio

The effect of sludge and water ratio on ultrasonic degradation of PHCs was studied. The sludge to water ratio was varied between 1:100, 1:75, 1:50 and 1:25 (Fig. 4). It was observed that for an decrease in sludge-to-water ratio the viscosity of the solution mixture got increased. Very less water content in sludge solution could bring about expanded consistency of the slurry blend which could then hinder the arrangement and collapse of cavitation bubbles, which reduces the impact of sonication in the treatment [31].

Feng and Aldrich [51] have shown that, increased solid concentration above 50% in the oily soil slurry could inhibit the ultrasonic cavitation process in the PHCs contaminated soil remediation. Higher amount of water usage to treat the sludge makes the process not feasible for scale up from an economical and technical point of view. As a result, an optimum level of sludge-to-water ratio (1:100) was selected for the ultrasonic irradiation of oily sludge.

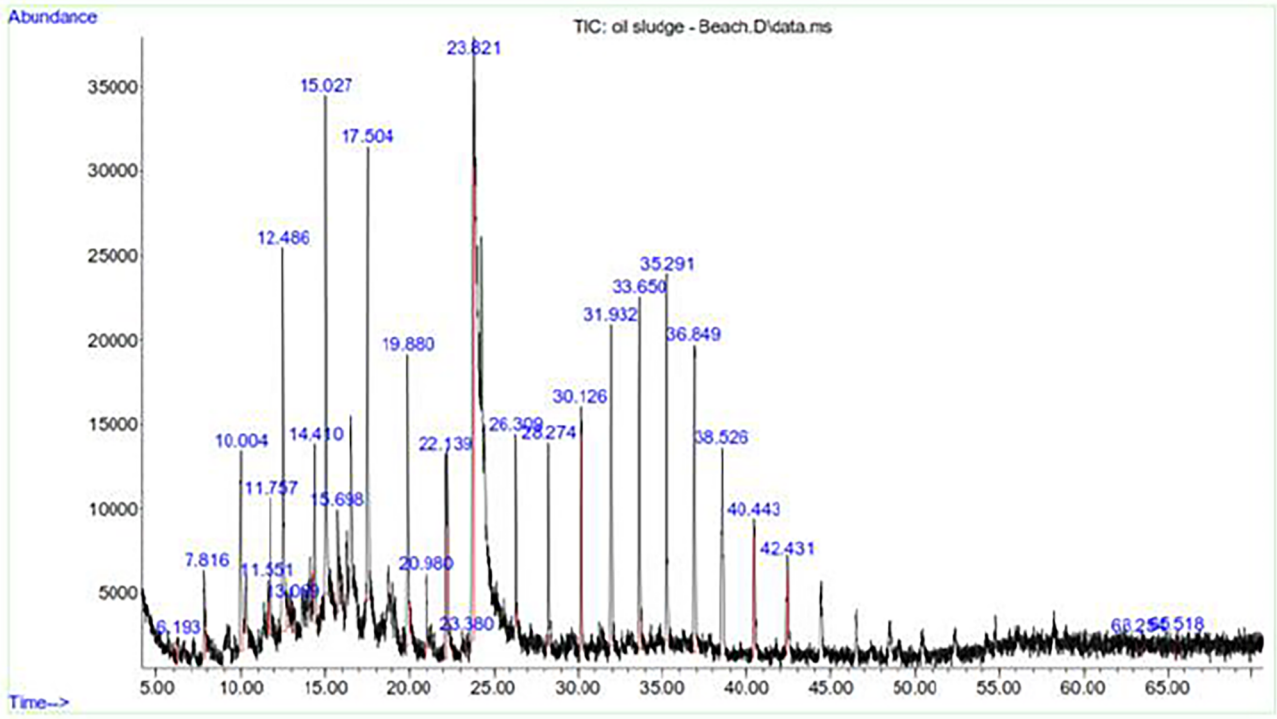

Fig. 1. Gas chromatograph of sludge sample collected 10 days after the oil spill.

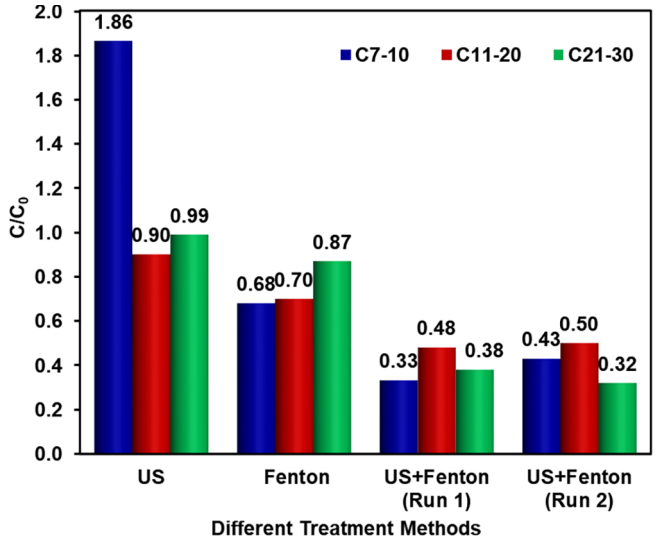

Fig. 2. Comparison between different treatment methods (Sludge/water ratio = 1:100, H_2O_2/Fe^{2+} weight ratio = 10:1, ultrasonic power intensity = 40%, contact time = 10 min).

3.2.2. Effect of pH

The pH of oil sludge is a key factor that controls sono chemical degradation due to the formation of hydroxyl radicals [43]. pH influences the physical and chemical properties of solution and bubble dynamics, which also affects the rate of degradation of PHC compounds present in the solution [15]. The effect of pH was investigated for oily sludge with 10:1 ratio of H_2O_2 to Fe^{2+}, ultrasonic amplitude of 40% and contact time of 10 min at pH 3.0, 5.0, 7.0 and 9.0. Kwon et al. [21] proved that Fenton process is more efficient in acidic conditions between pH 3.0–4.0. Fig. 5 shows that PHC reduction of oily sludge varies significantly with pH. Oil spill sludge had an initial pH of ~7. The GC–MS analysis results showed that pH 3.0 was favourable for overall degradation of PHCs. From pH 3.0–5.0, the solubilization of nC7–C10, nC11–C20, nC21–C30 range hydrocarbons increased. For a solution pH > 7, the release of carbon chain into the liquid got reduced. Similar pattern has been observed in the NaCl effect on solubilizing the sludge. When pH > 4.0, Fe^{2+} precipitates as hydroxide thereby reducing the degradation efficiency [35]. Lower reduction rate was observed in highly alkaline conditions since Fe^{2+} gets converted to iron hydroxide $Fe(OH)_3$, which reacts with H_2O_2 and inhibits the production of ·OH radicals [12]. Studies have proved the decline in oxidative potential of hydroxyl radicals with increase in pH [29,50]. GC–MS overlay chromatogram for effect of pH portrayed in Fig. S1 confirms maximum PHC degradation at pH 3.0.

3.2.3. Effect of ultrasonic power (Sonication amplitude)

The effect of ultrasonic power on PHC degradation was studied to treat 1% oily sludge (2 g in 200 ml) with different power amplitude of 20%, 30%, 40% and 50% with with 10:1 ratio of H_2O_2 to Fe^{2+} and sonication time of 10 min. Fig. 6 shows the PHC degradation pattern of nC7–C10 and nC11–C20 fractions present in the oil sludge. For an increase in ultrasonic power from 20% to 40% amplitude there was an increase in degradation of these PHC fractions. For an increase in ultrasonic power from 30–75% there was an increase in temperature from 34–55 °C. The initial reaction temperature was found to be 34 °C. The temperature was not controlled during the experiments. Cavitation bubbles produced were increased for higher temperature, but the resulting effects from cavitational collapse were reduced. Increase in ultrasonic amplitude from 40 to 75% did not improve PHC degradation. This was mainly due to the fact that increase in cavitation energy lowered the threshold limit of cavitations and increased the number of cavitation bubbles [17]. Mello et al. [28] also observed that increasing amplitude of ultrasonic wave beyond 40% did not greatly improve sulfur removal. Czechowska-Biskup et al. [52] reported that at higher power, the efficiency of sonication processes may be reduced due to scattering of ultra sound waves by the number of cavitation bubbles present in the sample.

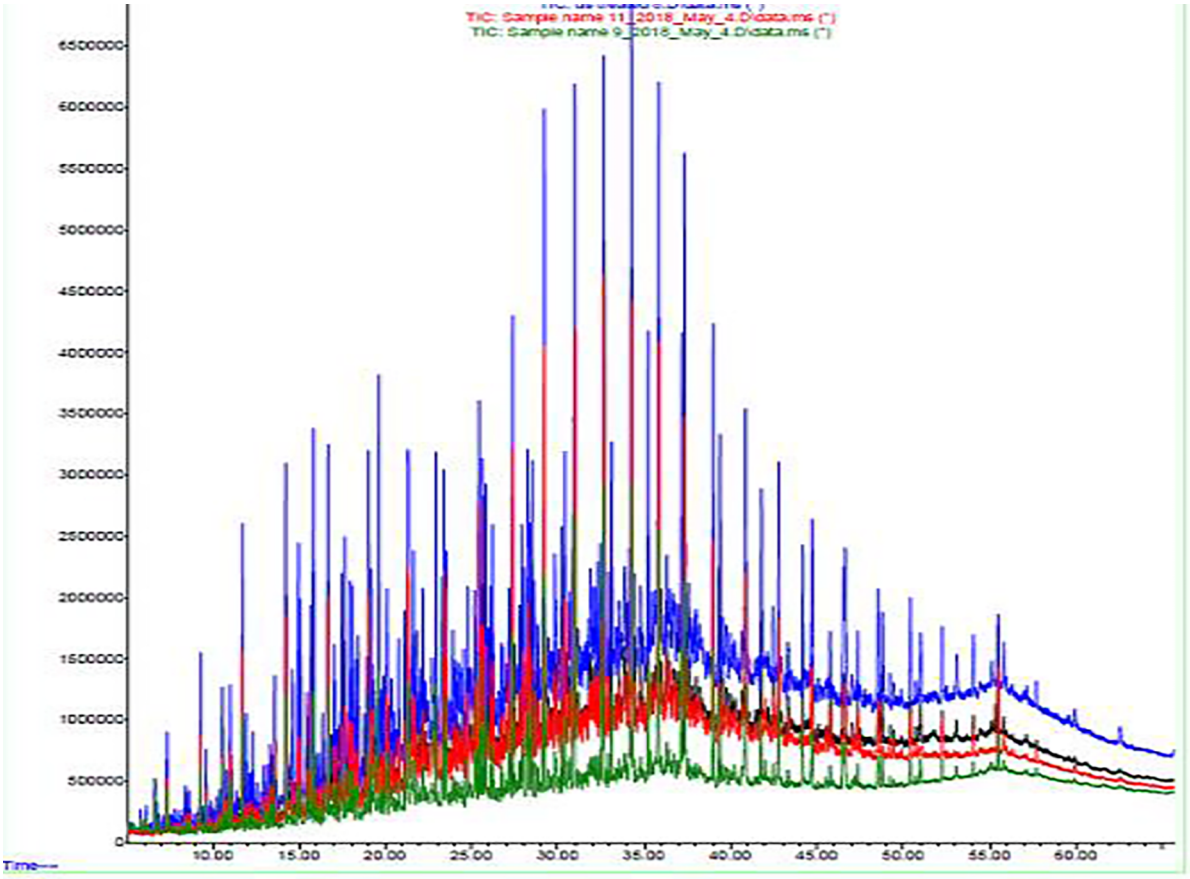

Fig. 3. GC–MS overlay chromatogram of untreated, ultra sound, Fenton and Sono Fenton treatment.

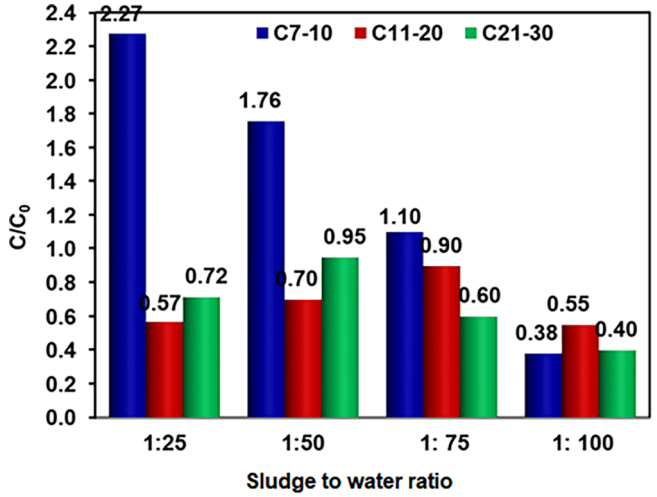

Fig. 4. Effect of sludge to water ratio on PHC degradation using sono-Fenton process (Sludge/water ratio = 1:100, H_2O_2/Fe^{2+} weight ratio = 10:1, ultrasonic power = 100, contact time = 10 min).

3.2.4. *Effect of H_2O_2/Fe^{2+} weight ratio*

The efficiency of Fenton treatment of oily sludge is less due to inadequate contact of hydroxyl radicals with PHCs present in the oil sludge. Combined sono-Fenton solubilizes and disperses the PHCs in the aqueous phase which enables the ·OH radicals to oxidize the PHC molecules to a greater extent. Determination of the optimum concentration of Fe^{2+} or H_2O_2 in solution is more important to enhance the degradation efficiency. The required Fenton reagent varies depending on the type of pollutant and complexity of reaction system. Excess iron would consume all generated hydroxyl radicals and prevent PHC degradation [24]. Degradation of oily sludge at varying iron and H_2O_2 concentrations were investigated. H_2O_2/Fe^{2+} weight ratio was initially varied as 3:1, 7:1, 10:1 and 20:1 keeping the H_2O_2 volume fixed (Fig. 7a). H_2O_2/Fe^{2+} ratio of 10:1 (300 mg/L Fe^{2+} and 3000 mg/L of H_2O_2) and gave the better removal efficiency.

H_2O_2 concentration was then varied as 1000, 2000, 3000 mg/L and 4000 mg/L with the fixed H_2O_2/Fe^{2+} ratio of 10:1. At lower H_2O_2 and Fe dose, lesser removal efficiency was observed, since there is not enough ·OH radicals are produced to oxidize the PHC and remains as the soluble fraction in the reaction mixture. At higher H_2O_2 and Fe concentration, solubilized fractions of PHC got oxidized which in turn reduced the peak intensity as observed in Fig. 7b. No significant difference was observed in PHC reduction of C11-20 and C21- 30 fractions for 3000 mg/L and 4000 mg/L of H_2O_2 concentration (10:1 and 20:1). This may be due to recombination and scavenging of ·OH radicals [35]. Farzadkia et al. [12] reported the optimum molar ratio of H_2O_2 to Fe^{2+} to be 10 for the removal of petroleum hydrocarbons from oily sludge in Shiraz oil refinery. Several studies show that higher H_2O_2/Fe^{2+} ratio results in higher PHC degradation of petroleum sludge. Zhang et al. [48] reported highest PHC reduction of oily sludge at an optimum H_2O_2/Fe^{2+} molar ratio of 4:1. Painmanakul et al. [30] determined the optimum H_2O_2/Fe^{2+} weight ratio to be 28:1 for treatment of cutting oily waste water. From the experimental results for this study, the optimal weight ratio was found to be 10:1.

3.2.5. *Effect of contact time*

Oil spill sludge was treated for different contact times (10 to 30 min), keeping the ultrasonic amplitude of 40%, H_2O_2/Fe^{2+} weight ratio of 10:1 and sludge/water ratio of 1:100 constant. Fig. 8 shows the removal of (nC7–C10, nC11–C20 and nC21–C30) PHC fractions for

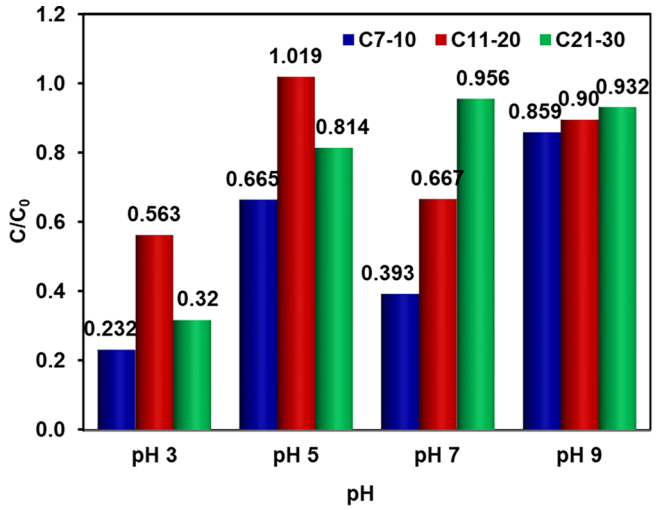

Fig. 5. Effect of pH on PHC degradation using sono-Fenton process (Sludge/water ratio = 1:100, H_2O_2/Fe^{2+} weight ratio = 10:1, ultrasonic power = 100, contact time = 10 min).

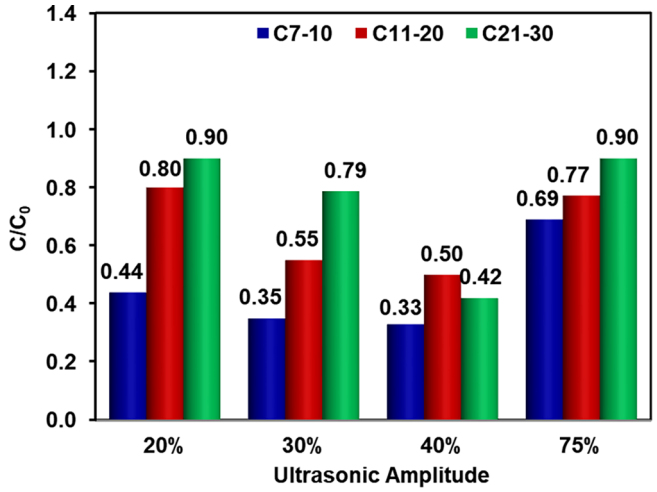

Fig. 6. Effect of ultrasonic amplitude on PHCs degradation in oil spill sludge (pH = 3, sludge/water ratio = 1:100, H_2O_2/Fe^{2+} weight ratio = 10:1, contact time = 10 min).

different ultrasonication times. Maximum variation in peak intensity was observed for 10 min treatment. PHC removal rate for 20 and 30 min of sono-Fenton treatment are lesser compared to that of 10 min. This shows that increasing the treatment time does not enhance the solubilisation and degradation of PHCs present in the oily sludge. Similar results were reported by Mello et al. [28] for the ultrasonic desulfurization treatment of petroleum feedstock at 9, 15 and 30 min. Sulfur removal efficiency did not improve with increase in sonication time.

Literature review also showed that treatment with high ultrasonic power-short sonication time was more effective than that with low ultrasonic power-long sonication time [20,46]. Lesser sonication time is also preferable when taking account the economical aspects, apart from high reduction efficiencies.

3.2.6. Effect of salt

The effect of addition of salts like sodium chloride, sodium sulphate and sodium hypo chlorite on the PHC reduction of oily sludge has been studied. The degradation of PHCs was investigated by adding salts (5% by weight) to the oil spill sludge and maintaining the other parameters constant (Fig. 9). Experimental results revealed that the presence of Na_2SO_4 salt increased solubilization of nC7–C10 fraction, which was

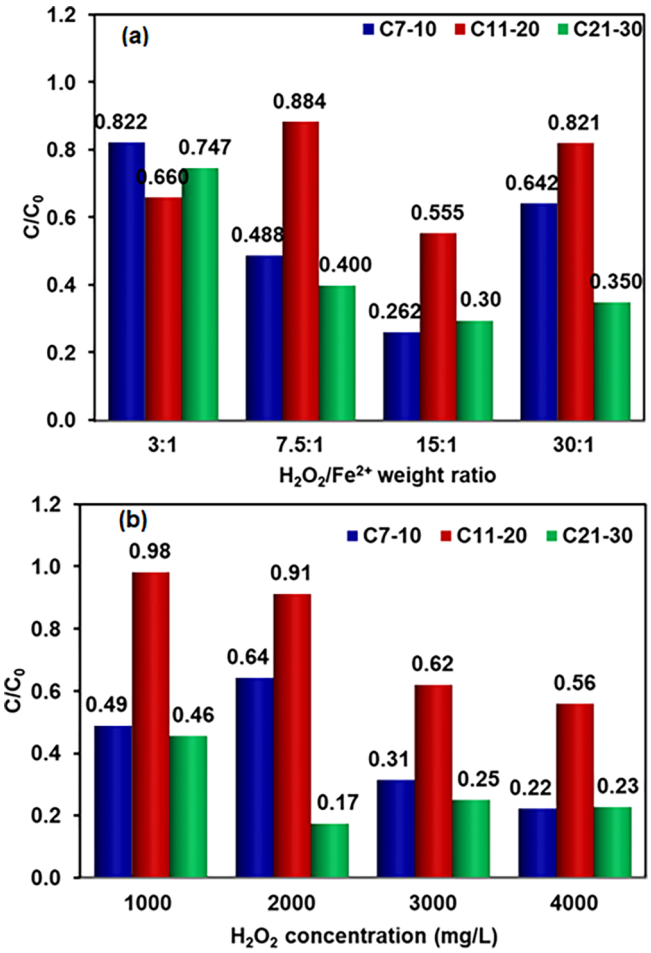

Fig. 7. (a) Effect of H_2O_2/Fe^{2+} weight ratio on PHC degradation in oil spill sludge (b) Effect of varying H_2O_2 concentration with the fixed H_2O_2/Fe^{2+} weight ratio of 10:1 (pH = 3, sludge/water ratio = 1:100, ultrasonic amplitude 40%, contact time = 10 min).

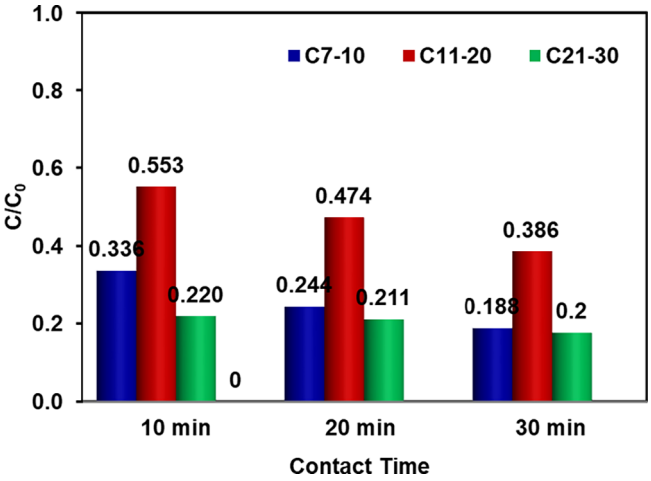

Fig. 8. Effect of retention time on PHC degradation in oil spill sludge (pH = 3, sludge/water ratio = 1:100, ultrasonic power = 100 W, H_2O_2/Fe^{2+} weight ratio = 10:1).

indicated by the increase in peak intensity after treatment. This is because unsaturated hydrocarbons have a tendency to react with sulphate groups and form esters by direct addition. NaOCl is a strong oxidizing agent [45]. It released OCl^- ions that helped in breaking down and oxidizing larger alkane chains. PHC peak intensity reduced to 45% in

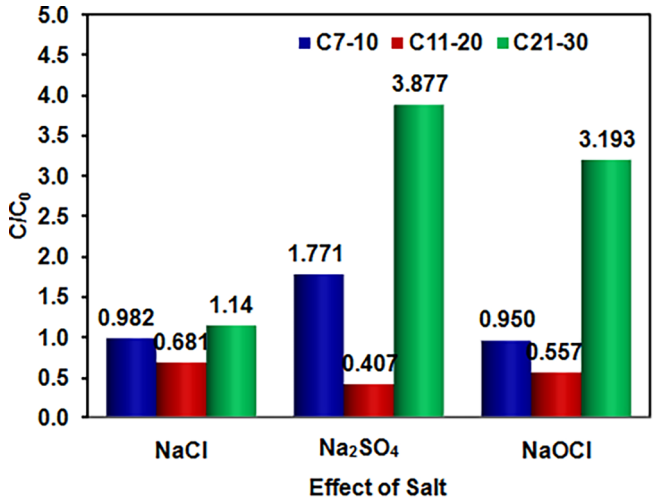

Fig. 9. Effect of PHC degradation in the presence of different salts (pH = 3, sludge/water ratio = 1:100, ultrasonic power = 100 W, H_2O_2/Fe^{2+} weight ratio = 10:1, treatment time = 10 min).

presence of Na_2SO_4 and 50% in the presence NaOCl for all three fractions. The increasing trend in the peak intensity for the heavier fraction (nC21–C30) was due to compound solubilization. Overall PHC reduction was good in the presence of NaCl. Abramov et al. [1], Suri et al. [36] also reported that the addition of sodium salts could enhance separation of oil from slurries. This was because the presence of NaCl in small amounts could improve cavitation bubble implosion and enhance ultrasonic power intensity. Duckhouse et al. [11] also observed that sonication and simultaneous chlorination significantly enhanced the biocidal effect of hypochlorite.

3.3. Investigation of PHCs degradation mechanism

The proposed sono-Fenton degradation pathway for petroleum hydrocarbons present in the oil sample has been schematically represented in Fig. 10. Mechanism of PHC degradation was studied for ultrasound and combined sono-Fenton treatment. Treatment of PHCs with ultrasound formed methyl intermediates of saturated alkanes which were then transformed to alcohols. Sonication of saturated alkanes like octane, tetradecanes resulted in the formation of alcohols (2-hexyl-1-octanol) and acetates (7-methyl-Z-tetradecen-1-ol acetate). Benzene present in the form of a methyl intermediate (Benzene,1,3-bis (1,1-dimethylethyl) hydrolysed to give a phenolic compound (Phenol,2,6-bis (1,1-dimethylethyl)). Octadecane was found to reduce to a long chained carboxylic acid. Solubilization and mineralization of nC21–C30 fraction of PHCs increased after fenton-assisted ultrasound treatment which was quite recalcitrant for the biological treatment [46]. Compounds like Heptadecane and Docosane got solubilized and converted to its ester in the combined Fenton-US treatment. Since oil sludge is a mixture of several complex petroleum hydrocarbons, the intermediates like carboxylic acids, ketones, alcohols, could have accumulated when large amounts of PHCs were degraded [48]. Consequently, a lower rate of PHC reduction of parent compound was observed.

3.4. Fourier Transform Infrared Spectroscopy (FT-IR) analysis of oil spill sludge

FT-IR Spectroscopy proved to be a very useful and common analysis technique by identifying the functional groups present in oil spill sludge before and after treatment [27,50]. The IR patterns for oil before and after treatment were similar. The bands at 2923 and 2859 cm^{-1} for both samples were related to stretching of alkyl $-CH_2$ and $-CH_3$ groups. Apart from the dominant C—H peaks, there are Si—O and O—H frequency peaks present due to the interaction of soil and water in the oily sludge. The presence of O–H stretching vibration at 3465 cm^{-1} in pre treated oil can be assigned either to hydroxyl (water) or carboxylic group functionalities. The O—H frequency peak disappeared completely after treatment due to the separation of water from oil sludge after treatment. On the contrary, the C═O stretch in carbonyl/carboxylic became significant after treatment which confirms the formation of carboxylic acids after ultrasonication by oxidation of alcohols. Comparing the IR spectra of oily sludge before and after degradation, the C═C stretch in aromatics reduced in intensity after treatment. This indicates degradation of some aromatic structures. FT-IR spectra of raw pretreated sludge and oil sludge after treatment were shown in Fig. 11.

3.5. Particle size distribution of oil spill sludge

Particle size measurement was done using a Nano-particle analyzer. Oily sludge was treated at optimized treatment conditions and the impact of sono–Fenton on size of particles present in the sludge was measured. Particle size plays a major role in releasing the oil from sludge. Pretreated oil sludge had a mean particle size of 2129.5 nm and treated sludge had a particle size of 290.2 nm. The particle size of oily sludge reduced almost ten times after sono–Fenton treatment. The disruption of oil flocs and volume occupied by particulate matter was enhanced by sonication. Lower the particle size, higher the release of pollutants into bulk liquid phase. Higher specific ultrasonic energy input and longer sonication time results in substantial reduction of particle size [38]. Kidak et al. [20] examined the effect of ultrasonication on particle size distribution for municipal and industrial sludges with ultrasound power of 100 W for 90 min. They reported that the average particle size reduced from 275 to 4.5 μm for industrial sludge and from 1000 to 70 μm for municipal sludge.

4. Conclusion

The combination of ultrasound and Fenton process was successfully demonstrated for the degradation of petroleum oil spill sludge. PHC degradation efficiency improved from 15.83% for to 62.99% in the combined Fenton-US treatment. It reveals that combined Fenton-ultrasound treatment method is an efficient and feasible solution for the degradation of PHCs. The pH and ultrasonic power had remarkable impact on the reduction of PHCs. The experimental results also confirms that the degradation of PHC fractions in oily sludge was greatly improved when using the combined process. Maximum PHC reduction rate of 84.25% and 23.58% (nC7–C10 and nC11–C20) was achieved for the at a pH of 3, sludge/water ratio of 1:100, 40% ultrasonic amplitude, H_2O_2/Fe^{2+} weight ratio of 10:1 and ultrasonic treatment time of 10 min. The addition of NaCl could enhance degradation by enhancing cavitation bubble implosion. The results of FT-IR analysis showed prominent changes in the C—H and C═O groups and reduction in some cyclic structures, which is in accordance with the proposed degradation mechanism. Hence, the combination of sono-Fenton technology could effectively degrade the PHCs in petroleum wastewater within a short treatment time and its treatment efficiency could be enhanced by appropriate combination of different parameters. The study showed that degradation efficiency by sonication alone is marginal. However, enhanced solubility of the higher carbon compounds was observed. Enhanced solubilisation is advantageous since the soluble fractions will be readily amenable to chemical or biochemical oxidation resulting in better overall reduction of PHCs. Further experiments where AOP treatment processes are conducted in series are required to quantify and compare overall degradation rates. Solubilisation followed by biodegradation may also result in cost effective treatment technologies.

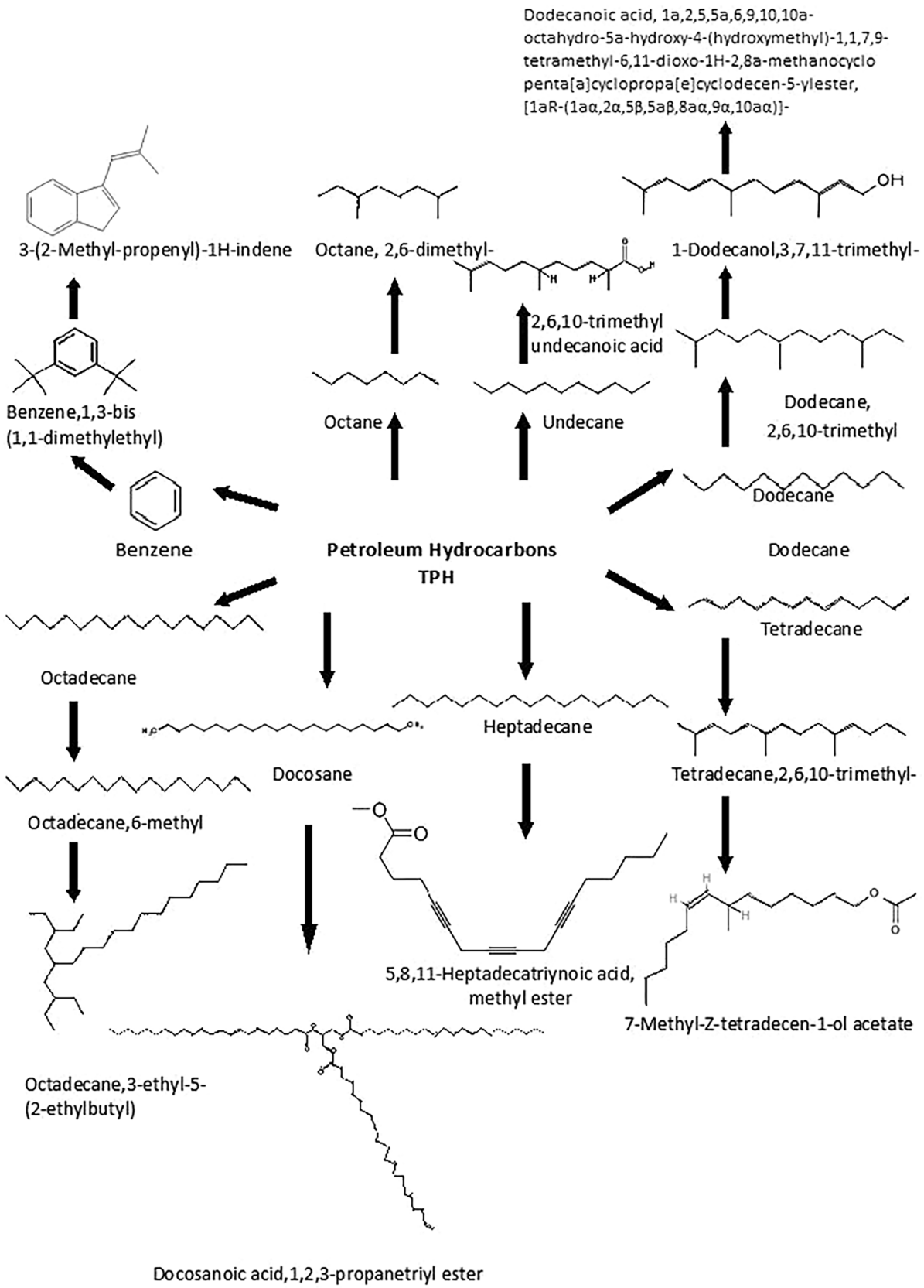

Fig. 10. Proposed mechanism for Fenton assisted ultrasound treatment.

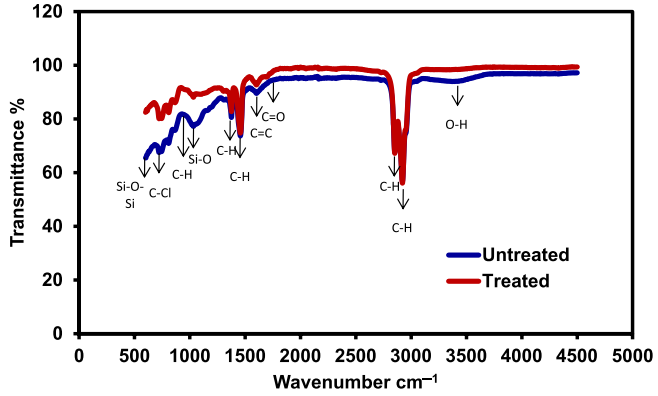

Fig. 11. FT-IR Spectra of raw and treated oil sludge after Sono Fenton treatment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ultsonch.2018.09.007.

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