



Remediation and optimization of petroleum hydrocarbons degradation in contaminated water using alkaline activated persulphate

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ABSTRACT

This study investigated the characterization of Nigerian crude oil using gas chromatography-mass spectrometry (GC-MS) and the efficiency of alkaline activated sodium persulphate in degrading petroleum hydrocarbons in crude oil-polluted water. Hydrocarbons (aliphatics and aromatics), non-hydrocarbons, and other constituents were characterized in crude oil samples. The ratio of hydrocarbons:non-hydrocarbons/others and aliphatics:aromatics is 86:14 and 45:55, respectively. Alkylated benzenes, toluene, o-xylene, fluorene, and naphthalenic compounds were the most common aromatic compounds. The majority of aliphatic compounds were n-alkanes and cyclic hydrocarbons, including cyclohexane and heptylcyclohexane. Degradation experiments were performed with different initial concentrations of sodium persulphate (0.3 M, 0.5 M and 0.7 M) with sodium hydroxide as an activator. Runs were carried out within 8 days. The total petroleum hydrocarbons (TPH) extraction was carried out and analyzed using gas chromatography flame ionization detector (GC-FID). From an initial TPH concentration of $\sim 137 \text{ mg L}^{-1}$ in water, near-complete degradation was achieved with 0.3 and 0.5 M oxidant dosage. With 0.7 M sodium persulphate, 76% TPH was degraded within 8 days. Radical quenching using sodium thiosulphate showed that the addition of the scavenger resulted in negligible changes in TPH concentration pre- and post-degradation using all three oxidant dosages. Thus, alkaline activated persulphate is effective for the remediation of petroleum hydrocarbon contamination.

1. Introduction

Hydrocarbon contamination of soil and groundwater has been a recurring challenge globally, and particularly, in oil-rich countries such as Nigeria. This has largely affected the availability of arable land and potable water in most communities in contaminated areas [1–3]. Several calls have been made for the remediation of contaminated aquifer by both local and international organisations. Treatment techniques such as remediation by enhanced natural attenuation (RENA) have been commonly adopted, however, studies have shown the ineffectiveness of this method because it leaves non-biodegradable residues resulting from incomplete mineralisation [4–8]. Over the years, remediation technologies have evolved to more advanced methods using activated chemical oxidants. The combination of high-tech methods over the past two decades has led to improved degradation of emerging, reluctant and recalcitrant contaminants [9–13]. Crude oils contain thousands of chemical constituents, of which hydrocarbons are the most abundant.

Carbon and hydrogen account for up to 98% of compounds in some crude oils, while nitrogen, sulphur, oxygen and several trace metals such as vanadium, iron, nickel, aluminium, sodium, copper, uranium and calcium are typically present [14].

Aliphatic hydrocarbons consist of normal (paraffins) and branched alkanes. Among the branched alkanes are isoprenoids like pristane and phytane, which are made up of isoprene building blocks. Naphthenes are also referred to as cycloparaffins or saturated ring structures. Many naphthenes have unique plant or animal precursors, making them useful as petroleum biomarkers. Aromatic hydrocarbons have one or two benzene rings that are fused or lined. They are less common than aliphatics which have more volatile compounds such xylenes as well as semi-volatile polycyclic aromatic compounds. The non-hydrocarbon components of petroleum are classified into nitrogen, sulphur, oxygen - also referred to as NSO compounds, asphaltenes, porphyrins and trace metals. Nitrogen compounds are present in all petroleum. Examples of these are pyridines, quinolines and indoles. Thiols and sulphides are the

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most common sulphur compounds. Although porphyrins are nitrogen-containing compounds, they are organometallic complexes of Ni and V, and consist of four pyrrole rings. Nickel and vanadium are the most abundant trace metal constituents of petroleum. Aside petroleum, other sources of hydrocarbons include incomplete combustion of fossils and anthropogenic activities.

Total petroleum hydrocarbon (TPH) refers to an extensive family of chemical compounds originating from crude oil. They mainly consist of hydrogen and carbon ranging from light, volatile to heavy, long-chain compounds such as BTEX (benzene, toluene, ethyl benzene and xylene), n-alkanes, PAHs (polycyclic aromatic hydrocarbons) and asphaltenes. TPHs are important environmental contaminants due to their ease and frequency of release via accidental spillage, pipeline vandalism and industrial accidents. They are found in most petroleum products, which are fundamental to humans due to their use in transportation, heating and power generation. TPH value varies depending on the constituents of petroleum products in a media. Classification of petroleum products is accounted for by the source and refining process of crude oil/petroleum. A common analytical technique for determination of TPH in a sample is the United States Environmental Protection Agency (USEPA) 8015 method. Based on this method, the TPH concentration in a sample is given as a single value and does not provide information on the individual hydrocarbon constituents such as aliphatics or aromatics.

Chemical oxidation is a process that converts organic contaminants into carbon dioxide and water or other non-hazardous substances. The strength of chemical oxidants derives from their oxidation/reduction potential – measured in volts (V) or millivolts (mV). Oxidation/reduction potential measures their tendency to be reduced when they acquire electrons. Prior to the emergence of persulphate, percarbonate and solid oxygen-supplying peroxides such as sodium percarbonate and peroxide, the use of hydrogen peroxide, ozone and permanganate has been widely reported in field and laboratory-scale studies [8,15]. Persulphates have been reportedly activated by heat [16,17,13], ultraviolet (UV), ultrasound, and electron beam in order to generate sulphate radicals. Other activation methods include metals [18,19], alkaline pH [20], nanoparticles [18], organic and inorganic chelates [21], electrochemical [22] and mineral-based activation [23]. Due to increased oxidation/reduction potential, activated sodium persulphate has found increasing application in degradation of several environmental contaminants including petroleum hydrocarbons. For field applications, the use of heat-activated persulphate for remediation studies may be limited due to energy requirements and cost implications (Matzek and Carter, [24]), while iron activation requires acidic pH to avoid precipitation (Liang et al. [25]) or chelating agents which could compete with contaminants for the chemical oxidant thereby reducing degradation efficiency [18].

The use of alkaline activation of persulphate has been on the increase. The reaction mechanism is shown in Eqs. (1) and (2) (Furman et al. [26]). Sodium and potassium hydroxide are the most widely employed alkaline activators [27,28]. At pH 10, sodium hydroxide reacts with sodium persulphate to produce hydroxyl, sulphate and superoxide radicals. At higher pH (12), hydroxyl radicals are predominate sulphate radicals [29].



Therefore, this work is aimed at elucidating the constituents of Nigerian crude oil using gas chromatography, and assessing the effectiveness of alkaline activated sodium persulphate for degradation of total petroleum hydrocarbons in crude oil contaminated water. The composition of crude oil has been classified into hydrocarbons, non-hydrocarbons and other constituents and study considers the effect of oxidant dosage on degradation of total petroleum hydrocarbons.

2. Materials and methods

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and sodium hydroxide purchased from Sigma Aldrich Merck KGaA, Darmstadt, Germany were used as oxidant and activator, respectively. Sodium thiosulphate pentahydrate 99.5% (Sigma Aldrich) was employed as a quenching agent. For the extraction of TPH, dichloromethane (Analar grade, 99.5%) purchased from Sigma Aldrich Merck KGaA, Darmstadt, Germany was used as received. Deionized water was produced with a Milli-Q system from Millipore. Complimentary crude oil was obtained from an indigenous company in Nigeria.

2.1. Chemical oxidation of TPH in water

This study involved pilot-scale petroleum-contaminated water samples. 200 mL of deionized water was spiked with 150 mg of crude oil (in 1 L hexane) and left for 100 days with intermittent/periodic stirring/shaking. This process can be used to simulate ageing and mimic oil weathering in natural environments, while evaporating the solvent. Analysis of TPH in the water prior to contamination and on contamination (prior to degradation) was carried out. Experiments were performed to evaluate the chemical oxidation of contaminated water by varying oxidant dosage with time (8 days) at pH 10. Batch studies were performed without pH adjustment (circumneutral), room temperature (20–25 °C), in the absence of light (by aluminum foil coverings). Blank experiments were performed by using petroleum-contaminated water alone without any oxidant but no pollutant degradation was observed. 0.1 M, 0.3 M, 0.5 M and 0.7 M of sodium persulphate were added to contaminated water samples and degradation of TPH determined at 2, 4, 6 and 8 days, respectively. The production of sulphate and hydroxyl radicals was then stopped by adding sodium thiosulphate to each and freezing these batches. Subsequently, liquid-liquid extraction was carried out using dichloromethane. Eight days contact time was chosen based on previous studies where no further degradation was observed after one week (Usman et al. [30]) while oxidants were fully consumed after this period as confirmed by iodometric titration (Rybnikova et al. [31]).

2.2. Extraction of TPH in water

Water samples were first extracted with dichloromethane before iodometric titration was carried out. The total petroleum hydrocarbons concentration was analysed using a GC-FID 7890B from Agilent Technologies. A standard mixture was used to define the integration limits of the chromatogram area, corresponding to $\text{C}_{10}\text{H}_{22}$ and $\text{C}_{34}\text{H}_{70}$. The extraction of TPH in water was carried out using United States Environmental Protection Agency (USEPA) Method 8015D. Contaminated water (200 mL) was measured into a pre-cleaned separatory funnel and mixed with 30 mL of dichloromethane. The mixture was mechanically shaken for few minutes and left to separate. Organic layer was collected into a beaker and the procedure repeated twice with 10 mL dichloromethane each time. All three organic fractions were mixed in a beaker before being concentrated to 1 mL using rotary evaporator [5].

2.3. Quantification of TPH using GC-FID

The TPH was analysed according to USEPA method 8015D procedure using a GC-FID 7890A (Agilent technologies). External calibration was carried out using hydrocarbon standard mixture (Sigma Aldrich Merck KGaA, Darmstadt, Germany). The integration limits of the chromatogram area ranged from $\text{C}_{10}\text{H}_{22}$ to $\text{C}_{40}\text{H}_{82}$ (n-decane to n-tetracontane). Five calibrations levels were prepared (0–200 mg L^{-1}) and injected in to the gas chromatograph to obtain calibration curves. A sample of pure dichloromethane, which served as a control was used to correct background noise by integrating with chromatogram area.

The GC-FID temperature program was as follows: initial temperature

of 50 °C, hold for of 2 min, ramp at 10 °C to 110 °C, hold for 2 min, then ramp at 5 °C to 260 °C and hold for 2 min, finally ramp at 3 °C to 300 °C and hold for 10 min. Helium was used as the carrier gas and TPH quantification/data analysis was carried out using Agilent Chemstation software.

3. Results and discussion

3.1. Crude oil characterization

The oil was characterized with Gas Chromatography-Mass Spectroscopy (GC-MS, Agilent 7890A GC/5977 MS), and the constituents were classified into aliphatic (cyclic and acyclic) and aromatic (BTEX, PAHs) hydrocarbons. Non-hydrocarbons such as β -sitosterol and other compounds not belonging to any of these groups were also identified and tabulated. Tables 1–6 present the percentage composition, Kovats retention time indices, molecular weight and molecular formula of identified compounds. The crude oil chromatogram is displayed in Fig. 1.

Aromatic constituents (monoaromatics, diaromatics and polyaromatics) are most abundant components in the crude oil. This is in agreement with previous studies on characterization of Nigerian (Gulf heavy) oil carried out by Odeunmi and Ismael [32]. Aliphatic constituents include both cyclic and acyclic compounds, and these make up about 39% of the analyzed crude oil. A distinct feature of the crude oil chromatogram (Fig. 2) is the high amount of hydrocarbon unresolved complex mixtures. This is consistent with crude oil characterization reported by Odeunmi and Ismael [32].

3.2. Aliphatic hydrocarbons

The crude oil exhibits distribution of n-alkanes between C₉-C₃₀. The presence of n-alkanes between C₉-C₁₃ is a likely indication of presence of volatile compounds, thereby signifying minimal weathering. This is further corroborated by the high percentage composition of monoaromatic components obtained from the analysis. A total of 20 acyclic hydrocarbons were identified, representing 22% of crude oil composition as depicted in Fig. 2. These acyclic compounds are presented in Table 1. The most significant acyclic hydrocarbons identified were tetracontane and undecane, both representing ~30% of the acyclic constituents and 6.5% of total crude oil composition. Table 2 presents the

Table 1
Acyclic hydrocarbons found in crude oil.

RT	Area %	Library/ID	Mol. weight	Formula
3.97	1.97	Hexane, 2,3,4-trimethyl-	128.255	C ₉ H ₂₀
4.43	0.46	3-Ethyl-3-methylheptane	142.2817	C ₁₀ H ₂₂
6.61	0.71	Heptane, 3-ethyl-2-methyl-	142.2817	C ₁₀ H ₂₂
9.26	0.34	Decane, 2-methyl-	156.3083	C ₁₁ H ₂₄
9.39	0.50	Decane, 3-methyl-	156.3083	C ₁₁ H ₂₄
10.08	2.73	Undecane	156.3083	C ₁₁ H ₂₄
10.60	0.33	Decane, 3,7-dimethyl-	170.3348	C ₁₂ H ₂₆
11.27	0.40	Undecane, 4-methyl-	170.3348	C ₁₂ H ₂₆
12.12	0.83	Dodecane	170.3348	C ₁₂ H ₂₆
12.47	0.85	Undecane, 2,6-dimethyl-	184.3614	C ₁₃ H ₂₈
15.66	1.32	Dodecane, 2,6,10-trimethyl-	212.4146	C ₁₅ H ₃₂
18.66	0.35	Decane, 2-methyl-	156.3083	C ₁₁ H ₂₄
20.42	1.24	Pentadecane, 2,6,10-trimethyl-	254.4943	C ₁₈ H ₃₈
21.87	0.57	Hexadecane, 7,9-dimethyl-		
23.66	0.41	Heptadecane, 3-methyl-		
30.62	1.86	Tetracosane	338.6538	C ₂₄ H ₅₀
31.71	1.77	Octacosane	394.7601	C ₂₈ H ₅₈
32.77	1.37	Hexacosane	366.7070	C ₂₆ H ₅₄
33.79	1.07	Tetracosane	338.6538	C ₂₄ H ₅₀
35.71	0.68	Nonacosane	408.7867	C ₂₉ H ₆₀
36.65	0.44	Triacontane	422.8133	C ₃₀ H ₆₂
37.56	0.55	Triacontane		
38.44	0.46	Tetracosane		
39.30	0.42	Tetracosane		

Table 2
Cyclic hydrocarbon constituents of petroleum sample.

RT	Area %	Library/ID	Mol. weight	Formula
3.66	3.47	Cyclohexane, 1,4-dimethyl-, trans-	112.2126	C ₈ H ₁₆
4.06	0.85	Cyclohexane, 1,4-dimethyl-, trans-		
4.54	2.81	Cyclohexane, ethyl-	112.2126	C ₈ H ₁₆
4.84	0.35	Cyclohexane, 1,2,4-trimethyl-, (1.alpha.,2.beta.,4.beta.)-	126.2392	C ₉ H ₁₈
4.90	0.41	Cyclohexane, 1,2,4-trimethyl-, (1.alpha.,2.beta.,4.beta.)-		
5.55	1.03	1-Ethyl-4-methylcyclohexane	126.2392	C ₉ H ₁₈
5.94	0.37	cis-1-Ethyl-3-methyl-cyclohexane	126.2392	C ₉ H ₁₈
6.39	0.55	Cyclohexane, propyl-	126.2392	C ₉ H ₁₈
8.58	0.99	Cyclohexane, butyl-	140.2658	C ₁₀ H ₂₀
9.09	1.10	Naphthalene, decahydro-	138.2499	C ₁₀ H ₁₈
10.63	0.73	1-Methyldecahydro-naphthalene	152.2765	C ₁₁ H ₂₀
10.78	0.61	Cyclohexane, pentyl-	154.2924	C ₁₁ H ₂₂
12.68	1.25	1,7,7-Trimethyl-2-vinylbicyclo [2.2.1]hept-2-ene	162.2713	C ₁₂ H ₁₈
12.95	0.85	Cyclohexane, hexyl-	168.3190	C ₁₂ H ₂₄
13.98	0.44	Cyclohexane, 1-ethyl-1-methyl-	126.2392	C ₉ H ₁₈
15.00	0.91	Heptylcyclohexane	182.3455	C ₁₃ H ₂₆

Table 3
Polycyclic aromatic hydrocarbon constituents.

RT	Area %	Library/ID	Mol. weight	Formula
11.89	1.65	Naphthalene	128.1705	C ₁₀ H ₈
14.14	3.57	Naphthalene, 1-methyl-	142.1971	C ₁₁ H ₁₀
14.50	1.66	Naphthalene, 1-methyl-		
15.74	0.69	Naphthalene, 2-ethenyl-	154.2078	C ₁₂ H ₁₀
16.55	2.41	Naphthalene, 1,6-dimethyl-	156.2237	C ₁₂ H ₁₂
16.91	0.75	Naphthalene, 2,7-dimethyl-	156.2237	C ₁₂ H ₁₂
17.17	0.59	Naphthalene, 1,3-dimethyl-	156.2237	C ₁₂ H ₁₂
18.24	0.30	Naphthalene, 1,4,6-trimethyl-	170.2503	C ₁₃ H ₁₄
18.35	0.38	Naphthalene, 1-(1-methylethyl)-	170.2503	C ₁₃ H ₁₄
18.43	0.78	Naphthalene, 1,4,6-trimethyl-		
18.53	0.93	Naphthalene, 2,3,6-trimethyl-	170.2503	C ₁₃ H ₁₄
18.79	0.98	Naphthalene, 1,6,7-trimethyl-	170.2503	C ₁₃ H ₁₄
18.85	0.53	Naphthalene, 2,3,6-trimethyl-		
19.07	0.59	Naphthalene, 1,6,7-trimethyl-		
19.38	0.93	Fluorene	166.2185	C ₁₃ H ₁₀
19.49	0.64	Naphthalene, 1,4,5-trimethyl-	170.2503	C ₁₃ H ₁₄
20.83	0.30	1,4,5,8-Tetramethylnaphthalene	184.2768	C ₁₄ H ₁₆

Table 4
Volatile organic compounds/BTEX and derivatives.

RT	Area %	Library/ID	Mol. weight	Formula
3.50	3.77	Toluene	92.1384	C ₇ H ₈
5.05	1.60	Benzene, 1,3-dimethyl-	106.1650	C ₈ H ₁₀
5.23	4.17	o-Xylene	106.1650	C ₈ H ₁₀
5.65	0.86	o-Xylene	106.1650	C ₈ H ₁₀
6.27	0.45	Benzene, (1-methylethyl)-	120.1916	C ₉ H ₁₂
6.89	1.79	Benzene, propyl-	120.1916	C ₉ H ₁₂
7.09	1.966	Benzene, 1-ethyl-3-methyl-	120.1916	C ₉ H ₁₂
7.24	1.32	Benzene, 1,2,3-trimethyl-	120.1916	C ₉ H ₁₂
7.45	0.42	Benzene, 1-ethyl-2-methyl-	120.1916	C ₉ H ₁₂
7.77	2.20	Benzene, 1,2,3-trimethyl-	120.1916	C ₉ H ₁₂
8.08	0.47	Benzene, (2-methylpropyl)-	134.2182	C ₁₀ H ₁₄
8.99	1.06	Benzene, 1-methyl-3-propyl-	134.2182	C ₁₀ H ₁₄
9.15	0.66	Benzene, 1-ethyl-3,5-dimethyl-	134.2182	C ₁₀ H ₁₄
9.73	1.06	Benzene, 4-ethyl-1,2-dimethyl-	134.2182	C ₁₀ H ₁₄
10.41	0.89	Benzene, 1,3-diethyl-5-methyl-	148.2447	C ₁₁ H ₁₆
10.51	0.73	Benzene, 1,2,4,5-tetramethyl-	134.2182	C ₁₀ H ₁₄
10.99	0.81	Benzene, (1,1-dimethylpropyl)-	148.2447	C ₁₁ H ₁₆
11.17	1.16	Benzene, 1,2,3,4-tetramethyl-	134.2182	C ₁₀ H ₁₄
11.64	0.68	Benzene, 1-methyl-4-(1-methylpropyl)-	148.2447	C ₁₁ H ₁₆

Table 5
Non-hydrocarbons characterized using GC-MS.

RT	Area %	Library/ID	Mol. weight	Formula
6.18	0.53	(Z)-Hex-3-enyl (E)-2-methylbut-2-enoate		
8.14	0.45	Benzeneacetaldehyde, .alpha.-methyl-	134.1751	C ₉ H ₁₀ O
13.07	0.34	2-Cyclopenten-1-one, 3-methyl-2-(1,3-pentadienyl)-, (E,Z)-		
13.19	1.15	7-Oxabicyclo[4.1.0]heptane, 1,5-dimethyl-		
13.67	0.98	Sulfurous acid, 2-ethylhexyl tridecyl ester		
15.10	0.32	Tetradecane, 1-chloro-	232.833	C ₁₄ H ₂₉ Cl
15.30	0.45	2,6-Heptadienal, 2,4-dimethyl-		
15.50	0.51	Sulfurous acid, butyl dodecyl ester		
20.03	0.28	[1,1'-Biphenyl]-4-carboxaldehyde	182.2179	C ₁₃ H ₁₀ O
34.76	0.88	Heptacosane, 1-chloro-	415.179	C ₂₇ H ₅₅ Cl
39.70	0.38	.beta.-Sitosterol	414.7067	C ₂₉ H ₅₀ O
40.08	1.07	2-Furancarboxamide, N-(8-methyl-2H-[1,2,4]thiadiazolo[2,3-a]pyridin-2-ylidene)-		
41.99	0.28	Acetic acid, 4,4,6a,6b,8a,11,12,14b-octamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14b-octadecahydricen-3-yl ester		

Table 6
Other components of crude oil sample.

RT	Area %	Library/ID	Mol. weight	Formula
8.38	2.60	o-Cymene	134.2182	C ₁₀ H ₁₄
9.55	0.64	o-Cymene		
8.68	0.86	Indane	118.1757	C ₉ H ₁₀
11.39	1.08	Naphthalene, 1,2,3,4-tetrahydro-	132.2023	C ₁₀ H ₁₂
11.94	0.46	1H-Indene, 2,3-dihydro-4,7-dimethyl-	146.2289	C ₁₁ H ₁₄
13.54	0.59	Naphthalene, 1,2,3,4-tetrahydro-6-methyl-	146.2289	C ₁₁ H ₁₄
14.62	1.10	Benzene, cyclohexyl-	160.2554	C ₁₂ H ₁₆
16.01	0.71	Naphthalene, 1,2,3,4-tetrahydro-1,4-dimethyl-	160.2554	C ₁₂ H ₁₆
17.69	1.31	1,1'-Biphenyl, 4-methyl-	168.2344	C ₁₃ H ₁₂
17.83	0.60	1,1'-Biphenyl, 4-methyl-		

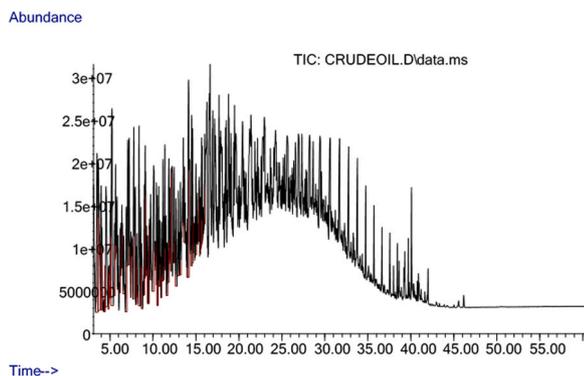


Fig. 1. GC-MS chromatogram of crude oil.

chromatographic data for cyclic hydrocarbons. A total of 14 compounds representing 17% of total crude oil composition were identified. Cyclohexanes such as propylcyclohexane, butylcyclohexane and heptylcyclohexane accounted for > 80% of the cyclic constituents. Of the 14 compounds, only decahydronaphthalene (1.10%), 1-methyldecahydronaphthalene (0.73%) and 1,7,7-trimethyl-2-vinylbicyclo[2.2.1]hept-2-ene are non-cyclohexanes.

3.3. Aromatic hydrocarbons

The monoaromatic constituents of the crude oil sample are dominated by C₇-C₁₁ hydrocarbons. Polycyclic aromatic hydrocarbons and monoaromatic hydrocarbons (volatile organic compounds (VOCs)/BTEX and derivatives) are presented in Tables 3 and 4, respectively. A total of 13 PAHs ranging from C₁₀-C₁₃ and constituting 18% of crude oil composition were identified using GCMS. PAHs were dominated by 2-

ring structured naphthenic compounds (fluorene is the only non-naphthalenic compound). Naphthalene and fluorene are important aromatic compounds which have been classified as priority PAHs owing to their neurotoxicity and carcinogenicity [33]. Di- and tri- substituted naphthalenes account for about 40% of total PAHs in the crude oil analyzed. 1-methylnaphthalene, one of only two monosubstituted PAHs found in the analyzed crude oil corresponds to nearly 30% of the PAHs constituents. Alkylated PAHs are known to be more toxic than their unsubstituted congeners [34]. Table 4 presents Kovats retention time, molecular weight and formula of monoaromatic constituents, mostly BTEX-based compounds. The high percentage of volatile compounds in the analysed crude oil (29%) signifies minimal weathering has occurred. Of these compounds, benzene and its substituted derivatives account for about 60% of total monoaromatics. Toluene (3.78%), o-cymene (3.24%) and o-xylene (5.03%) are the only non-alkyl substituted monoaromatics.

3.4. Non-hydrocarbons and other constituents

Tables 5 and 6 present the chromatographic data for non-hydrocarbons and other crude oil constituents not belonging to any of the groups already identified. A total of 13 non-hydrocarbons representing 7% of total crude oil composition were identified. Two halogenated alkanes namely 1-chlorotetradecane and 1-chloroheptacosane were identified. Of the other constituents – comprising of 7 compounds, 1,2,3,4-tetrahydro-naphthalene, (1.0817%), cyclohexyl-benzene (1.0988%) and 4-methyl-1,1'-biphenyl (1.9145%) are the most abundant. Although these are all aromatic compounds, they are not generally classified as PAHs or BTEX derivatives.

Different analytical methods are used for conventional crude oil characterization such as GC-FID, GCMS, Fourier Transform Infrared Spectroscopy (FTIR), Thermo-gravimetric Analysis (TGA)-FTIR, TGA-MS, TGA-Differential Thermal Analysis (DTA), and Nuclear Magnetic Resonance (NMR) Spectrometry [32,35-39]. American Society for Testing and Materials (ASTM) D-2425, D2786, and D-3239 standard methods have prescribed chromatographic conditions for separation of saturates and aromatics in petroleum and its products. Some other standard ASTM methods include D-7213 and D-7169 for simulated distillation (Sim Dis) and high temperature methods for crude oils, respectively (Annual Book of ASTM Standards. Vol. 05.04). While ASTM D-7213 has been extensively employed for Sim Dis analysis of crude oil, one major drawback is the use of carbon disulfide (CS₂) – a foul-smelling, toxic and highly flammable solvent.

A gas chromatographic technique that acquires both FID and MS spectra data for group type analysis of petroleum products using controlled carrier gas flow in the capillary column was reported by [35]. Crude oil, diesel and lube fractions were analysed using ASTM D-7213 and D-7169. Chromatograms obtained were correlated with a reference quality control standard. Previous studies on GCMS characterization of Nigerian crude oil samples indicate abundance of n-alkanes [40,41]. Odeunmi and Ismael [32] studied the effect of alumina and

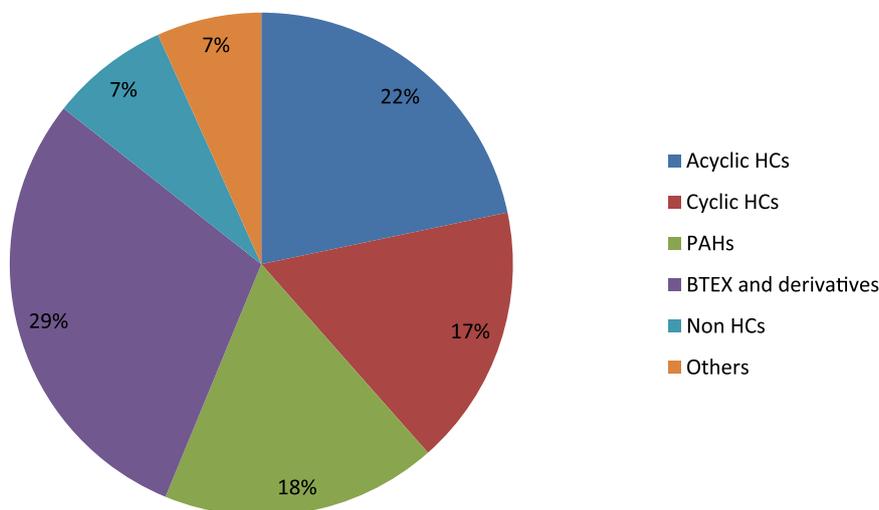


Fig. 2. Chart showing percent of crude oil composition after GC-MS analysis.

silica-alumina stationary phases on separation of Nigerian crude oil into constituent fractions prior to GC-MS characterization. Crude oil fractions were eluted with 100% n-hexane (saturates), 5% benzene + 95% n-hexane (monoaromatics), 15% benzene + 85% n-hexane + 60% methanol (diaromatics), 20% diethyl ether + 20% benzene (polyaromatics) using both alumina and silica-alumina phases. Results obtained suggested that the nature of stationary phase used may affect the quantity of petroleum constituents obtained. Crude oil studied (Gulf heavy oil) was found to contain higher quantity of aromatics than saturates, with alumina stationary phase giving better separation.

3.5. Chemical oxidation of TPH in crude oil contaminated water

The degradation of TPH in petroleum contaminated water was studied over a period of 8 days. The initial concentration of TPH in contaminated water after analysis using GC-FID was found to be 137.33 mg L^{-1} (Fig. 3). This represents a recovery of about 96% from initial contamination of $15 \text{ mg}/100 \text{ mL}$ in each reaction vessel.

The % TPH degradation increased with time and oxidant dosage. The maximum TPH degradation (about 96%) was obtained with 0.5 M sodium persulphate after 8 days. With 0.7 M sodium persulphate, TPH degradation increased steadily from 31% to 74% within the first 6 days, then slowly during the 6th - 8th day. For the 0.3 and 0.5 M sodium persulphate, > 90% TPH degradation was achieved with ~ 80%

degradation within the first 2 days. This represents 85% and 84% of total degradation respectively. In contrast, the increase in degradation efficiency between the last two days (days 6–8) corresponds to ~1.5% and 1.6% respectively. This also applies to oxidant dosage of 0.7 M with 2.9% increase in TPH degradation efficiency between days 6–8. The results indicated that increasing contact time increased the percentage of TPH removal, with steady degradation observed within the first 6 days. This can be attributed to the decrease in surface activity for the uptake of pollutant particles. From the results obtained, it can be seen that increasing contact beyond 6 days only achieved marginal increase (<3% for all oxidant dosages) in % TPH degradation.

The activation of persulphates, achieved under alkaline condition, result in the production of sulphate radicals, thereby initiating a radical chain reaction (Eqs. (1) and (2)). The radicals produced immediately react with hydrocarbon contaminants, oxidizing them. Eventually, both contaminants and intermediates are degraded. However, continued increase in oxidant dosage results in instant production of large amount of sulphate radicals (SO_4^-). These radicals are consumed upon reacting with each other, resulting in termination of the reaction via formation of persulphate ions (Eq. (3)) [42]. The steady rate of degradation observed with 0.3 and 0.5 M sodium persulphate is absent with 0.7 M oxidant. The termination reaction (Eq. 3) probably accounts for the decrease in % TPH removal observed with 0.7 M sodium persulphate. This could be attributed to the rapid increased production of sulphate radicals with

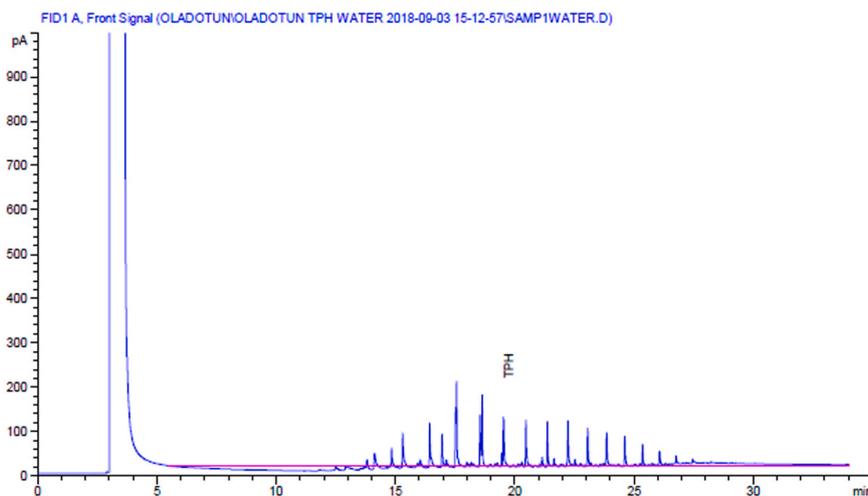
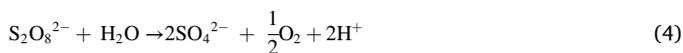


Fig. 3. GC chromatogram of initial concentration of TPH in water prior to degradation.

higher oxidant concentration, thereby reducing alkalinity. Considering that 0.3 M sodium persulphate (pH 10) achieved about 92% TPH degradation within 6 days, the use of higher oxidant dosage and more time may not be optimal. The plot of % TPH degradation with time for alkaline activated persulphate degradation using varying oxidant dosage is presented in Fig. 4.



From the results obtained, it is likely that increasing concentration of sodium persulphate leads to corresponding increase in acidity of contaminated media. Thus, the effect of oxidant dosage on the experimental set up – prior to pH adjustment was studied. The initial pH of petroleum-contaminated water was observed to be 7.8. On addition of sodium persulphate to the contaminated water, it was observed that the pH of the mixture changed in relation to oxidant dosage. The addition of 0.3, 0.5 and 0.7 M sodium persulphate resulted in pH decrease from an initial 7.8–4.7, 3.9 and 3.1, respectively. Thus, the higher the concentration of sodium persulphate, the more acidic the mixture. This indicates that the alkalinity of the water - persulphate mixture decreased with increasing persulphate concentration. It is possible that persulphate itself serves as a source of oxygen during hydrolysis, and the equation could be represented as follows (4):



Since the hydrolysis of persulphate generates H^+ ion, it is expected that acidity increases and the pH of the mixture is lowered. This perhaps explains the decrease in pH from 7.8 to 3.1, on addition of 0.7 M sodium persulphate, prior to pH adjustment with sodium hydroxide.

3.6. The role of thiosulphate in radical quenching/scavenging

Scavengers are used to demonstrate the occurrence of a radical reaction process. Termination in a radical chain reaction results from the production of unreactive radicals [43,44]. To investigate the generation of hydroxyl and sulphate radicals, sodium thiosulphate was used as a scavenger. Fig. 5 presents a chart showing the initial concentration of TPH (pre-degradation) and the effect of thiosulphate as a scavenger after 8 days using all three oxidant dosages. In the presence of the scavenger, the TPH concentration with all oxidant dosages (131, 141 and 139 mg L^{-1} TPH with 0.3, 0.5 and 0.7 M sodium persulphate, respectively) was similar to the initial concentration of TPH prior to degradation (137 mg L^{-1}). Therefore, since no considerable change was observed in TPH concentration after 8 days, TPH degradation was almost completely inhibited in the presence of sodium thiosulphate.

Several radical scavengers have been employed in previous studies such as potassium iodide, alcohols (mannitol, methanol, ethanol), ice and sodium bicarbonate. Alcohols have been reported to possess lower scavenging power, especially in thermally-activated persulphate oxidation processes due to evaporation at high temperatures [44–47].

4. Conclusion

GC-MS characterization of crude oil from Nigeria was carried out. Crude oil was characterized as hydrocarbons (aliphatics and aromatics), non-hydrocarbons and other constituents. The percentage composition of petroleum hydrocarbons was about 86%. Of the hydrocarbons identified, aromatics made up 55% of total constituents. Aromatic compounds were mainly alkylated benzenes, toluene, o-xylene, fluorene and naphthalenic compounds. Aliphatic compounds were mostly n-alkanes ($\text{C}_9\text{-C}_{30}$) and cyclic hydrocarbons ($\text{C}_8\text{-C}_{13}$) such as cyclohexane and heptylcyclohexane. Different concentrations of sodium persulphate were evaluated to remediate petroleum hydrocarbon contamination in water at alkaline pH. Near complete degradation of total petroleum hydrocarbons (TPH) was achieved within 8 days. Oxidant dosage of 0.5 M showed highest degradation efficiency (96%) within this period,

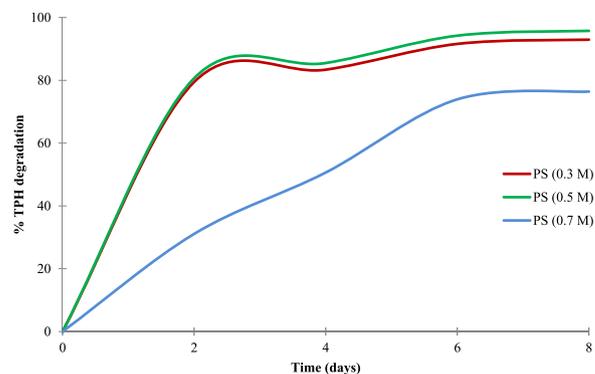


Fig. 4. Effect of nanoparticles-mediated persulphate activation on TPH degradation.

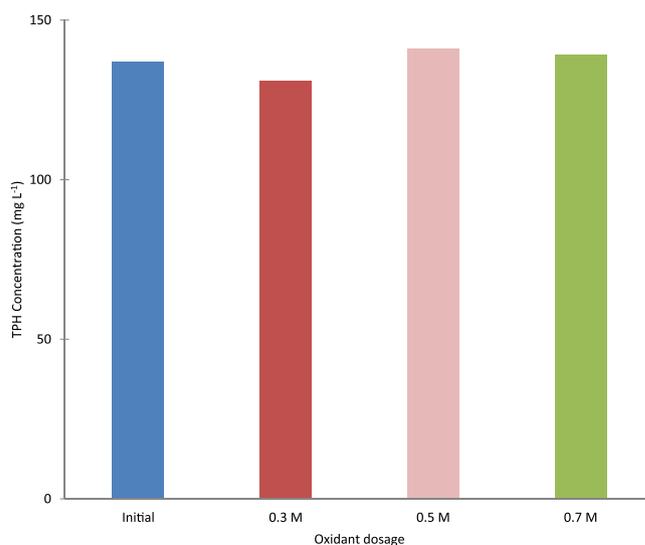


Fig. 5. Effect of radical quenching on TPH degradation with varying oxidant dosage.

while lowest degradation was achieved with 0.7 M oxidant. Optimum degradation was achieved within 6 days for all oxidant concentrations. With 93% TPH degraded at day 6 using 0.3 M oxidant, this condition suggests optimum degradation for the experiment. Radical quenching was studied using sodium thiosulphate. The results obtained showed that addition of sodium thiosulphate to the reaction set-up resulted in negligible changes between initial concentration of TPH in contaminated water pre-degradation and TPH concentration after 8 days using all three oxidant dosages. Hence, thiosulphate acted as an effective scavenger for hydroxyl and sulphate radicals.

CRediT authorship contribution statement

Oladotun Bolade, Nsikak Benson: Conceptualization; **Oladotun Bolade:** Data curation; **Oladotun Bolade, Nsikak Benson:** Formal analysis; **Nsikak Benson:** Funding acquisition; **Oladotun Bolade, Akan Williams, Nsikak Benson:** Investigation; **Oladotun Bolade, Nsikak Benson:** Methodology; **Nsikak Benson:** Project administration; **Nsikak Benson, Akan Williams:** Supervision; **Oladotun Bolade:** Writing - original draft; **Nsikak Benson, Oladotun Bolade, Akan Williams:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that there is no conflict of interest.

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