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Research Article

Photodegradation of Ghana Crude Oil by Sunlight Irradiation

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Abstract: Photochemical degradation of crude oil in seawater is critical in the protection of the marine environment during oil spillages. In this study, the photochemical weathering of Ghana Crude Oil (GCO) was investigated, by irradiation with natural sunlight. The analytical techniques of Gas chromatography-Mass Spectrometry (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR) were applied in the identification of aromatic and aliphatic components after 10 weeks of irradiation. The aliphatic components exhibited low susceptibility for photo-chemical degradation, while the aromatic components were mainly affected by photo-oxidation. The results showed a decrease in the number of aromatic and aliphatic compounds detected by 39% and 35% respectively. These results confirm photo-oxidation by natural sunlight as an effective remediation process for GCO, especially under high solar radiation environmental conditions.

***Keywords*:** sunlight, photo-oxidation, crude oil degradation, Gas chromatography-Mass Spectrometry

1. Introduction

The exploration and utilisation of crude oil and its derived products have significantly contributed in advancing human civilisation. Crude oil and its derivatives find applications in various aspects of human existence, spanning from industry, trade, households, and nation-building.[1,2] Crude oil has served as a primary energy source for many decades for both developed and developing nations worldwide driving extensive exploration and extraction activities.[3,4]

A significant issue associated with crude oil and its refined products is the occurrence of spillage on land and over the oceans, which may emanate from accidents or during transportation.[5,6] Most compounds originating from petroleum consist primarily of non-toxic saturated hydrocarbons.[7] However, these compounds serve as precursors for the formation of other photo-degraded products. Hence, it is essential to identify and measure them to track and monitor the presence, transformation, and chemical composition changes of petroleum products.[8-10] Various analytical tools can be used for the identification of these components. Liquid-liquid extraction (LLE) can extract constituents from water samples. Infrared spectroscopy is effective for recognising components by detecting functional group absorptions, even at low concentrations. Additionally, Gas Chromatography-Mass Spectrometry (GC-MS) is a high-sensitivity method for analysing aliphatic and aromatic components.[11-13]

Sunlight plays a crucial role in breaking down various naturally occurring chemical substances in both aquatic and terrestrial environments.[14,15] The process of photochemical degradation has the potential to transform the original

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compounds found in crude oil and petroleum derivatives into photodegraded products, inducing alterations in their chemical composition, reactivity, and, consequently, their toxicity.[16,17] In the aftermath of an oil spillage, sunlight exposure can trigger a sequence of chemical reactions in floating slicks, leading to the conversion of the oil into new compounds.[18,19]

Both natural and artificial sunlight exposure have been observed to enhance the solubility of oil due to the generation of photoproducts derived from the polar aliphatic and aromatic compounds present in petroleum fractions. The initial reduction and subsequent decline in the quantities of oil and petroleum products may be attributed to photochemical reactions.[20,21]

The Ghana Crude Oil (GCO) used in this study, is a dry oil with low water content (< 1%) which reduces its ability for microbial growth and collection of water soluble metals and salts. It has an acceptable API and sulphur content of 35 and 0.237 respectively and hence classified as a sweet crude oil.[22] Given the distinctiveness of each crude oil, it becomes crucial to understand how crude oil from Ghana reacts when exposed to sunlight. The data generated through this research will serve as a foundational resource for making well-informed choices regarding remediation approaches and policy formulation in the event of an oil spillage.

2. Material and methods

2.1 *Chemicals and materials*

The Ghana Crude Oil (GCO) composite sample was sourced from the Jubilee Field in the Western Region of Ghana and preserved in an amber reagent bottle sealed with a plastic cap. The reagents, including acetone, hexane, diethyl ether, ethyl acetate, toluene, and methanol, were of analytical grade from British Drug House (BDH) Chemicals, UK.

2.2 *Analytical methods*

2.2.1 *Sample irradiation*

The irradiated samples were prepared following the modified method outlined by King et al.[23] A 100 ml aliquot of GCO was transferred into three 600 ml beakers, each filled with 400 ml of distilled water, and left to float. These beakers were covered with plastic wrap. Over a period of ten weeks, the samples were exposed to natural sunlight with an average temperature of 25.9 °C on the third floor of the Chemistry building at Kwame Nkrumah University of Science and Technology (KNUST), from 10 am to 4 pm. Dark controls, wrapped in aluminum foil, were prepared and stored in the dark in the laboratory. The sample identification used during the irradiation period were as follows: C_0 (before), C_1 (2 weeks), C_2 (4 weeks), C_3 (6 weeks), C_4 (8 weeks), and C_5 (10 weeks).

2.2.2 *Liquid-liquid extraction (LLE) of crude oil*

A 20 ml aliquot of the aqueous solution and a separate 5 ml aliquot of the oil layer from the irradiated Ghana Crude Oil (GCO) were subjected to extraction using various organic solvent systems in a 50 ml separatory funnel. The mixtures were shaken for 5 minutes and allowed to stand for 10 minutes. The organic phase was then collected into 50 ml glass tubes with aluminum-coated screw caps. This involved shaking each with 10 ml of hexane for aliphatics (F_1), 10 ml of a 1:1 hexane-methanol mixture for polycyclic aromatic hydrocarbons (PAHs) (F_2), and 10 ml of a 9:1 ethyl acetate-diethyl ether combination for polar oxygenated products (F_3). The extracts F_1, F_2, and F_3 were combined and concentrated using a Buchi Rota Vap rotary evaporator at 50 °C and 100 Pa, resulting in a volume of approximately 1 ml. This concentrate was reconstituted in 5 ml of hexane for subsequent GC-MS and FT-IR analysis. For additional extraction details adopted from Gawel el al.[24]

2.2.3 *Full-scan GC-MS analysis*

The extracts were subjected to analysis for aromatic and aliphatic components using a 450-GC interfaced with a Varian 220-MS detector, GC-MS. The GC column chosen for this analysis was VF-ms 5 (CP8944) with dimensions of 30 m × 0.25 mm × 0.25 µm, sourced from Agilent, USA. Helium was utilized as the carrier gas, flowing at a rate of 1 ml/min. A 1 µl extract was manually injected in splitless mode. The GC oven followed a prescribed temperature program: initially held at 50 °C for 5 minutes, followed by a ramp of 5 °C/min to 300 °C, and maintained at 300 °C for 20 minutes. The Varian MS operated in EI mode at 70 eV, employing a full scan mode within the range of 50-500 m/z. The MS source temperature was set at 200 °C, the transfer line at 250 °C, and the manifold temperature at 80 °C.

2.2.4 *FTIR analysis*

FTIR analysis were conducted on the extracts using an FTIR-ATR Spectrophotometer from Agilent, USA. Spectra were acquired in the wavelength range of 4,000-400 cm^{-1} with 32 scans and a resolution of 4 cm^{-1}. The samples were applied dropwise directly onto the Attenuated Total Reflectance (ATR) cell, and spectra were recorded after solvent evaporation at room temperature. Following each analysis, the cell was cleaned three times with propanol, as per the procedure outlined by Gawel et al.[25]

3. Results and discussion

3.1 *Irradiation products of GCO*

The impact of photo-oxidation as a weathering phenomenon on the degradation of GCO is evident in the chromatograms depicted in Figures 1 and 2 for C_0 and C_5, respectively.

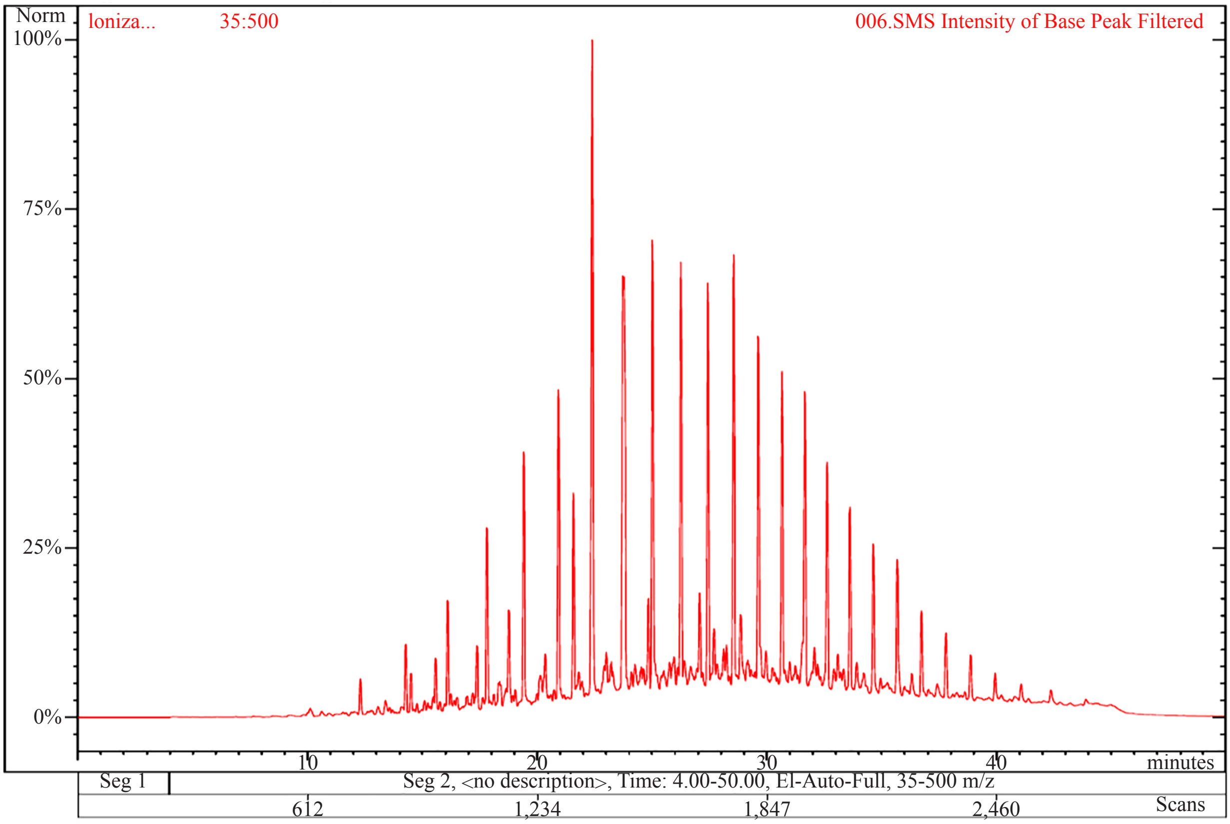

Figure 1. GC-MS chromatogram of GCO extract before irradiation (C_0) 0 week

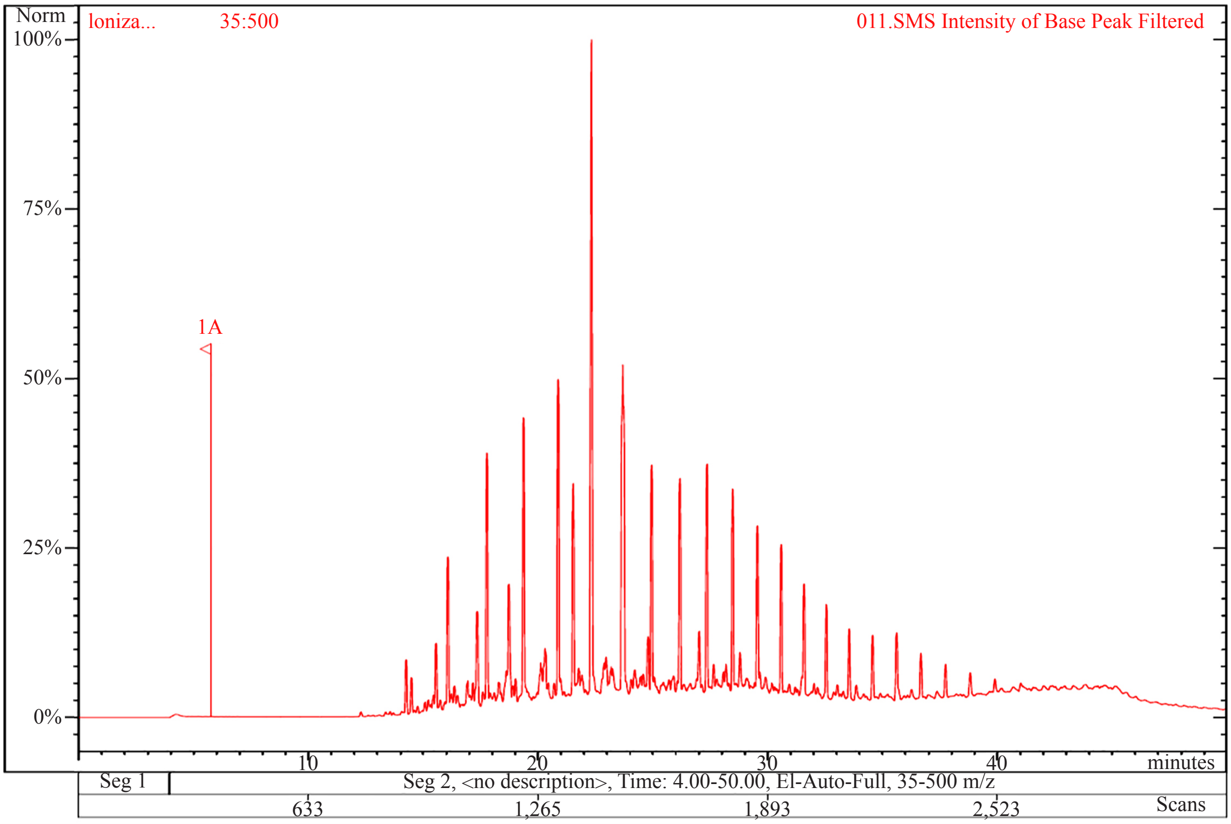

Figure 2. GC-MS chromatogram of GCO extracts after 10 weeks(C_5) irradiation

While the chromatograms of the irradiated extracts (refer to Appendix A) generally share similarities, a more detailed examination reveals noticeable differences in both the quantity and retention times of the major peaks identified. The chromatogram of the non-irradiated extract displayed the highest peak count compared to the irradiated samples. Specifically, the number of identified peaks was 88, 86, 61, 59, and 49 for extracts C_1, C_2, C_3, C_4, and C_5, respectively. This indicates a reduction of approximately 56% in the number of peaks after the ten-week duration. The decline in the number of peaks, as illustrated in Figure 2, is attributed to photochemical transformations and evaporation, especially affecting the early eluting lower boiling point constituents over the duration of solar radiation.[26] The study focused exclusively on the aliphatic and aromatic components, given the intricate nature of crude oils.

3.2 *Identified aromatic components*

In all the extracts, the number of aromatic compounds was consistently higher than that of aliphatics, indicating that aromatics constitute a significant portion of the GCO composition (refer to Figure 3). The non-irradiated sample (C_0) exhibited the highest count for both aliphatic and aromatic components. Nevertheless, there was an overall decrease in the number of components in the irradiated samples. Specifically, aromatics experienced an average reduction of 39.2%, while aliphatics showed a 35% decrease in terms of the number of compounds (see Figure 3).

For the C_5 extract, the number of aromatic compounds exceeded that of the other extracts (refer to Figure 3). The extended duration of irradiation had a notable impact on the degradation, leading to an increase in aromatics and the subsequent formation of other components. The aromatic compounds (Figure 3) experienced a significant decrease of approximately 32% when comparing samples before irradiation with those after 10 weeks of irradiation. This observation underscores the susceptibility of aromatic components to photo-oxidation.[27] The identified aromatics were predominantly parent compounds, likely originating from the initial crude oil (see Table 1). However, they act as precursor compounds that may undergo photo-oxidation to yield corresponding products.

Among the identified aromatics, alkylated naphthalenes constituted the majority compared to other classes, with alkylated benzene homologues and PAHs accounting for 20% and 80%, respectively, of the identified aromatics (refer to Table 1).

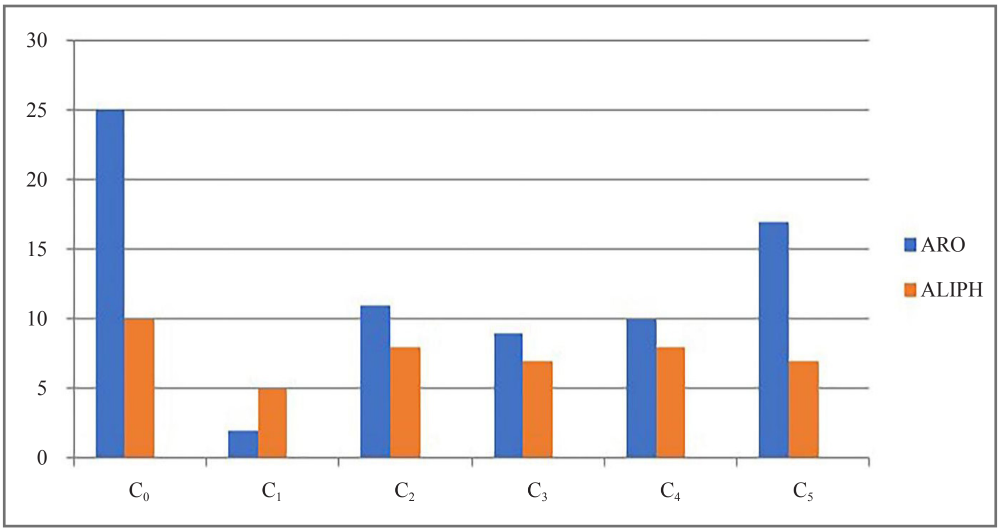

Figure 3. Aromatic (ARO) and Aliphatic (ALIPH) compounds of the crude oil extracts

Table 1. Identification Data for identified Aromatics

ID	t_R (min)	MW	CAS NUMBER	COMPOUND
C_1	18.733	112	632-15-5	3,4-dimethylthiophene
C_2	10.634	120	108-67-8	1,3,5-trimethylbenzene
	13.047	152	4683-95-8	2-methyldecahydronaphthalene
	13.399	134	488-23-3	1,2,3,4-tetramethylbenzene
	16.505	142	91-5- 6	2-methylnaphthalene
	18.089	156	575-37-1	1,7-dimethylnaphthalene
	18.375	156	575-43-9	1,6-dimethylnaphthalene
	20.875	170	2131-42-2	1,4,6-trimethylnaphthalene
	22.096	184	3031-15-0	1,2,3,4-tetramethylnaphthalene
	24.200	194	4612-63-9	2,3-dimethylfluorene
	24.474	194	2294-82-8	1-ethylfluorene
	27.031	178	65996-93-2	Phenanthrene

Table 1. (cont.)

ID	t_R (min)	MW	CAS NUMBER	COMPOUND
C_3	10.617	120	108-67-8	1,3,5-trimethylbenzene
	12.701	152	4683-95-8	2-methyldecahydronaphthalene
	13.399	134	488-23-3	1,2,3,4-tetramethylbenzene
	13.818	148	700-12-9	C_5-benzene
	14.077	166	1618-22-0	1,2-dimethyldecahydronaphthalene
	28.216	220	30232-26-9	C_3-phenanthrene
C_4	12.701	152	4683-95-8	2-methyldecahydronaphthalene
	13.393	134	934-80-5	4-ethyl-o-xylene
	13.672	148	700-12-9	C_5-benzene
	13.800	148	700-12-9	C_5-benzene
	16.205	142	2471-83-2	1-ethylidene-1H-Indene
	20.093	170	2245-38-7	1,6,7-trimethylnaphthalene
C_5	13.052	152	2958-75-0	1-methyldecahydronaphthalene
	13.390	134	934-80-5	4-ethyl-o-xylene
	16.203	142	2471-83-2	1-ethylidene-1H-Indene
	18.086	156	575-37-1	1,7-dimethylnaphthalene
	18.316	156	571-58-4	1,4-dimethylnaphthalene
	20.288	170	819871-70-0	3-(2-methyl-1-propenyl)-1H-Indene
	22.098	184	3031-15-0	1,2,3,4-tetramethylnaphthalene
	24.057	212	89816-98-8	2-ethyl-dibenzothiophene
	24.237	194	4569-45-3	C_2-fluorene
	26.186	212	1207-12-1	C_2-dibenzothiophene
	27.023	156	581-42-0	2,6-dimethylphenanthrene
	28.292	220	30232-26-9	C_3-phenanthrene

Source: From this study

3.3 *Identified aliphatic components*

The count of identified aliphatics remained relatively constant, except for C_1, which displayed only 5 aliphatic compounds, making it as an experimental outlier (see Figure 3). This aligns with the observation that aliphatics tend to exhibit low degradation when exposed to sunlight.[5] The aliphatic compounds identified in the GCO encompassed branched, linear, cyclic, and alkenes, as detailed in Table 2. The peak with a retention time of 22.315 minutes showed no significant decrease in area across all extracts and consistently appeared as a broad peak. This behavior is consistent with either phytane or pristane, both recognised for their notable resistance to photo-oxidation.[27]

The majority of the identified aliphatics were substituted n-alkanes, with approximately equal number of alkenes and cyclohexane. The number of branched aliphatic were higher relative to the other classes, mainly ascribed to the photo-oxidation of linear aliphatics.

Table 2. Identification Data for identified Aliphaticss

ID	t_R (min)	MW	CAS NUMBER	COMPOUND
C_1	12.280	170	17312-44-6	2,3-dimethyldecane
	14.255	156	13151-34-3	3-methyldecane
	17.346	170	17312-54-8	3,7-dimethyldecane
	23.728	296	54833-48-6	2,6,10,15-tetramethylheptadecane
C_2	12.276	170	17312-44-6	2,3-dimethyldecane
	14.484	154	13157-29-6	4-methyl-1-decene
	16.376	168	54410-98-9	4,6,8-trimethyl-1-Nonene
	17.609	154	62238-33-9	1-ethyl-2-propylcyclohexane
	17.754	170	1002-43-3	3-methylundecane
	17.914	156	6975-98-0	2-methyldecane
	20.858	212	629-62-9	Pentadecane
	21.546	212	3891-98-3	2,6,10-trimethyldodecane
C_3	12.276	170	17312-44-6	2,3-dimethyldecane
	15.095	140	7058-01-7	1-methylpropylcyclohexane
	15.224	266	13151-93-3	7-cyclohexyltridecane
	21.563	212	31295-56-4	2,6,11-trimethyldodecane
	23.747	268	629-92-5	Nonadecane

Table 2. (cont.)

ID	t_R (min)	MW	CAS NUMBER	COMPOUND
C_4	12.274	170	17312-44-6	2,3-dimethyldecane
	14.480	154	13157-29-6	4-methyl-1-decene
	14.741	160	29493-00-3	6-dodecene
	17.609	154	62238-33-9	1-ethyl-2-propylcyclohexane
	21.563	212	31295-56-4	2,6,11-trimethyldodecane
	24.795	268	25117-35-5	5-methyloctadecane
	28.189	296	629-94-7	Heneicosane
C_5	12.284	170	17312-44-6	2,3-dimethyldecane
	14.485	154	13157-29-6	4-methyl-1-decene
	19.351	156	1120-21-4	Undecane
	21.543	212	3891-98-3	2,6,10-trimethyldodecane
	22.325	198	61141-72-8	C_2-dodecane
	23.688	268	54105-67-8	2,6-dimethylheptadecane
	31.587	324	638-67-5	n-Tricosane

Source: From this study

3.4 *FTIR findings for Ghana crude oil*

The FTIR spectra of both the irradiated GCO samples (see Figure 4) and the non-irradiated sample reveal absorption bands associated with C-H bonds in aliphatics, along with additional bands corresponding to other major functional groups.[28]

The peaks around 2,900 cm^{-1} and 1,600 cm^{-1} display subtle changes in the irradiated samples. These slight increases in the absorption bands suggest the occurrence of photo-oxidation in the crude oil.[26] The strong bands in the 3,000-2,800 cm^{-1} range, characteristic of hydrocarbons, indicate the stretching vibrations of C-H alkyl bonds. The band at 722 cm^{-1} is attributed to the presence of long-chain alkyl groups, specifically $(CH_2)n$, where n is greater than or equal to 3.[28] The absorption bands at 870, 810, and 743 cm^{-1} arise from the aromatic nucleus, with mono-substituted, di-substituted (1,2-), and tri-substituted (1,2,3-) configurations, respectively, of the precursor aromatics. Absorptions in the region between 870 cm^{-1} and 720 cm^{-1} consist of four peaks characteristic of hydrogen atoms adjacent to aromatic C-H bonds, representing out-of-plane bend vibrations.

Absorptions between 1,710 cm^{-1} and 1,640 cm^{-1} are attributed to various carbonyl groups, including carboxylic acids, ketones, aldehydes, esters, and amides.[29] The broad absorptions of C-O bonds in the irradiated samples (see Figure 4) can be attributed to the interaction with oxygen, leading to the formation of carbon-oxygen bonds and the consequent generation of carbonyl compounds such as esters, alcohols, and acids due to photo-oxidation.[30]

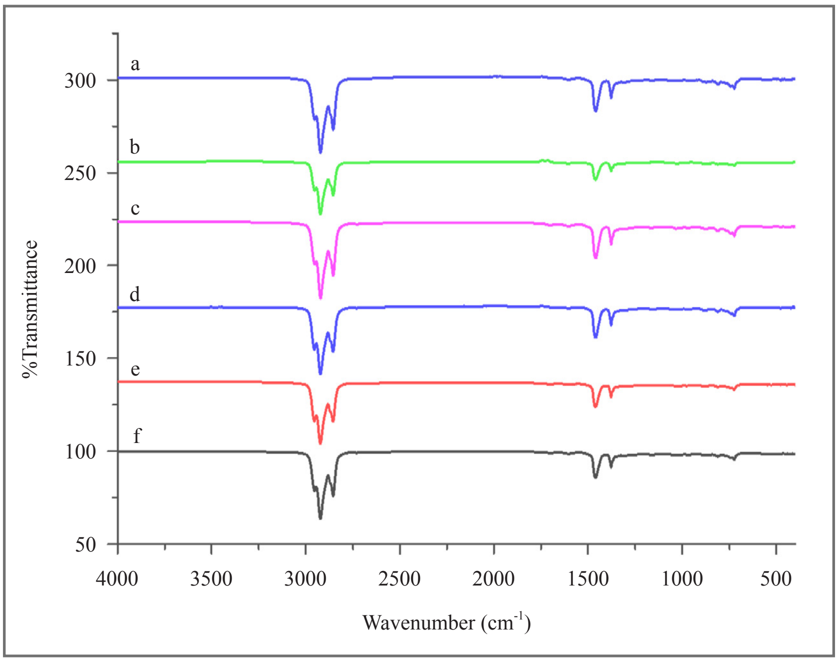

Figure 4. Presents the FTIR spectrum of GCO, with Spectrum (a) representing the state before irradiation, Spectrum (b) after 2 weeks of irradiation, Spectrum (c) after 4 weeks of irradiation, Spectrum (d) after 6 weeks of irradiation, Spectrum (e) after 8 weeks of irradiation, and Spectrum (f) after 10 weeks of irradiation.

4. Conclusion

Analysis conducted using GC-MS and FTIR on GCO extracts unveiled both the degradation and formation of various crude oil products. The primary aromatic compounds identified were alkyl naphthalenes, while aliphatic compounds encompassed branched, cyclic, linear compounds, and alkenes. Additionally, polycyclic aromatic hydrocarbons (PAHs) such as phenanthrene and its alkylated derivatives like C_3-phenanthrene, as well as alkyl fluorenes and dibenzothiophene, were identified. These findings suggest that the photoproducts of GCO have a higher concentration of aromatic compounds compared to aliphatics. Importantly, it is worth noting that these photooxidation products show increased susceptibility to biodegradation compared to their resistant precursor compounds. Consequently, the application of photooxidation induced by natural sunlight emerges as a viable remediation approach for addressing crude oil spillage in the tropical environment of Ghana.

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Conflict of interest

The authors declare no competing financial interest.

References

[1] Lawson, L. Y. D.; Adiku, S. G. K.; Danso, S. K. A. The petroleum find: Its possible impact on the agricultural sector in ghana: The role of soil science. *West Afr. J. Appl. Ecol.* **2014,** *22*, 45-55.

[2] Sumaila, U. R.; Cisneros-Montemayor, A. M.; Dyck, A.; Huang, L.; Cheung, W.; Jacquet, J.; Watson, R. Impact of the deepwater horizon well blowout on the economics of US Gulf fisheries. *Can. J. Fish. Aquat. Sci.* **2012,** *69*, 499-510.

[3] Yang, G.; Li, Z.; Sun, X.; Jing, W. Photochemical degradation of crude oil in seawater. *Chin. J. Oceanol. Limnol.* **2006,** *24*, 264-269.

[4] International Energy Agency (IEA). Key World Energy Statistics, 2015. https://www.iea.org/publications/freepublications/publication/KeyWorld_Statistics_2015.pdf.

[5] Garrett, R. M.; Pickering, I. J.; Haith, C. E.; Prince, R. C. Photooxidation of crude oils. *J. Environ. Sci. Technol.* **1998,** *32*, 3719-3723.

[6] Maki, H.; Sasaki, T.; Harayama, S. Photo-oxidation of biodegraded crude oil and toxicity of the photo-oxidized products. *Chemosphere* **2001,** *44*, 1145-1151.

[7] Yasin, G.; Bhanger, M. I.; Ansari, T. M.; Naqvi, S. M. S. R.; Ashraf, M.; Khizar, A.; Talpur, F. N. Quality and chemistry of crude oils. *J. Pet. Technol. Altern. Fuels* **2013,** *4*, 53-63.

[8] Najafi, M.; Kashi, G. Removal of poly aromatic hydrocarbons and total petroleum hydrocarbon by using of bio-enzyme; a batch study. *J. Med. Bioeng.* **2012,** *1*, 42-47.

[9] Pavlova, A.; Ivanova, R. Determination of petroleum hydrocarbons and polycyclic aromatic hydrocarbons in sludge from wastewater treatment basins. *J. Environ. Monit.* **2003,** *5*, 319-323.

[10] Ukiwe, L. N.; Ergereonu, U. U.; Njoku, P. C.; Nwoko, C. I. A.; Allinor, J. I. Polycyclic aromatic hydrocarbons degradation techniques. *Int. J. Chem.* **2013,** *5*, 43-55.

[11] Yue, Z.; Shi, Q.; Ai, J.; Peng, S.; Micio, X.; Wang, Z. A review on analytical methods of petroleum hydrocarbons in water and sediments of aquatic systems. *IOP Conf. Ser. Earth Environ. Sci.* **2021,** *621*, 012011.

[12] Yolchuyeva, U.; Japharova, L.; Vakhshouri, R. A.; Salmanova, C.; Khamiyeva, G. Photochemical investigation of aromatic hydrocarbons of Balakhani crude oil as petroleum luminophores. *Appl. Petrochem. Res.* **2020,** *10*, 139-148.

[13] Fathalla, E. M. *Degradation of crude oil in the environment: Toxicity arising through photochemical oxidation in the aqueous phase*; Doctoral dissertation, PhD Thesis, University of Münster, Germany, 2007.

[14] Almeda, R.; Harvey, E. T.; Connelly, L. T.; Baca, S.; Buskey, J. E. Influence of UVB radiation on the lethal and sublethal toxicity of dispersed crude oil to planktonic copepod nauplii. *Chemosphere* **2016,** *152*, 446-458.

[15] Griffiths, M. T.; Da Campo, R.; O'Connor, B. P.; Barrow, P. M. Throwing light on petroleum: simulated exposure of crude oil to sunlight and characterization using atmospheric pressure photoionization fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2014,** *86*, 527-534.

[16] Aeppli, C. Recent advances in understanding photooxidation of hydrocarbon after oil spills. *Curr. Opin. Chem. Eng.* **2022,** *36*, 100763.

[17] Xhelilaj, E.; Sinanaj, S. The behaviour and effects of oil pollution into marine environment and oceans. *Sci. J. Mar. Res.* **2010,** *24*, 19-25.

[18] Freeman, H. D. Sunlight-driven dissolution is a major fate of oil at sea. *Sci. Adv.* **2022,** *8*, 7605.

[19] Ganjali, S. T.; Niknafi, B. N.; Khosravi, M. Photooxidation of crude petroleum maltenic fraction in natural simulated conditions and structural elucidation of photoproducts. *Iran. J. Environ. Health Sci. Eng.* **2007,** *4*, 37-42.

[20] Richard, F. L. Photo-oxidation and photo-toxicity of crude and refined oils. *Spill Sci. Technol. Bull.* **2003,** *4*, 157-162.

[21] Ward, C. P.; Reddy, C. M.; Overton, E. B. Why sunlight matters for marine oil spills. *Eos.* **2020,** *101*, 1-12.

[22] Appenteng, M. K.; Golow, A. A.; Carboo, D.; Nartey, V. K.; Kaka, E. A.; Salifu, M.; Aidoo, F. Physicochemical characterization of jubilee crude oil. *Elixir. Appl. Chem.* **2013,** *54*, 12513-12517.

[23] King, S. M.; Leaf, P. A.; Olson, A. C.; Ray, P. Z.; Tarr, M. A. Photolytic and photocatalytic degradation of surface oil from the deepwater horizon spill. *Chemosphere* **2014,** *95*, 415-422.

[24] Ziolli, R. L.; Jardim, W. F. Photochemical transformations of Water-Soluble Fraction (WSF) of crude oil in marine waters. *J. Photochem. Photobiol. Anal. Chem.* **2003,** *155*, 243-25.

[25] Gawel, B.; Eftekhardadkhah, M.; Oye, G. An elemental composition and ft-ir spectroscopy analysis of crude oils and their fractions. *Energy & Fuels.* **2014,** *28*, 997-1003.

[26] Nicodem, D. E.; Guedes, C. L. B.; Correa, R. J.; Fernandes, M. C. Z. Photochemical processes and the environmental impact of petroleum spills. *Biochemistry* **1997,** *39*, 121-138.

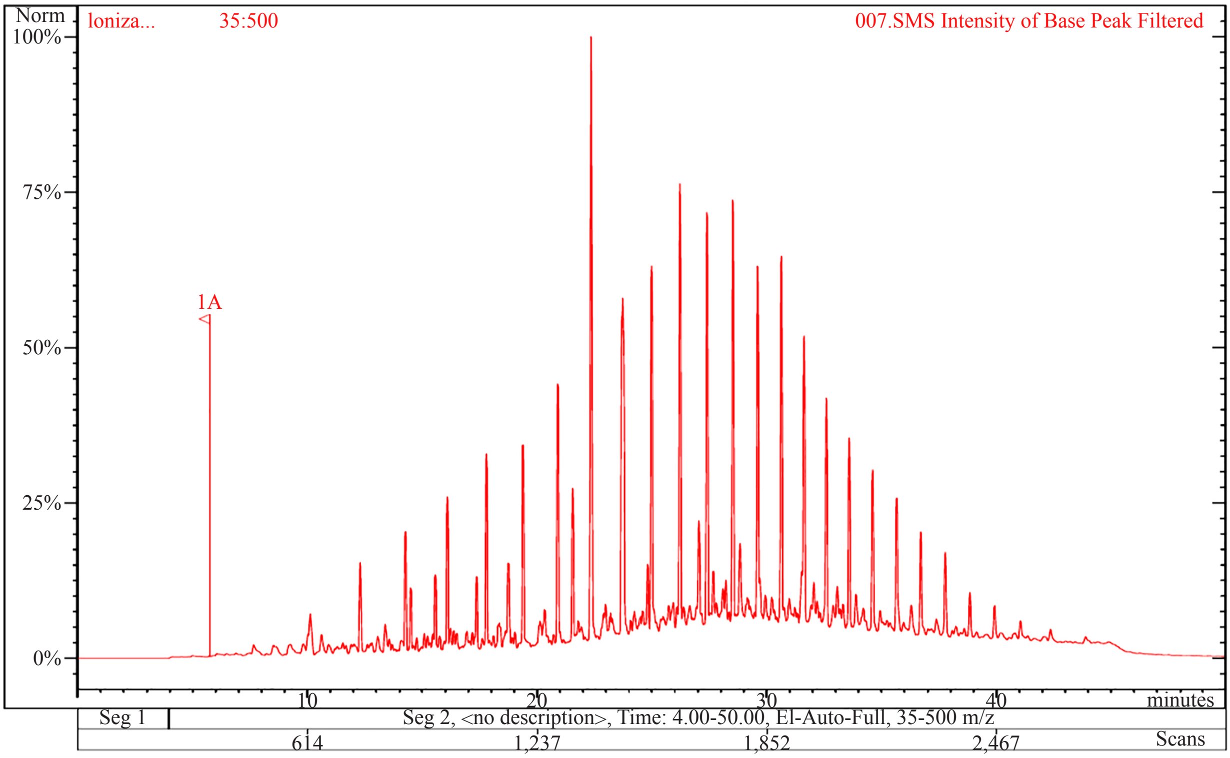
[27] D'Auria, M.; Emanuele, L.; Racioppi, R.; Velluzzi, V. Photochemical degradation of crude oil: Comparison between direct irradiation, photocatalysis, and photocatalysis on zeolite. *J. Hazard. Mater.* **2009,** *164*, 32-38.

[28] Coates, J. Interpretation of infrared spectra, a practical approach. In *Encyclopedia of Analytical Chemistry*; Meyers, R. A., Ed.; John Wiley & Sons Ltd: Chichester, 2000; pp 10815-10837.

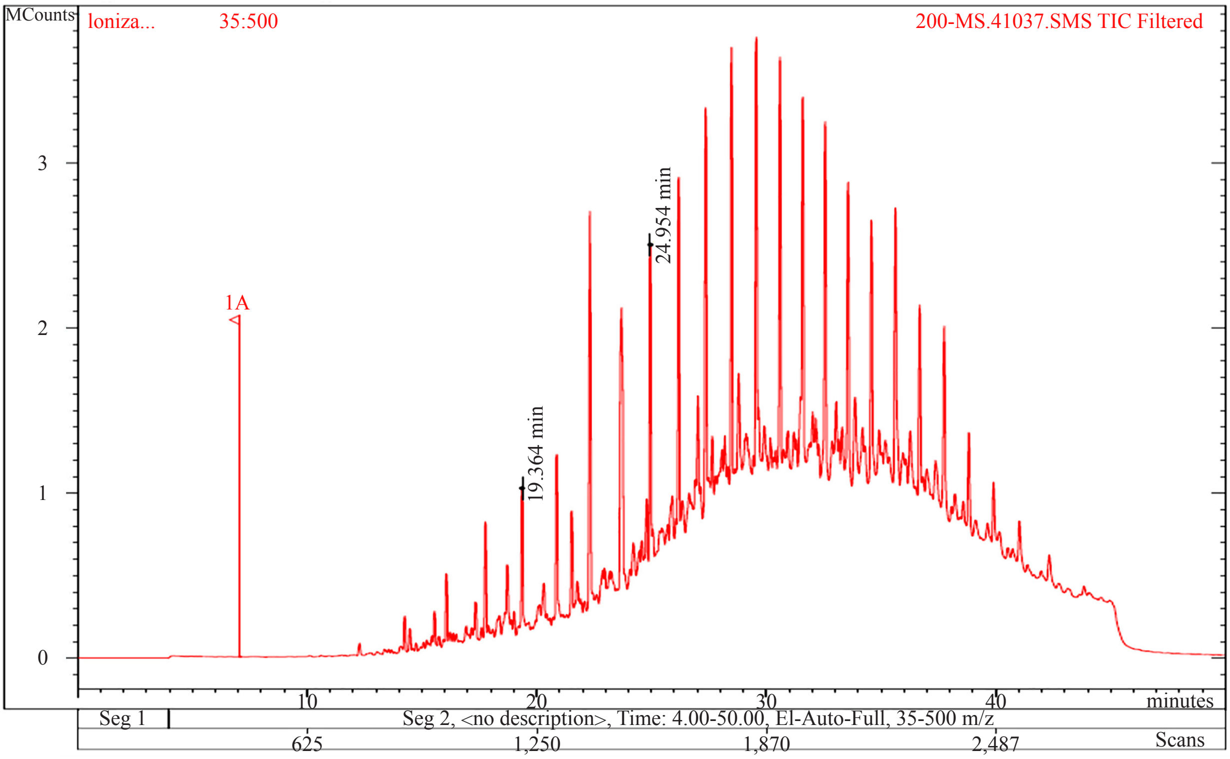
[29] Castro, L. V.; Vazquez, F. Fractionation and characterization of mexican crude oils. *Energy & Fuels.* **2009,** *23*, 1603-1609.

[30] Dutta, T. K.; Harayama, S. Fate of crude oil by the combination of photooxidation and biodegradation. *Environ. Sci. Technol.* **2000,** *34*, 1500-1505.

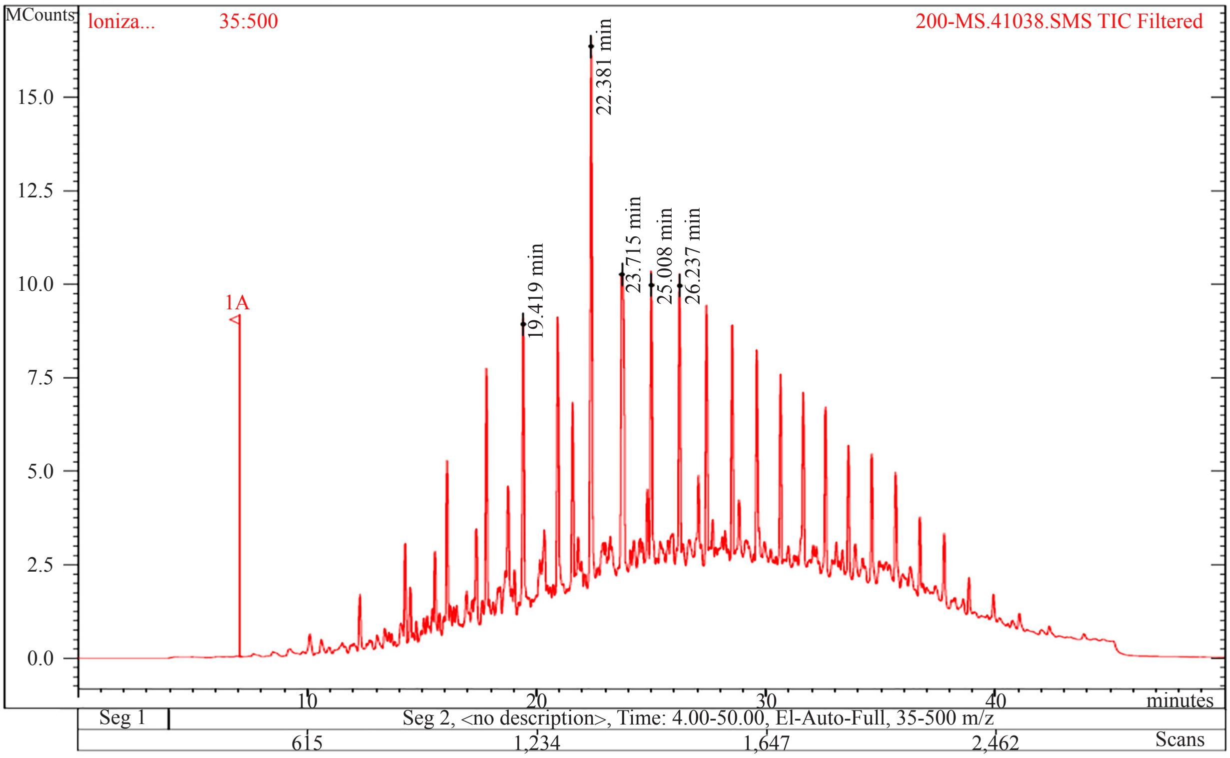
Appendix A



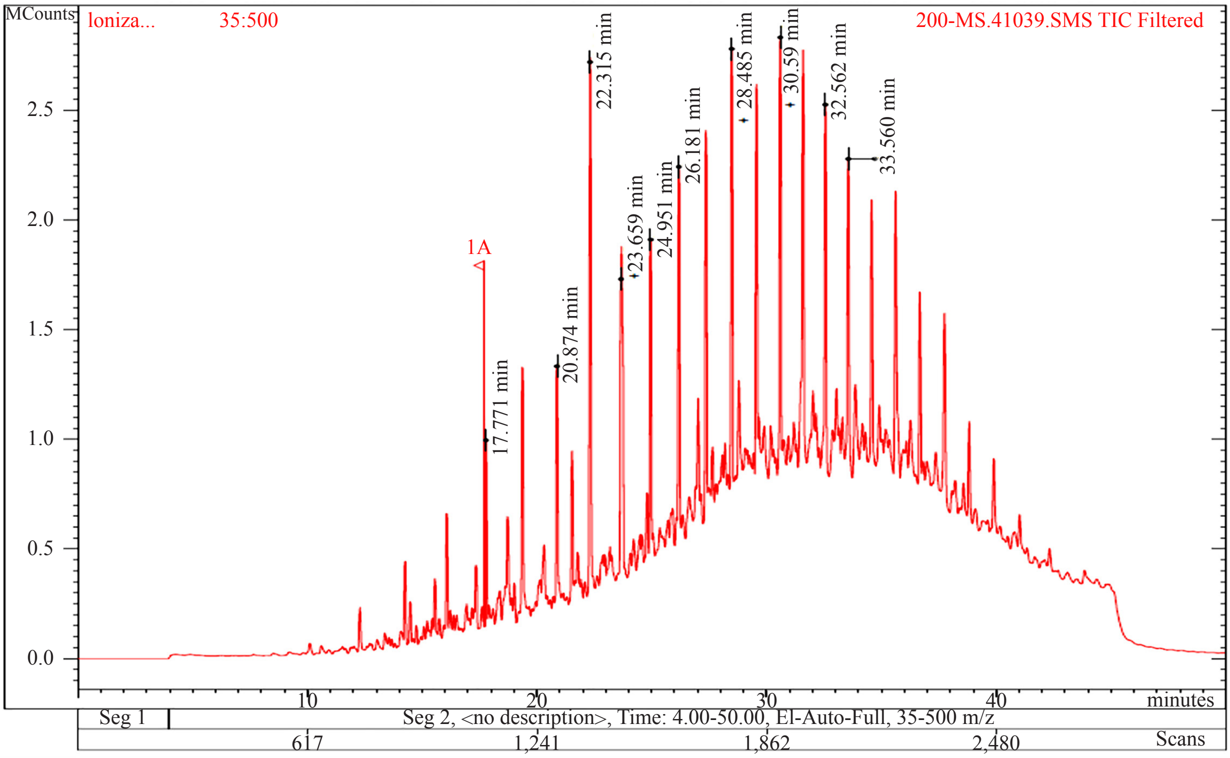
A1. (C_1) : GC-MS chromatogram of crude oil extra after 2 weeks irradiation



A2. (C_2): GC-MS chromatogram of crude oil extra after 4 weeks irradiation



A3. (C_3): GC-MS chromatogram of crude oil extracts after 6 weeks irradiation



A4. (C_4): GC-MS chromatogram of crude oil extracts after 8 weeks' irradiation