Comparative Study of Physicochemical Properties and Metal Contents in Crude Oil from Different Fields in Iraq

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Abstract— **This research evaluates the physical and chemical properties and concentration of trace elements and heavy metals in Iraqi crude oil. The way in which geographical locations affect oil quality is not widely known, especially in the Middle East. Therefore, crude oils from three locations (East Baghdad, Khurmala, and Nahr Omar) were selected. The physical and chemical data showed apparent variations in the properties of crude oils from different fields. Nahr Umr oil was the lightest (D = 0.8199 g/cm^3, API = 40.57°) and the lowest in sulfur content (1.327 wt%), East Baghdad oil was the heaviest (D = 0.9067 g/cm^3, API = 24.39°) and the highest in sulfur content (3.842 wt%), while Khurmala was (D = 0.8518 g/cm^3, API = 34.12°) and (2.44 wt%) of sulfur content, reflecting the differences in the quality of crude oils. Advanced techniques such as the rotating disc electrode optical emission spectrometer (RDE-OES) and inductively coupled plasma (ICP-OES/MS) were used to measure the element content after sample preparation using microwave acid digestion. The content of metals in crude oil indicates that East Baghdad oil contains the highest rate of V, Al, Ag, and Hg. At the same time, Ni, Fe, Na, Ca, Pb, Se, and Li were higher in Khurmala oil, while Mo, Ti, Sr, Bi, Ba, and Hg were higher in Nahr Umr. The statistical analysis of the least significant difference (LSD) test was used to show the significant differences between the measured element concentrations at the 0.05 level.**

Keywords— **Crude Oil Quality; Physicochemical Parameters; Wear Metals; Heavy elements, ICP-OES and ICP-MS.**

I. INTRODUCTION

Crude oil is one of the most valuable natural resources and is a complex mixture of hydrocarbons, metals, non-metals, and other traces [1,2]. These components not only influence the chemical and physical properties of crude oil but also substantially impact refining processes, environmental management, and the economic viability of oil production [3-5]. Among the key factors influencing crude oil's behavior during refining is its mineral and metal content, which can vary widely depending on the geographic location, geological formation, and extraction methods [6,7]. Metals such as vanadium, nickel, iron, lead, and non-metals like sulfur are commonly found in crude oil, often posing challenges for refineries [8,9]. Therefore, understanding the detailed composition of metals and minerals in crude oil is essential for optimizing refining processes, extending the lifespan of catalysts, and ensuring environmental compliance [10]. Iraq possesses some of the world's largest crude oil reserves, playing a pivotal role in the global energy market [11]. The oilfields spread across the country, offering diverse crude oil profiles due to their distinct geological characteristics. This diversity results in variations in crude oil quality, among other things, the mineral and metal content [12].

The occurrence of metals, distribution patterns, and concentrations in crude oils can indicate the origin, migration, environment of deposition, maturation of petroleum, and the geochemical characterization of source rocks [13,14]. The presence and concentration of specific minerals can provide valuable information about the origin and geography of the crude oil. For instance, certain trace metals can be used as biomarkers to determine the source rock and depositional environment, helping to understand the age, location, and quality of oil deposits [15]. Wear metals like vanadium and nickel act as catalyst poisons during the refining process. When these metals accumulate on refining catalysts, they reduce the efficiency of methods such as catalytic cracking, hydrodesulfurization, and hydrocracking [16], and this leads to lower yields of high-value products like gasoline and diesel, increasing operational costs. The metals can form stable and insoluble residues [17]. which can clog equipment, reduce efficiency, and require additional energy and chemicals to process. Over time, such deposits may cause blockages or decrease the effectiveness of refining units. Minerals like sulfur can cause severe corrosion of pipelines, storage tanks, and refinery equipment [18]. Heavy metals such as lead, mercury, arsenic, and cadmium are highly toxic and pose significant environmental and health risks when released into the atmosphere, water, or soil [19,20]. During refining, combustion, or disposal of waste products, these metals can enter the environment, leading to contamination of ecosystems, food chains, and drinking water sources. Other

metals, like sodium (Na), calcium (Ca), and magnesium (Mg), may also be present in significant amounts and be transferred to fuel fractions, decreasing their quality and performance [21].

Rotary disc electrode optical emission spectroscopy (RDE-OES) inductively coupled plasma emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) offer rapid methods for elemental analysis. The techniques are employed to identify and quantify even trace quantities in petroleum products, including crude oils, automotive fuels, and lubricating oils, with low detection limits [22,23]. Microwave-acid digestion (MAD) is one of the most used methods to efficiently decompose organic and inorganic matrices by increasing the reaction rate between the sample and the digestion reagents [24]. The high temperature and pressure conditions created by microwaves enhance the solubilization of metals and other analytes from complex matrices, soils, biological tissues, and crude oil. For example, the extraction of metals using microwave digestion is far more efficient compared to conventional methods. MAD is widely used in preparing samples for atomic absorption spectroscopy (AAS), ICP-OES, and ICP-MS [25].

The objective of this study is to determine physicochemical parameters, heavy metals, and wear metals in crude oils using advanced and cutting-edge techniques. The crude oils were collected in several different locations across Iraq. Furthermore, the crude oil quality among the collected sites should be compared, and their economic and environmental potentials should be evaluated. This study provides insight into the crude oil quality as well as the environmental factors that are controlling the local conditions.

II. MATERIALS AND METHODS

A. Materials

Nitric acid (70%) and hydrogen peroxide (30%) were purchased from Merck-Germany, and toluene (99%) and n-heptane (99%) were purchased from Central Drug House (CDH)-India. ICP multi-element standard solution VI (dilute in HNO3) from Sigma Aldrich- Germany, calibration standard solution CS21 for Spectroil M from Spectro Scientific-USA, certified reference materials (CRMs) (Sulfur Conc.: 4.5 wt%) from ASI standards-USA, asphaltene standard liquid (APD-006, 1gr/100 ml Toluene) from Cosmo Instruments Co., Ltd/Japan. An ultrapure water system produced deionized water (TOC < 5 ppb, resistivity 18.2MΩ·cm at 25°C degrees) PURIST-USA.

B. Sample collection

The crude oil samples were collected from three different oil fields in Iraq, namely East Baghdad (EB), Khurmala (KH), and Nahr Umr (NH), as shown in Fig. 1. These sites were chosen due to their significance in local oil production and their diverse geochemical properties. East Baghdad oil field is located east of the capital and is 20 km east, and its daily production capacity is 40 thousand barrels. Khurmala oil field is located approximately 35 km southwest of Erbil, and the field's oil production is 200 thousand barrels per day. Nahr Umr oil field is located 25 km north of Basra city, and its average oil production is 40 thousand barrels. Approximately 1 liter of crude oil was collected from each site. This quantity was sufficient to perform multiple analyses, including the physicochemical characterization and trace element detection using ICP-MS/OES and RDE-OES, as outlined in the study. Crude oil samples were collected directly from the wellhead or pipeline at each selected site using clean, metal-free sampling containers to avoid contamination. The containers were rinsed with the respective oil sample three times before final collection to ensure sample purity. After collection, the containers were tightly sealed to prevent any exposure to air or moisture. After collection, the crude oil samples were immediately stored in glass bottles to protect them from light exposure, which could alter their composition. The samples were kept at ambient temperature and transported in insulated containers upon arrival to prevent temperature fluctuations during transit. At the laboratory, they were stored in a cool, dark environment until analysis.

Bedrock geology of the Arabian peninsula and selected adjacent areas from the united states geological survey (USGS) are used to create geological maps. The GIS ArcMap version 10.6 (Esri company, USA) program created the map [26].
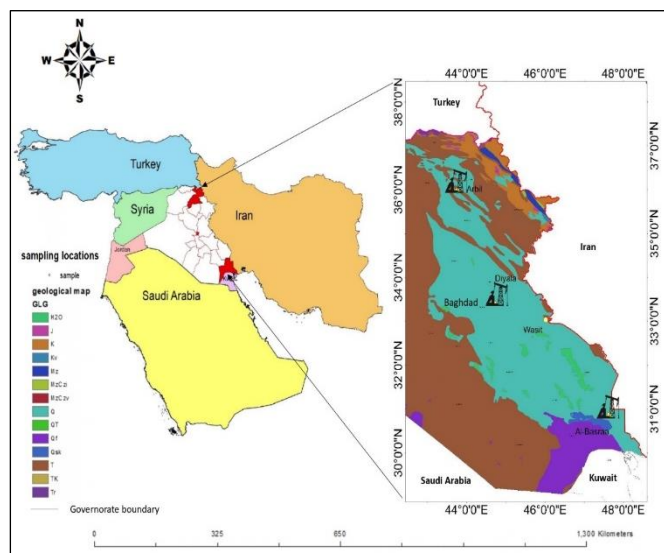

Fig. 1: Crude oil fields in Central, North, and South Iraq are being investigated.

C. Crude oil processing for metal analysis

Crude oil samples were digested with a Titan MPS closed-vessel microwave digestion system (Perkin Elmer, USA) before elemental analysis by ICP-OES and ICP-MS using the method described in [27]. Titan MPS closed-vessel has 10 high-pressure TFM vessels with an internal volume of 100 mL (maximum temperature and pressure are 300 °C and 100 bar, respectively). For digestion, crude oil samples (100 mg) were transferred into the digestion vessel, followed by the addition of nitric acid (HNO$_3$, 70%; 8 mL) and hydrogen peroxide (H$_2$O$_2$, 30% (v/v); 2 mL). The filled vessels with crude oils were stirred gently for 10 min, and then the vessels were sealed. The digestion processes applied were (1) heating at 150 °C target temperature with 30 bar pressure for 5 min ramp time and holding for 10 min, (2) heating at 190 °C target temperature with 35 bar pressure limit, and 5 min ramp time, holding for 30 min, and (3) heating 50 °C target temperature with 35 bar pressure limit, and 1 min ramp time, holding for 30 min. After the

digestion process was completed, the vessels were cooled down to room temperature for about 10 min. The solutions were diluted with 30 mL of distilled water and shaken for an hour on a table shaker. The mixtures were filtered through filter paper before heavy metal analysis by ICP-OES.

D. Solid suspended particles

Crude oil characteristics, such as contaminants in crude oil, gas turbine, and diesel engine fuel, were analyzed using rotating disc electrode optical emission spectroscopy (RDE-OES) [28]. Specifically, the rotating disc electrode was used to determine soil impurity particles dissolved or suspended in an oil sample. Spectroil disc electrode M series has critical features for analyzing samples without any preparation in 30 seconds. It was used to analyze ash-metal-based impurities in the fuel for the elements V, Ni, Fe, Na, Ca, and Al in triplicate.

E. Total sulfur content

The total sulfur content of the crude oil was analyzed using energy-dispersive X-ray fluorescence (EDXRF), Horiba Scientific Company-USA, by the method described in [29]. The portable analyzer has a measurement range from 0 to 5 wt% of total sulfur content, according to ASTM D4294, with a detection limit of 20 ppm and repeatability of 15 ppm. The instrument was calibrated using sulfur standard solutions ranging from 0.0 to 4.5 wt%. After the calibration, 5 g of the crude oil sample was used in triplicate to measure total sulfur content.

F. Asphaltene content

The asphaltene content of the crude oil was measured by ASTM D3279 asphaltene analyzer (A Cosmo APD-600A asphaltene analyzer Japan) by the method described in [30]. The asphaltene analyzer has a measurement range from 0.5 to 15 wt%, and it has excellent repeatability. Crude oil samples were heated at 80 °C for 10 min and then mixed with 1 mL of toluene, followed by heating at 80 °C for 10 min. The mixture was vigorously shaken for 15 min to ensure complete dissolution. After that, 100 mL of heated n-heptane (heated to 80 °C) was added to the mixture, followed by stirring for 10 min. The mixture was incubated for 40 min to cool down before the analysis. The asphaltene content was measured in triplicate.

G. Instrumentation for elemental analysis

The concentrations of metals Ag, Mo, Sr, Bi, and Ba were analyzed using a method adapted from [31], with slight modifications, by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (iCAP PRO ICP-OES Duo) from Thermo Fisher Scientific-Germany. ICP-MS (Agilent 7500, California, USA) analyzed the concentrations of the remaining elements and metals. Quantification involved external standard stock solutions prepared from multi-element standard solution VI for ICP (TraceCERT® in 2% nitric acid) within the 1–100 µg/L concentration range. Calibration curves were generated by plotting the measured peak areas against corresponding standard concentrations, and linear regression was applied to each curve, achieving R^2 values of 0.938, indicating excellent linearity. To reduce interference and matrix effects, both standard solutions and samples were prepared in 2% HNO_3.

The method's linearity was checked using standard solutions outside the calibration range (500, 1000, and 5000 µg/L). Samples were diluted when their concentrations exceeded the linearity range of the method. To monitor instrument stability, a 25 ng/L analytical standard solution was analyzed every 20 injections, and a blank (100% deionized water) was analyzed to check for cross-contamination.

In the ICP-OES, a cross-flow nebulizer attached to a glass spray chamber vaporized the solution. The plasma cell was parameterized to the following conditions: RF power of 1150 W, plasma flow fixed at 12.5 L/min, auxiliary flow of 0-2.25 L/min, nebulizer flow of 0-1.3 L/min, repeat read time of 5 seconds, sample incubated for 25 seconds, and pump rate of 45 rpm. The absorbance was recorded from 167 to 852 nm to maximize signal intensity while minimizing matrix-specific spectral interferences. At the same time, in the ICP-MS, a concentric nebulizer was equipped with a quartz spray chamber, a Babington nebulizer, and a quartz torch. An axial injector with an inner diameter of 2.5mm was employed. RF power was set to 1500 W. Argon gas was used to follow the system, with a purity of 99.9%, at a regulated pressure of 700kPa (100 psi). The nebulizer gas flow rate was set to 0.19 L min−1. The sample injection was 0.7 ml/min. The sample injection was for 35 seconds, followed by washing for 45 seconds.

H. Statistical analysis

A comparison of crude oil samples was performed using the Least Significant Difference (LSD) test in IBM SPSS Statistics 29 (USA). Results were reported as mean ± standard deviation, with comparisons made between EB and KH, EB and NU, and KH and NU. Statistical significance was determined at the 0.05 level.
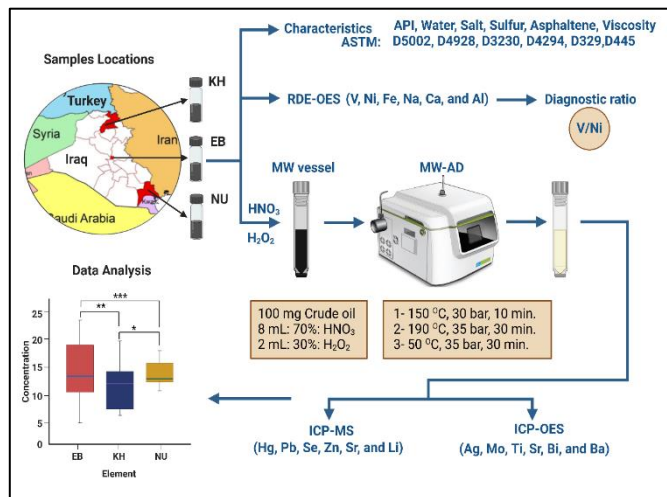

Fig. 2: Crude oil processing for physicochemical properties and metal contents tests.

III. RESULTS AND DISCUSSION

A. Physicochemical parameters of the crude oils

The physicochemical properties of the crude oil samples showed variation across the crude oil collected from different geographical locations. The physicochemical properties of the crude oils are summarized in Table 1. The API gravities of the crude oils varied between 27.16 and 40.57. Nahr Umr crude oil had the highest value (more than 40), and it is classified as super light crude oil. Khurmala crude oil is also categorized as light crude, while East Baghdad crude oil is considered medium grade. The light crude oil has a lower viscosity and lighter chemical composition [32]. Heavy

crude oil is considered less desirable than light oil since it produces a lower yield of oil byproducts. Khurmala crude oil had the highest water content of 0.1%, and water content variation is caused by the pumping mechanism used during the oil extraction process or reservoir water [33]. The presence and movement of water within the reservoir can influence the water content of the crude oil. The highest salt content was in Khurmala crude oil at 295.12 ppm, where the lowest content was 7.99 ppm for Nahr Umr. Salts in crude oils can present significant obstacles to refining and transporting petroleum, like corrosion, pumping issues, difficulties drilling and filling oil wells, catalyst deactivation, scaling issues, and pipeline clogging. The mineral salts frequently found in crude oils are primarily sodium chloride, with trim levels of calcium and magnesium chlorides [34].Abbreviations and Acronyms

Table 1. The physicochemical parameters of crude oil are collected from different locations in Iraq.

Characteristics	Standard Method	Location of the Oil Fields		
		Baghdad	Erbil	Basrah
Oil Filed	-	East Baghdad	Khurmala	Nahr Umr
Symbol	-	EB	KH	NU
Formation	-	Zubair	Qamchuqa	Zubair
Well no.	-	21	3	7
Depth (m)	-	3045	3650	3620
Longitude	-	44.700° E	43.763° E	47.650° E
Latitude	-	33.408° N	35.977° N	30.871° N
Density@ 15°C (g*cm^{-3})	ASTM D5002	0.9067	0.8518	0.8199
Specific gravity @ 15°C	ASTM D5002	0.9083	0.8544	0.8223
API gravity @ 15°C	ASTM D5002	24.39	34.12	40.57
Water content (%)	ASTM D4928	0.07	0.1	0.08
Water and sediment (%)	ASTM D4007	0.04	0.5	0.13
Salt content (ppm)	ASTM D3230	10.15	295.12	7.99
Sulfur content (%)	ASTM D4294	3.842	2.44	1.327
Asphaltene content (%)	ASTM D3297	15.422	1.367	0.923
Viscosity @ 10 °C	ASTM D445	36.12	21.13	18.26
Viscosity @ 21 °C	ASTM D445	27.75	13.46	6.83
Viscosity @ 37.8 °C	ASTM D445	19.94	7.09	2.78
Viscosity @ 50 °C	ASTM D445	12.81	4.28	1.75

Sulfur contents of Nahr Umr crude oil (1.327 wt%) were the lowest, followed by Khurmala crude oil (2.44 wt%) and East Baghdad crude oil (3.842 wt%). The sulfur content depends on the thermal maturity of the crude oil; the higher the maturity, the lower the sulfur content. Further, the higher the maturity, the higher the API value [35]. Nahr Umr crude oil (sulfur content = 1.327 wt%, API = 40.57) indicates it is more mature than the rest of the crude oils under study. The asphaltene content level in Khurmala crude oil was 1.367 wt%, which is considered the highest value among the three crude oil samples, while Nahr Umr crude oil was 0.923 wt% as the lowest content. Asphaltenes, one of the densest components in crude oil, have significant importance since they considerably influence the characteristics of crude oil [36]. The characterization above can help the refineries by

selecting the most suitable crude oil or combination of crude oils based on their specific product and taking advantage of the distinct qualities of different types of crude oil.

B. Wear metals

The concentration of 6 distinct wear metals, V, Ni, Fe, Na, Ca, and Al, were found in all crude oils, as presented in Table 2. and shown in Figure 3. Vanadium (V) showed exceptionally high concentrations, especially in East Baghdad (55.65 ppm), which could be attributed to a rich source of vanadium in these areas, possibly from vanadium-bearing rocks [37]. Conversely, Nahr Umr and Khurmala exhibit lower vanadium levels (12.39 and 12.48 ppm, respectively). Nickel (Ni) concentrations are notably high, particularly in Khurmala (20.62 ppm) and East Baghdad (14.54 ppm). These high levels could be due to naturally nickel-rich geological deposits [38]. Iron (Fe) content is elevated in Khurmala (1.57 ppm) and Nahr Umr (1.28 ppm) compared with East Baghdad, indicating iron-rich soils in these regions, possibly due to the presence of iron-bearing minerals. Sodium (Na) is highest in Khurmala (5.12 ppm), indicating sodium-rich water or soil sources in the area [39]. In comparison, East Baghdad (2.01 ppm) showed significantly lower sodium concentrations, highlighting variability across the locations.

Table 2. Wear metal concentrations (ppm) in crude oil samples (n=3) collected for this investigation.

Metal	Site	Max	Min	Mean	St.D.	P Value Between Two Locations	
V	EB	56.44	54.87	55.65	1.15	EB and NU	1.6*10^{-9}
	KH	13.79	12.48	13.27	0.69	EB and KH	1.7*10^{-9}
	NU	13.72	12.39	12.91	0.70	KH and NU	0.636
Ni	EB	15.91	13.82	14.76	1.05	EB and NU	1.1*10^{-6}
	KH	20.42	18.97	19.58	0.75	EB and KH	2.3*10^{-4}
	NU	2.88	2.54	2.71	0.17	KH and NU	1.5*10^{-7}
Fe	EB	0.68	0.53	0.61	0.07	EB and NU	0.011
	KH	1.57	1.39	1.51	0.07	EB and KH	6.2*10^{-6}
	NU	1.37	1.22	1.28	0.08	KH and NU	0.028
Na	EB	2.39	2.01	2.18	0.19	EB and NU	0.003
	KH	11.59	11.12	11.29	0.25	EB and KH	1.6*10^{-9}
	NU	3.02	2.88	2.93	0.07	KH and NU	2.7*10^{-9}
Ca	EB	1.27	1.03	1.14	0.12	EB and NU	0.041
	KH	5.51	4.73	5.13	0.39	EB and KH	8.6*10^{-7}
	NU	0.68	0.46	0.57	0.04	KH and NU	0.045
Al	EB	1.82	1.53	1.71	0.15	EB and NU	0.532
	KH	1.56	1.27	1.41	0.13	EB and KH	0.027
	NU	1.71	1.59	1.64	0.06	KH and NU	0.066

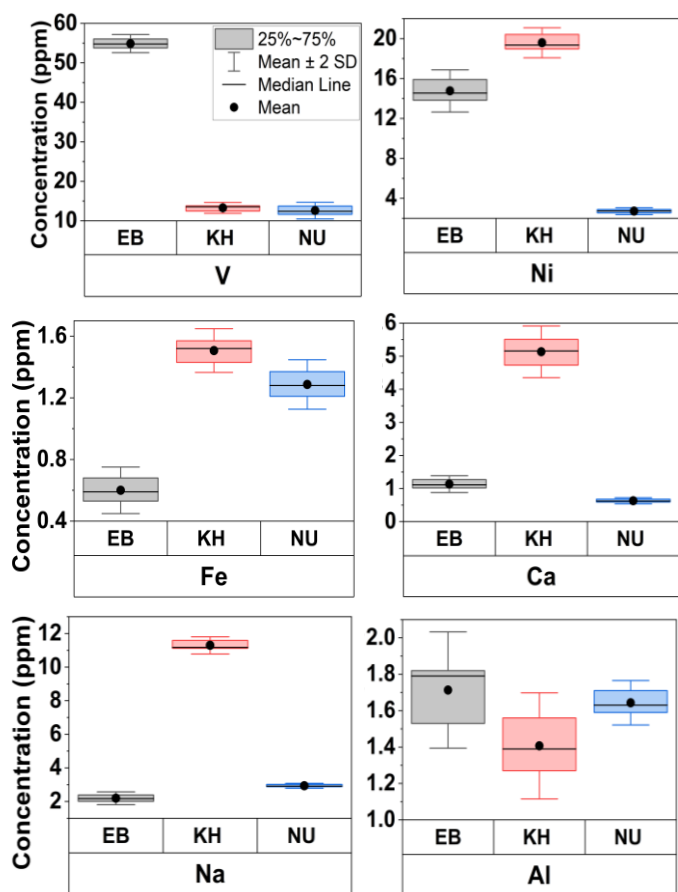The mean difference is significant at the 0.05 level.

Fig. 3: The concentrations (ppm) of metal analysis by RDE-OES: V, Ni, Fe, Na, Ca, and Al in crude oil samples were collected at different locations in Iraq. Multiple box plots represent the mean (n=3) ± SD. Zero means the metals are not detected.

Calcium showed high levels in Khurmala (5.51 ppm), indicating the presence of calcium-rich deposits in this area [40]. However, Ca levels were much lower in other sites, such as East Baghdad and Nahr Umr. These areas may be rich in calcareous materials or limestone deposits, factors that may affect calcium levels. Aluminium element was found in close content in the three samples (1.82, 1.56, and 1.71 ppm) of East Baghdad, Khurmala, and Nahr Omar, respectively.

The LSD test showed a very significant correlation between the crude oil samples under investigation. Significant differences in the contents of Ni, Fe, Na, and Ca were observed among the three crude oils, with $p < 0.05$. The concentrations of V and Al were significantly different between EB and KH, EB and NU, and EB and KH. However, the concentrations of V and Al were not significant ($p = 0.636$, $p = 0.532$, and $p = 0.066$) between KH and NU; EB and NU, respectively.

Crude oils can be classified into four families based on their V/Ni ratios. Ratios higher than 3, with Ni concentrations typically below 90 ppm (Family A), indicate marine organic material derived from carbonate shales or limestone deposited under anoxic conditions. V/Ni ratios between 1.9 and 3 (Family B) suggest that source rocks formed under disoxic-oxic conditions, with precursor organic material of mixed origin, are primarily marine with some continental input. Ratios below 1.9 (Family C) point to terrestrial organic matter, with source rocks deposited under predominantly oxic conditions. Lastly, ratios exceeding 3

and Ni concentrations above 90 ppm (Family D) are associated with marine carbonate source rocks formed in euxinic or highly reducing environments. In this study, East Baghdad and Nahr Umr had V/Ni ratios of 4.53 and 3.69, respectively, placing them in Family A and indicating marine organic material and argillaceous limestone as source rocks formed under oxygen-deprived conditions. Conversely, the Khurmala sample, with a V/Ni ratio of 0.61, belongs to Family C, suggesting terrestrial organic matter deposited under disoxic-oxic conditions.

C. ICP-OES

The concentration of 6 elements, Ag, Mo, Ti, Sr, Bi, and Ba, by ICP–OES in the crude oils is presented in Table 3 and Figure 4. For silver (Ag), East Baghdad recorded the highest concentration at 1.99 ppm, while concentrations were below 0.6 ppm in Nahr Umr and Khurmala. Titanium (Ti) showed the highest concentrations at 0.46, 042, and 0.038 ppm in Nahr Umr and East Baghdad, respectively, and a trace amount in Khurmala. Strontium (Sr) concentrations were highest in Nahr Umr and East Baghdad, ranging between 1.565 and 0.537 ppm, while concentrations in Khurmala were lower. Bismuth (Bi) concentrations do not exceed 0.09, 0.07, and 0.03 ppm in Nahr Umr and East Baghdad, respectively. Barium (Ba) concentrations ranged from 0.372 to 0.215 ppm, indicating its natural presence in the soil or rocks in all the studied locations. Molybdenum (Mo) concentrations were highest in Nahr Umr and East Baghdad, ranging between 3.82 and 3.51 ppm, while concentrations in Khurmala were lower, not exceeding 1.6 ppm. The significant level of molybdenum in crude oil may be ascribed to many reasons, primarily associated with the geochemical processes and properties of the source rocks and the reservoir environment [42]. One primary factor is the composition of the source rock. The source rocks consist of mudrocks that are abundant in organic matter and have elevated amounts of molybdenum. During the maturation and migration phases, the high concentration of Mo in the source rocks may be transmitted to the crude oil. The redox conditions of the source rock depositional environment influence the concentration of molybdenum [43]. Molybdenum concentrations in organic-rich mudrocks formed under euxinic (anoxic and sulfidic) conditions are often high due to molybdenum behavior. The high molybdenum concentration in crude oil is also affected by the intense attraction between asphaltenes and molybdenum and several reservoir processes, such as thermochemical sulfate reduction and biodegradation [44].

Notable variations in the concentrations of Ag and Sr were detected across the three crude oils, with $p < 0.05$ by LSD test. The concentrations of Mo, Ti, Bi, and Ba showed no significant differences between EB and NU ($p = 0.528$ for Mo), EB and NU ($p = 0.109$ for Ti), KH and NU ($p = 0.643$ for Bi), and across various comparisons for Ba, including EB and KH ($p = 0.27$), EB and NU ($p = 0.15$), and EB and NU ($p = 0.679$). In contrast, other correlations exhibited high significance.

Table 3. Trace element concentrations (ppm) in crude oil samples (n=3) were collected for this investigation.

Element	Site	Max	Min	Mean	St.D.	P Value Between Two Locations	
Ag	EB	0.605	0.489	0.551	0.053	EB and NU	$5.6*10^{-9}$
	KH	0.041	0.023	0.032	0.01	EB and KH	$8.7*10^{-10}$
	NU	0.546	0.528	0.358	0.032	KH and NU	$2.2*10^{-6}$
Mo	EB	3.527	3.465	3.496	0.036	EB and NU	0.528
	KH	1.512	1.389	1.44	0.062	EB and KH	$9.3*10^{-5}$
	NU	3.816	2.879	3.446	0.46	KH and NU	$1.4*10^{-4}$
Ti	EB	0.421	0.312	0.373	0.055	EB and NU	0.109
	KH	0.038	0.027	0.033	0.006	EB and KH	$2.3*10^{-4}$
	NU	0.458	0.412	0.428	0.025	KH and NU	$9.9*10^{-6}$
Sr	EB	0.543	0.504	0.531	0.017	EB and NU	$8.1*10^{-7}$
	KH	0.422	0.354	0.407	0.043	EB and KH	0.036
	NU	1.688	1.497	1.689	0.096	KH and NU	$3.9*10^{-7}$
Bi	EB	1.631	1.096	1.115	0.303	EB and NU	0.044
	KH	0	0	0	0	EB and KH	0.036
	NU	1.712	1.586	1.703	0.066	KH and NU	0.643
Ba	EB	0.299	0.194	0.247	0.029	EB and NU	0.27
	KH	0.347	0.269	0.298	0.025	EB and KH	0.15
	NU	0.372	0.253	0.288	0.062	KH and NU	0.679

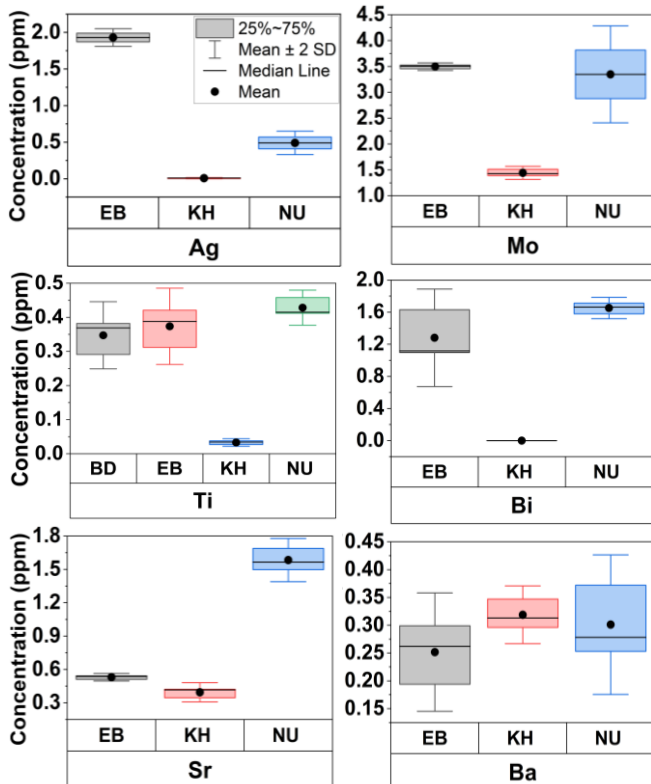The mean difference is significant at the 0.05 level.

Fig. 4: The concentration (ppm) of elemental analysis by ICP-OES: Ag, Mo, Ti, Sr, Bi, and Ba in crude oils samples were collected at different locations in Iraq. Multiple box plots represent the mean (n=3) ± SD. Zero means the metals are not detected.

D. ICP-MS

Heavy metal concentrations (ppb) of Hg, Pb, Se, Zn, Sn, and Li by ICP-MS analysis are presented in Figure 5 and Table 4. Mercury (Hg) showed low concentrations across crude oil samples, ranging from 39 to 16 ppt for Nahr Umr and East Baghdad, respectively, and was not detected in Khurmala. Lead (Pb) concentration in Khurmala was higher than that of other sites, which was 650 ppt. In contrast, other sites were lower than 331 and 228 ppt for Nahr Umr and East Baghdad, respectively, indicating uniform geological distribution. Elevated lead levels in these areas may be due to geological deposits containing lead. High lead concentrations pose environmental and health risks due to the toxic nature of lead [45]. Selenium (Se) showed high content in Khurmala (190 ppt), while the other crude oil samples showed lower content (17 and 9 ppt) for Nahr Umr and East Baghdad, respectively. Zinc (Zn) concentrations were highest in East Baghdad (230 ppb) and lower concentrations in Nahr Umr (9 ppt). Tin (Sn) had a concentration ranging from 285 to 157 ppt. Finally, Lithium (Li) had low concentrations (71-22 ppb) in all sites .

The crude oil samples under investigation exhibited a highly significant correlation in the LSD test. The p values were less than 0.05, indicating that the concentrations of Hg, Pb, Zn, and Sn were highly significant among the three crude oils. The concentrations of Se and Li were also highly significant between EB and KH, as well as between EB and NU. The concentrations of Se and Li were not statistically significant (p = 0.636, p = 0.211, and p = 0.901) between EB and NU for both elements, respectively.

Table 4. Heavy metals concentrations (ppm) in crude oil samples (n=3) were collected for this investigation.

Element	Site	Max	Min	Mean	St.D.	P Value Between Two Locations	
Hg	EB	16	11	13.12	2.64	EB and NU	$1.2*10^{-3}$
	KH	0	0	0	0	EB and KH	$6.6*10^{-3}$
	NU	39	27	32.32	6.24	KH and NU	$5.7*10^{-5}$
Pb	EB	228	211	219.3	8.08	EB and NU	$3.4*10^{-3}$
	KH	651	632	636.6	11.93	EB and KH	$6.4*10^{-4}$
	NU	331	308	317.6	12.28	KH and NU	$3.1*10^{-3}$
Se	EB	9	5	7.88	1.52	EB and NU	0.211
	KH	190	169	178.3	10.69	EB and KH	$5.5*10^{-8}$
	NU	17	11	14.81	3.21	KH and NU	$7.2*10^{-8}$
Zn	EB	239	221	238.7	8.02	EB and NU	$2.4*10^{-8}$
	KH	214	203	205.4	8.73	EB and KH	$1.5*10^{-3}$
	NU	17	8	11.71	4.93	KH and NU	$6.1*10^{-8}$
Sn	EB	156	142	148.6	7.5	EB and NU	$1.4*10^{-6}$
	KH	45	27	31.96	4.04	EB and KH	$4.5*10^{-6}$
	NU	12	7	8.16	7.19	KH and NU	0.017
Li	EB	29	22	24.71	4.04	EB and NU	0.901
	KH	71	59	64.43	6.12	EB and KH	$2.5*10^{-5}$
	NU	31	16	25.66	5.14	KH and NU	$2.7*10^{-4}$

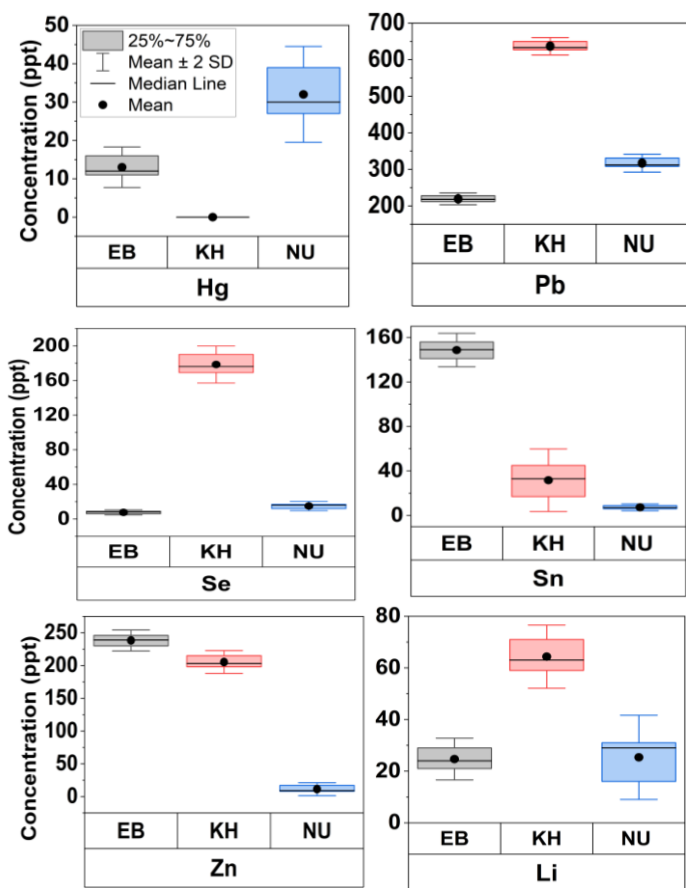The mean difference is significant at the 0.05 level.

Fig. 5: The concentration (ppt) of heavy metals analyzed by ICP-MS: Hg, Pb, Se, Zn, Sr, and Li in crude oil samples were collected at different locations in Iraq. Multiple box plots represent the mean (n=3) ± SD. Zero means the metals are not detected.

IV. CONCLUSION

The current study revealed the physiochemical parameters and elemental and heavy metal concentrations of the crude oil collected at different locations in Iraq. In our study comparing the characteristics of three crude oil samples, East Baghdad (EB), Khurmala (KH), and Nahr Umr (NU), Nahr Umr (NU) is the most favorable due to its high API gravity (40.57), low sulfur content (1.327%), low water content (0.08%), low asphaltene content (0.923%), and low viscosity, making it easier to refine and process. In contrast, East Baghdad (EB) is the least desirable with low API gravity (24.39), high sulfur (3.842%), high water content (0.07%), high asphaltene content (15.422%), and high viscosity, which complicate refining. The concentrations of elemental and heavy metals in the oil samples provide insights into their quality and potential issues. High levels of Vanadium and Nickel, especially in Khurmala, suggest challenges in refining due to catalyst poisoning. Lead levels, also high in Khurmala, raise environmental concerns. Sodium, particularly in Nahr Umr, indicates potential corrosion issues in refining equipment. Generally, lower levels of Calcium, Iron, and Mercury are positive, suggesting fewer operational and environmental problems. Overall, Nahr Umr is the best sample for refining, while East Baghdad and Khurmala pose more refining challenges and environmental risks.

CONFLICT OF INTEREST
Authors declare that they have no conflict of interest.

REFERENCES

[1] M. T. Khathi and A. A. Ali, "A comparative study of Iraqi crude oil taken from the Nasiriyah refinery with various local and global crude oils.," *University of Thi-Qar Journal of Science*, vol. 6, no. 1, pp. 70–77, Dec. 2016.

[2] M. Q. Saleh, Z. A. Hamad, and J. R. Hama, "Assessment of some heavy metals in crude oil workers from Kurdistan Region, northern Iraq," *Environmental Monitoring and Assessment*, vol. 193, no. 1, Jan. 2021.

[3] A. Abdulrazzaq Hadi and A. Abdulkhabeer Ali, "A review of petroleum emulsification types, formation factors, and demulsification methods," *Materials Today: Proceedings*, vol. 53, pp. 273–279, 2022.

[4] L. S. Tiewsoh, M. Sivek, and J. Jirásek, "Traditional energy resources in India (coal, crude oil, natural gas): A review," *Energy Sources, Part B: Economics, Planning, and Policy*, vol. 12, no. 2, pp. 110–118, Feb. 2017.

[5] X. F. Wu and G. Q. Chen, "Global overview of crude oil use: From source to sink through inter-regional trade," *Energy Policy*, vol. 128, pp. 476–486, May 2019.

[6] A. Abdulrazzaq Hadi and A. Abdulkhabeer Ali, "Chemical demulsification techniques in oil refineries: A review," *Materials Today: Proceedings*, vol. 53, pp. 58–64, 2022.

[7] K. Salim Abdul-Baqi, N. Rao Lakkimsetty, and V. Manappallil Joy, "Demulsification of water in oil emulsion via non– ionic surfactants: Statistical modeling and optimization," *Materials Today: Proceedings*, vol. 92, pp. 841–848, Apr. 2023.

[8] D. E. Adanenche, A. Aliyu, A. Y. Atta, and B. J. El-Yakubu, "Residue fluid catalytic cracking: A review on the mitigation strategies of metal poisoning of RFCC catalyst using metal passivators/traps," *Fuel*, vol. 343, p. 127894, Jul. 2023.

[9] A. Habib, H. N. Bhatti, and M. Iqbal, "Metallurgical Processing Strategies for Metals Recovery from Industrial Slags," *Zeitschrift für Physikalische Chemie*, vol. 234, no. 2, pp. 201–231, Feb. 2020.

[10] D. LI, "Crucial technologies supporting future development of petroleum refining industry,"

Chinese Journal of Catalysis, vol. 34, no. 1, pp. 48–60, Jan. 2013.

[11] T. AL-Saadi, A. Cherepovitsyn, and T. Semenova, "Iraq Oil Industry Infrastructure Development in the Conditions of the Global Economy Turbulence," *Energies*, vol. 15, no. 17, p. 6239, Aug. 2022.

[12] Z. Caineng et al., "Geological features, major discoveries and unconventional petroleum geology in the global petroleum exploration," *Petroleum Exploration and Development*, vol. 37, no. 2, pp. 129–145, Apr. 2010.

[13] A. B. Ogbesejana, B. Liu, and M. Ostadhassan, "Stable Isotope Geochemistry of the Organic Elements within Shales and Crude Oils: A Comprehensive Review," *Molecules*, vol. 27, no. 1, p. 34, Jan. 2022.

[14] Z. Wang, C. Yang, Z. Yang, C. E. Brown, B. P. Hollebone, and S. A. Stout, "4 - Petroleum biomarker fingerprinting for oil spill characterization and source identification," *ScienceDirect*, Jan. 01, 2016.

[15] L. M. Wu, C. H. Zhou, J. Keeling, D. S. Tong, and W. H. Yu, "Towards an understanding of the role of clay minerals in crude oil formation, migration and accumulation," *Earth-Science Reviews*, vol. 115, no. 4, pp. 373–386, Dec. 2012.

[16] A. G. Okunev, E. V. Parkhomchuk, A. I. Lysikov, P. D. Parunin, V. S. Semeikina, and V. N. Parmon, "Catalytic hydroprocessing of heavy oil feedstocks," *Russian Chemical Reviews*, vol. 84, no. 9, pp. 981–999, May 2015.

[17] J. Liu, Y. Huang, H. Li, and H. Duan, "Recent advances in removal techniques of vanadium from water: A comprehensive review," *Chemosphere*, vol. 287, p. 132021, Jan. 2022.

[18] U. Bharatiya, P. Gal, A. Agrawal, M. Shah, and A. Sircar, "Effect of Corrosion on Crude Oil and Natural Gas Pipeline with Emphasis on Prevention by Ecofriendly Corrosion Inhibitors: A Comprehensive Review," *Journal of Bio- and Tribo-Corrosion*, vol. 5, no. 2, p. 35, Feb. 2019.

[19] M. Balali-Mood, K. Naseri, Z. Tahergorabi, M. R. Khazdair, and M. Sadeghi, "Toxic Mechanisms of Five Heavy Metals: Mercury, Lead, Chromium, Cadmium, and Arsenic," *Frontiers in Pharmacology*, vol. 12, no. 643972, Apr. 2021.

[20] A. Waseem, J. Arshad, F. Iqbal, A. Sajjad, Z. Mehmood, and G. Murtaza, "Pollution Status of Pakistan: A Retrospective Review on Heavy Metal Contamination of Water, Soil, and Vegetables," *BioMed Research International*, vol. 2014, pp. 1–29, 2014.

[21] N. Saqib and M. Bäckström, "Chemical association and mobility of trace elements in 13 different fuel incineration fly ashes," Fuel, vol. 165, pp. 193–204, Feb. 2016.

[22] K. Jankowski and E. Reszke, "Recent developments in instrumentation of microwave plasma sources for optical emission and mass spectrometry: Tutorial review," *Journal of Analytical Atomic Spectrometry*, vol. 28, no. 8, p. 1196, 2013.

[23] F. Laborda et al., "Detection, characterization and quantification of inorganic engineered nanomaterials: A review of techniques and methodological approaches for the analysis of complex samples," *Analytica Chimica Acta*, vol. 904, pp. 10–32, Jan. 2016.

[24] M. C. Zuma, J. Lakkakula, and N. Mketo, "Recent trends in sample preparation methods and plasma-based spectrometric techniques for the determination of rare earth elements in geological and fossil fuel samples," *Applied Spectroscopy Reviews*, vol. 57, no. 5, pp. 353–377, Dec. 2020.

[25] M. A. Gab-Allah and A. B. Shehata, "Determination of iron, nickel, and vanadium in crude oil by inductively coupled plasma optical emission spectrometry following microwave-assisted wet digestion," *Chemical Papers*, vol. 75, no. 8, pp. 4239–4248, Apr. 2021.

[26] Ismail Elkhrachy, A. Alhamami, and S. H. Alyami, "Landfill Site Selection Using Multi-Criteria Decision Analysis, Remote Sensing Data, and Geographic Information System Tools in Najran City, Saudi Arabia," *Remote Sensing*, vol. 15, no. 15, pp. 3754–3754, Jul. 2023.

[27] A. K.-T. Mohammad, A. T. Hameed, M. A. Alhamdany, K. Mohammad Al Azzam, and G. A. A. Talk, "Characterization and screening of metals, metalloids and biomarkers in crude oil by ICP-MS/OES, and GC-MS techniques after digestion by microwave-induced combustion," *Biomedical Chromatography*, vol. 33, no. 4, p. e4481, Feb. 2019.

[28] Ö. Doğan, H.J. Köroğlu, and V. Pelitli, "Waste oil management: Analyses of waste oils from vehicle crankcases and gearboxes," *Global Journal of Environmental Science and Management*, vol. 3, no. 1, 2017, Accessed: Nov. 29, 2024.

[29] A. T. Khadim, T. M. Albayati, and N. M. Cata Saady, "Desulfurization of actual diesel fuel onto modified mesoporous material Co/MCM-41," *Environmental Nanotechnology, Monitoring & Management*, vol. 17, p. 100635, Dec. 2021.

[30] A. Abdulrazzaq Hadi, K. Abbas Al-Rudaini, A.Thamer Hameed, S. Mohsen Alardhi,, & Talib Mohammed

Albayati, "Utilizing A Millifluidic Approach And Three Variables To Reduce Asphaltene Content Of Crude Oil," *Azerbaijan Chemical Journal*, vol.3, pp. 29-24, Sep. 2024.

[31] M. A. Ajeel, A. A. Ajeel, A. M. Nejres, and R. A. Salih, "Assessment of Heavy Metals and Related Impacts on Antioxidants and Physiological Parameters in Oil Refinery Workers in Iraq," *Journal of Health and Pollution*, vol. 11, no. 31, Aug. 2021.

[32] A. R. Rahmani, M. T. Samadi, M. Ghaymali, and H. Motaghipoor, "Determination of Sawdust Efficiency for Cyanide Removal from Aqueous Solutions," *Journal of Water and Wastewater*; vol. 22, no. 3, pp. 53–58, Oct. 2011.

[33] A. Abdulrazzaq Hadi, M. Turki, and A. Abdulkhabeer, "Upgrading API and Specific Gravity Specifications of Iraqi Crude Oil Using a Laboratory-Built Multipumping Fuel Analysis (MPFA) System," *Journal of Kufa for Chemical Sciences*, vol. 2, no. 9, pp. 353–368, Aug. 2023.

[34] Saja Mohsen Alardhi et al., "Artificial neural network and response surface methodology for modeling oil content in produced water from an Iraqi oil field," *Water Practice & Technology*, Aug. 2024.   [35] S. Fakher, M. Ahdaya, M. Elturki, and A. Imqam, "Critical review of asphaltene properties and factors impacting its stability in crude oil," *Journal of Petroleum Exploration and Production Technology*, vol. 10, no. 3, pp. 1183–1200, Dec. 2019.

[36] F. Galarraga, K. Reategui, A. Martínez, M. I. Martínez, J. F. Llamas, and G. Marquez, "V/Ni ratio as a parameter in palaeoenvironmental characterisation of nonmature medium-crude oils from several Latin American basins," *Journal of Petroleum Science and Engineering*, vol. 61, no. 1, pp. 9–14, Apr. 2008.

[37] J. A. Ali et al., "Investigating the Influence of Environmental Factors on Corrosion in Pipelines Using Geospatial Modeling," *UHD Journal of Science and Technology*, vol. 8, no. 1, pp. 1–12, Jan. 2024.

[38] S. N. Abdulhamid, A. M. Hasan, and S. Q. Aziz, "Solidification / Stabilization of Contaminated Soil in a South Station of the Khurmala Oil Field in Kurdistan Region, Iraq," *Applied Sciences*, vol. 11, no. 16, p. 7474, Aug. 2021.

[39] V. K. Yadav et al., "The Processing of Calcium Rich Agricultural and Industrial Waste for Recovery of Calcium Carbonate and Calcium Oxide and Their Application for Environmental Cleanup: A Review," *Applied Sciences*, vol. 11, no. 9, p. 4212, Jan. 2021.

[40] C. Scott and T. W. Lyons, "Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: Refining the paleoproxies," *Chemical Geology*, vol. 324–325, pp. 19–27, Sep.2012. [41]A. Abdulrazzaq Hadi, and A. Abdulkhabeer, M. Turki, "Desulfurization of Crude Oil by Laboratory Developed Multipumping Flow Injection Analysis System with Optimization by Response Surface Methodology," *Journal of Ecological Engineering*, vol. 24(2), pp.382-339, 2023.

[42] A. B. Ogbesejana, B. Liu, and M. Ostadhassan, "Stable Isotope Geochemistry of the Organic Elements within Shales and Crude Oils: A Comprehensive Review," *Molecules*, vol. 27, no. 1, p. 34, Jan. 2022.

[43] G. R. Helz, E. Bura-Nakić, N. Mikac, and I. Ciglenečki, "New model for molybdenum behavior in euxinic waters," *Chemical Geology*, vol. 284, no. 3–4, pp. 323–332, May 2011.

[44] Abdula, Rzger A. "Crude oil classification based on age and provenance from the Southern Iraq: A review." *Bulletin of the Geological Society of Malaysia*, vol. 70, p. 87-102, Nov. 2020.

[45] A. Kumar et al., "Lead Toxicity: Health Hazards, Influence on Food Chain, and Sustainable Remediation Approaches," *International Journal of Environmental Research and Public Health*, vol. 17, no. 7, p. 2179, Jan. 2020.