Comprehensive Analysis of Oil Sludge from The Absheron Peninsula to Solve Environmental Problems

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Abstract. The Absheron Peninsula, historically known for its oil production, is home to several key oil fields including Bibi-Eybet, Balakhani, Surakhani and Ramana. Decades of oil production have resulted in the accumulation of significant quantities of oil sludge, which poses significant environmental and economic challenges. The objective of this study is to conduct a comprehensive chemical analysis of oil sludge from these fields using an Agilent Technologies ICP-OES 5810 for elemental analysis and a Cary 630 FTIR for molecular characterization. The results provide valuable information on the composition of these sludges, which can facilitate more effective remediation and disposal strategies.

Keywords: Oil sludge, Absheron Peninsula, ICP-OES, FTIR, environmental remediation, elemental analysis.

1 Introduction

The Absheron Peninsula in Azerbaijan is one of the world's oldest oil-producing regions, with its key oil fields - Bibiheybet, Balakhani, Surakhani, and Ramana contributing significantly to Azerbaijan's oil history. While these oil fields have been central to energy production for over a century, they have also contributed to the accumulation of vast quantities of oil sludges. Oil sludge is a complex waste product generated from oil extraction, refining, storage, and transportation processes. It contains a mixture of hydrocarbons, heavy metals, and solid particles, along with water and other contaminants. Improper handling of oil sludge can lead to severe environmental degradation, impacting soil and water quality and presenting long-term ecological risks [1].

1.1 Problem of Oil Sludge Accumulation and Environmental Concerns

The oil fields on the Absheron Peninsula have witnessed prolonged production activities, and the disposal of oil sludges has created both economic and environmental challenges. The

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environmental concern is compounded by the toxic nature of many components in oil sludge, such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals, which pose hazards to both terrestrial and aquatic ecosystems. The presence of heavy metals like lead (Pb), arsenic (As), cadmium (Cd), nickel (Ni), vanadium (V), iron (Fe), sodium (Na), calcium (Ca), zinc (Zn) and non-metals Silicon (Si) phosphorus (P) can result in soil contamination, leaching into groundwater, and bioaccumulation in the food chain. Therefore, a thorough understanding of the chemical composition of oil sludges is essential for both assessing their environmental impact and developing appropriate remediation strategies [2].

1.2 Objective of the Study

The main objective of this study is to conduct a comprehensive chemical analysis of oil sludge samples from the Bibieybet, Balakhany, Surakhany and Ramana fields on the Absheron Peninsula. The aim of the study is to determine the concentrations of major heavy metals and characterize the hydrocarbon composition of the oil sludge. This information will provide valuable information on the level of contamination and serve as a basis for developing appropriate reclamation and waste management strategies.

1.3 Overview of the Analytical Methods

To achieve the objectives of the study, we used a combination of advanced analytical techniques. Elemental analysis was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES), specifically using an Agilent Technologies ICP-OES 5810. This technique is highly effective for the detection and quantification of trace metals and is widely known for its accuracy and sensitivity. For molecular characterization, Fourier transform infrared spectroscopy (FTIR) was performed using an Agilent Technologies Cary 630 FTIR. This technique allows for the identification of functional groups in organic compounds, making it suitable for the analysis of the hydrocarbon fraction of oil sludge. In line with industry standards, the analytical method used for this study follows IP 501/05 (2019), a standardized procedure for the analysis of metals and hydrocarbons in oil sludge. This method provides recommendations for sample preparation, digestion, and analysis, ensuring consistency and reliability of the results obtained. By using the IP 501/05 (2019) methodology, we ensure that the study meets international standards of environmental analysis and contributes to the global understanding of oil sludge pollution [1-3].

1.4 Relevance and Significance of the Study

The analysis of oil sludges using these advanced techniques offers critical data that can inform remediation efforts and regulatory policies. Given the increasing global emphasis on environmental sustainability and the remediation of contaminated sites, this study is highly relevant to the ongoing efforts to clean up oil-contaminated areas on the Absheron Peninsula. Furthermore, the insights gained from this research can be applied to similar oil-producing regions worldwide, where oil sludge accumulation poses similar environmental challenges [4-6].

In the following sections, the materials and methods used for the analysis will be described in detail, followed by the presentation of the results and a discussion of their implications for environmental management and remediation strategies [7, 8].

2 Materials and Methods

2.1 Sample Collection and Preparation

The study was conducted in four historically significant oil fields on the Absheron Peninsula: Bibiheybet, Balakhani, Surakhani, and Ramana. These fields have been under continuous oil production for more than a century, leading to substantial accumulation of oil sludge in both active and abandoned extraction sites. Each field was selected based on its unique production history and sludge accumulation patterns, providing a comprehensive understanding of the different characteristics and contaminant levels present in these areas [9, 10].

- Bibiheybet Field: This site is one of the oldest oil fields in the world, located on the southern shore of the peninsula. Its proximity to the Caspian Sea also makes it a region of particular environmental concern, as oil sludge runoff can impact marine ecosystems.
- Balakhani Field: Known for being the first field to undergo industrial-scale oil production in Azerbaijan, this site has a long history of oil sludge accumulation, primarily near old wellheads and storage facilities.
- Surakhani Field: Located inland, this field has experienced extensive sludge generation due to both extraction activities and oil refining operations nearby.
- Ramana Field: Situated east of Baku, this field represents one of the smaller, but equally important, oil-producing areas, with a high concentration of aged sludge pits and waste disposal sites.

Sampling Procedure:

Oil sludge samples were collected using a standardized sampling protocol to ensure consistency and reliability across the different fields. Sampling points were selected based on sludge deposition zones identified during a preliminary field survey. These points included:

- Surface pits and lagoons: Areas where oil sludge is openly stored or discarded.
- Drill sites and wellheads: Locations where active drilling and extraction result in the buildup of oily residues.
- Historical waste sites: Older deposits that have been left undisturbed for decades, representing aged and weathered sludge.

From each of the four fields, three representative sampling sites were selected, resulting in a total of 12 sampling points. At each site, both surface and subsurface sludge samples were collected to capture variations in composition. Surface samples (0–10 cm) were taken to assess fresh sludge material, while subsurface samples (10–30 cm) were collected to study aged and more degraded sludge.

Samples were collected using stainless steel trowels and placed in pre-cleaned, air-tight polyethylene containers to prevent contamination. Each sample was immediately labeled with the field name, sampling location, depth, and date of collection. The containers were sealed and stored in cool conditions during transportation to the laboratory to prevent any changes in composition due to evaporation, oxidation, or biodegradation [11-13].

Sample Preservation and Transport:

To maintain the integrity of the collected oil sludge samples, proper preservation methods were followed:

- Temperature Control: Samples were transported in coolers with ice packs to maintain a temperature of around 4°C. This prevented microbial degradation and volatilization of hydrocarbons during transportation.
- Avoiding Cross-Contamination: Sampling equipment was thoroughly cleaned between sample collections using deionized water and acetone to avoid cross-contamination between different field locations. New gloves were worn at each sampling point.
- Sealing and Labeling: After collection, the containers were double-sealed to prevent leaks and exposure to air. Each sample container was labeled with detailed information, including the field location, coordinates of the sampling site, and a unique identification number.

2.2 Physical-Chemical Analysis

The physical-chemical properties of the oil sludge samples were analysed to provide insights into their characteristics, such as moisture content, pH, and organic matter composition. These parameters are crucial for understanding the behaviour of oil sludge in the environment and for developing remediation strategies. The results of the physical-chemical analysis are shown in Table 1.

Table 1. The results of the physical-chemical analysis.

Parameter	Method	Unit	Description
Moisture Content	ASTM D2216	%	Determined by drying a sample at 105°C
pH	ASTM D1293	-	Measured using a digital pH meter
Total Organic Carbon (TOC)	Walkley-Black method	%	Quantifies organic matter content
Ash Content	ASTM D2974	%	Determined by combustion at 550°C
Bulk Density	ASTM D7263	g/cm³	Measures the density of the dried sludge
Particle Size Distribution	ASTM D422	%	Analyzes the distribution of particle sizes
Oil and Grease Content	EPA 9071B	mg/kg	Extracted using n-hexane and gravimetric analysis

2.3 Positioning

The physical-chemical properties of oil sludges are essential for understanding their environmental behaviour, degradation patterns, and suitability for different remediation approaches. In this study, key physical-chemical parameters such as moisture content, pH, total organic carbon (TOC), ash content, bulk density, particle size distribution, and oil/grease content were analysed. These parameters help elucidate the complex nature of oil sludges from the four studied fields and offer insight into their pollutant load and potential impact on the surrounding environment.

Moisture Content:

Moisture content is a critical factor in determining the stability and handling of oil sludge. High moisture levels can increase the mobility of contaminants and complicate remediation efforts.

Bibiheybet Field: The moisture content of samples from the Bibiheybet field averaged 25.6%. Due to the proximity of the field to the Caspian Sea, atmospheric humidity and groundwater intrusion into sludge pits may contribute to the higher moisture levels observed in this area.

Balakhani Field: Samples from the Balakhani field showed slightly lower moisture content, averaging 21.3%. The region's relatively dry climate and open-air sludge disposal methods may lead to the evaporation of water, resulting in drier sludge.

Surakhani Field: Sludges from Surakhani exhibited moisture levels around 23.8%. The field's inland location and the potential for rainwater accumulation in open pits are key factors influencing the moisture content.

Ramana Field: Ramana samples had the lowest moisture content, averaging 18.7%. This may be due to more controlled disposal practices and lower rainfall in this region compared to the others.

pH:

The pH of oil sludge influences the mobility of heavy metals and other pollutants, as well as microbial activity in the sludge. Acidic or highly alkaline conditions may enhance the leaching of toxic elements.

Bibiheybet Field: The average pH of Bibiheybet sludge was 6.5, indicating slightly acidic conditions. This may be due to the presence of acidic compounds from oil refining activities and the influence of seawater.

Balakhani Field: Sludges from the Balakhani field had a neutral pH of 7.0. Given the long history of oil production, this pH level likely reflects the balance between acidic and basic substances in the sludge.

Surakhani Field: The pH of sludge from Surakhani averaged 5.9, showing more acidic conditions compared to the other fields. This could be attributed to the higher concentration of sulfur-containing compounds in the sludge.

Ramana Field: Ramana sludge exhibited a near-neutral pH of 7.2. This may reflect a higher level of buffering agents or lower concentrations of sulfur compounds in this field.

Total Organic Carbon (TOC):

TOC represents the fraction of organic material in the sludge, which can be indicative of hydrocarbon content. High TOC levels suggest a significant amount of residual oil, which could be of interest for recovery efforts or present challenges for biodegradation.

Bibiheybet Field: The TOC of Bibiheybet sludges averaged 14.2%, highlighting the high hydrocarbon content present due to historical crude oil spills and refinery waste.

Balakhani Field: Samples from Balakhani showed a slightly lower TOC content of 12.6%. This may be due to the more advanced age of the sludge and subsequent weathering, leading to some natural degradation of hydrocarbons.

Surakhani Field: Surakhani sludges had the highest TOC levels, averaging 16.8%. This suggests that the field's waste contains significant hydrocarbon residues, possibly from more recent production or insufficient oil recovery processes.

Ramana Field: The Ramana samples had a TOC of 10.1%, indicating a lower proportion of organic material compared to the other fields. This may reflect the advanced age of the sludges and natural attenuation processes over time.

Ash Content:

Ash content refers to the inorganic residue left after complete combustion of the sludge and can be indicative of mineral content, including metals and silicates.

Bibiheybet Field: The ash content of Bibiheybet sludges averaged 45.5%, which is relatively high. This may be due to the accumulation of inorganic materials from surrounding soil, sand, and industrial debris.

Balakhani Field: Sludges from Balakhani had an ash content of 39.2%. This suggests that the field's sludge contains a lower mineral load compared to Bibiheybet, likely due to the different disposal methods and the composition of waste materials.

Surakhani Field: The Surakhani samples exhibited an ash content of 41.8%, reflecting the presence of both organic and inorganic contaminants. The higher ash content may be due to industrial activities nearby, contributing to mineral buildup.

Ramana Field: Ramana sludge had the lowest ash content at 35.3%. This may indicate a lower level of contamination by external minerals and a higher organic fraction in the sludge.

Bulk Density: Bulk density reflects the compactness of the sludge material, which can influence its behavior in landfills and during transport. Denser sludge is more difficult to manage and may require special handling techniques.

Bibiheybet Field: The bulk density of Bibiheybet sludge was measured at 1.21 g/cm^3. The relatively high density may be due to the presence of heavy metals and other mineral content in the sludge.

Balakhani Field: Balakhani sludges showed a bulk density of 1.14 g/cm^3. The slightly lower density compared to Bibiheybet could be a result of lower inorganic contamination and a more weathered sludge matrix.

Surakhani Field: Surakhani samples exhibited a bulk density of 1.18 g/cm^3. This value reflects the compactness of the sludge, which is likely influenced by the high TOC content and ash content in this field.

Ramana Field: Ramana sludge had the lowest bulk density at 1.10 g/cm³. The lower density may reflect a higher organic content and lower accumulation of heavy metals and other inorganics.

Particle Size Distribution: Particle size distribution in sludge influences the ease of pollutant leaching and the potential for solid-phase contaminant transport. Fine particles tend to increase the mobility of toxic elements like heavy metals.

Bibiheybet Field: Bibiheybet sludges showed a relatively even particle size distribution, with approximately 45% of the particles smaller than 75 µm, indicating a significant proportion of fine-grained material.

Balakhani Field: Samples from Balakhani exhibited a coarser distribution, with only 35% of particles smaller than 75 µm. This suggests that the sludge in this field is more granular, which could limit the mobility of contaminants.

Surakhani Field: Surakhani sludges had a finer particle distribution, with around 50% of the particles below 75 µm. This fine texture could enhance the leaching potential of contaminants from the sludge.

Ramana Field: Ramana samples showed 40% of particles smaller than 75 µm. The moderately fine texture may facilitate the leaching of organic and inorganic pollutants in the sludge.

Oil and Grease Content: Oil and grease content is a measure of the residual hydrocarbons in the sludge. Higher values indicate a higher degree of contamination by crude oil or refined petroleum products.

Bibiheybet Field: The oil and grease content in Bibiheybet sludges averaged 26,000 mg/kg, indicating significant hydrocarbon contamination likely due to both historical spills and ongoing production activities.

Balakhani Field: Balakhani sludge samples had an oil and grease content of 20,500 mg/kg. While still high, this suggests that some natural degradation or weathering has reduced the hydrocarbon load over time.

Surakhani Field: The Surakhani field exhibited the highest oil and grease content, averaging 32,100 mg/kg, likely due to insufficient recovery of oil from the sludge and the presence of recent production waste.

Ramana Field: Ramana samples had an oil and grease content of 17,800 mg/kg, the lowest among the fields, indicating that the sludge here has undergone more extensive natural degradation processes or has been subjected to partial remediation.

3 Results and Discussion

The elemental composition of the oil sludge samples from the Bibiheybet, Balakhani, Surakhani, and Ramana fields was determined using ICP-OES in accordance with the methods IP 501/05 (2019), IP 377, and IP 470. The ICP-OES calibration was performed using Agilent-manufactured standard solutions with known concentrations. The stock solution was 1000 ppm, and the calibration standards were prepared at concentrations of blank, 5 mg/L, 10 mg/L, and 50 mg/L.

The calibration curve was generated by diluting the 1000 ppm stock solution to achieve the target concentrations for the standards. The calibration standards covered the concentration range expected for the metal elements in the sludge. The accuracy of the calibration was verified using quality control samples, including certified reference materials and blank solutions. The calibration curve displayed excellent linearity with a correlation coefficient (R^2) greater than 0.999 for all elements.

The detection limit for each element varied based on the sensitivity of the method but was sufficient to detect trace concentrations in the oil sludge samples. Analytical precision was ensured by running each sample in triplicate, and the relative standard deviation (RSD) was maintained below 5%.

The elemental analysis of oil sludge samples from the Bibiheybet, Balakhani, Ramana, and Surakhani fields revealed significant concentrations of various metals and non-metals, which have important implications for environmental safety and regulatory compliance.

1. Heavy Metals: The presence of heavy metals, particularly lead (Pb), cadmium (Cd), mercury (Hg), vanadium (V), nickel (Ni), and zinc (Zn), is a critical concern. The concentrations of lead across all fields exceeded the regulatory limit of 10 mg/kg, with Bibiheybet (45.3 mg/L) and Balakhani (50.0 mg/L) showing particularly high levels. This elevated presence indicates potential contamination from industrial activities and highlights the need for stringent monitoring and remediation efforts in these areas.

Cadmium and mercury levels were also of concern, although they remained below the regulatory limits in most locations. However, the detected values, especially in Balakhani (1.5 mg/L for Cd and 0.5 mg/L for Hg), suggest a potential risk for bioaccumulation and toxicity in the surrounding ecosystems. Given that mercury is highly toxic even at low concentrations, ongoing surveillance is essential.

2. Vanadium and Nickel: Vanadium concentrations were significantly high, with values reaching up to 110 mg/L in Balakhani, far exceeding the 50 mg/L regulatory limit. Nickel levels were also elevated, particularly in Balakhani (100.0 mg/L) and Bibiheybet (98.5 mg/L). The presence of these metals may be associated with oil production and refining processes, and their environmental impacts should be assessed, particularly in terms of soil and water quality.

3. Iron, Sodium, and Calcium: Iron concentrations were within the acceptable limits across all fields, although the observed levels (ranging from 190.0 to 210.0 mg/L) suggest significant mineral content in the oil sludge. Sodium and calcium levels also showed variability, with values between 150.0 and 320.0 mg/L. High sodium concentrations may indicate salinity issues that can adversely affect soil health and plant growth.

4. Non-Metals: The analysis of non-metals such as silicon (Si) and phosphorus (P) revealed high concentrations, particularly silicon, which ranged up to 1100.0 mg/L. While silicon is generally less toxic, elevated levels may impact soil characteristics and plant uptake. Phosphorus concentrations were also notable, particularly in Balakhani (35.0 mg/L), where it can contribute to nutrient loading in nearby water bodies, potentially leading to eutrophication.

5. Implications for Environmental Management: The results underscore the need for careful management of oil sludge in these regions. The high concentrations of toxic heavy metals and nutrients necessitate immediate attention to mitigate environmental risks. Strategies could include implementing stricter waste management practices, enhancing remediation technologies, and conducting regular monitoring to track changes in sludge composition over time.

6. Future Research Directions: Further research should focus on the bioavailability of these metals and their ecological impacts. Longitudinal studies that monitor the effects of oil sludge contamination on local flora and fauna would be beneficial. Additionally, evaluating the effectiveness of remediation strategies in reducing metal concentrations over time will be crucial for improving environmental health in the Absheron Peninsula.

The FTIR analysis of oil sludge samples from the Bibiheybet, Balakhani, Ramana, and Surakhani fields yielded critical insights into their molecular composition, revealing a complex mixture of organic compounds that pose significant environmental considerations.

1. Functional Group Identification: The spectra obtained from the FTIR analysis exhibited distinct absorption peaks that correspond to various functional groups, providing a comprehensive overview of the molecular components in the oil sludge. Notably, the presence of hydroxyl groups (–OH) observed in the range of 3050-3300 cm^{-1} suggests moisture content as well as the potential for hydrogen bonding interactions in the sludge

matrix. The intensity of these peaks varied among the samples, indicating differences in water content, which can influence the physical and chemical properties of the sludge.

2. Aliphatic Hydrocarbons: The absorption bands detected between 3050-2950 cm^{-1} are indicative of C–H stretching vibrations commonly associated with aliphatic hydrocarbons. The presence of these hydrocarbons is expected, given the nature of oil sludge derived from crude oil. The variations in peak intensities suggest differences in the saturation levels and the complexity of the hydrocarbon chains among the different locations. For instance, Balakhani exhibited stronger peaks, potentially indicating a higher concentration of saturated hydrocarbons, which could affect the sludge's reactivity and biodegradability.

3. Aromatic Compounds: Aromatic compounds, reflected by peaks in the 1500-1600 cm^{-1} range, were prevalent across all samples. The presence of these compounds is concerning due to their potential toxicity and persistence in the environment. Notably, the highest intensities were observed in samples from Ramana, suggesting a greater impact from industrial activities. These aromatic compounds could contribute to the adverse environmental effects associated with oil sludge, such as soil and water contamination.

4. Carbonyl and Carboxylic Acid Functional Groups: The presence of carbonyl groups (C=O) indicated by peaks around 1700-1750 cm^{-1} points to the occurrence of oxidized organic materials, which may have arisen from degradation processes. This finding suggests that some components of the sludge have undergone oxidation, potentially influencing the sludge's reactivity and its interactions with environmental matrices.

Additionally, the identification of carboxylic acid groups, indicated by peaks in the 1200-1300 cm^{-1} range, raises concerns about the potential corrosiveness and environmental impact of the sludge. Carboxylic acids can enhance the solubility of metals in contaminated soils, potentially leading to increased leaching into groundwater.

5. Environmental Implications: The molecular composition of the oil sludge, as revealed by FTIR, underscores significant environmental implications. The presence of both aliphatic and aromatic hydrocarbons suggests that these sludges can have prolonged ecological effects, including bioaccumulation and toxicity in local flora and fauna. The functional groups identified also highlight potential pathways for biodegradation and the chemical interactions that may occur in the environment.

The variability in molecular composition among the different sampling sites suggests that localized industrial activities may influence the types and concentrations of compounds present. For example, higher aromatic content in Ramana may reflect specific industrial discharges or contamination sources that warrant further investigation.

4 Conclusion

Chemical analysis of oil sludge from the Bibi-Eybet, Balakhany, Surakhany and Ramana fields revealed a complex mixture of heavy metals and hydrocarbons that pose significant environmental hazards. Use of the Agilent Technologies ICP-OES 5810 allowed for accurate quantification of toxic metals, while the Cary 630 FTIR provided molecular data on the hydrocarbon composition. The results highlight the need for targeted remediation efforts with an emphasis on heavy metal stabilization and hydrocarbon degradation.

Future work should focus on developing tailored remediation technologies that address the specific contaminants identified in this study. Additionally, continuous monitoring of these fields is recommended to track changes in sludge composition and assess the effectiveness of remediation efforts.

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