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The Impact of Environmental Pollution on Oil-Contaminated Soil Properties and Its Improvement Using Biodiesel in the Dora Refinery Area

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ABSTRACT

In this research, oil-polluted soil in the vicinity of the Dora refinery was focused on. Soil samples were collected at appropriate depths and analyzed for their physical and chemical properties to determine the degree of pollution. The analyses included pH, organic matter content, electrical conductivity, bulk density, moisture content, and soil texture measurements. GC-MS was utilized for the identification of petroleum organic compounds. Used cooking oil was utilized to produce biodiesel, which was subsequently applied to the contaminated soil at a 10% by weight. Corn seedlings (*Zea mays*) were subsequently sown in treated and untreated soils, and growth parameters—height, number of leaves, and dry biomass—were quantified. The results indicated significant improvements in soil quality and plant growth in treated soil compared to untreated soil, showing the efficiency of biodiesel as an environmentally friendly bioremediation process for enhancing oil-contaminated soil quality and promoting plant growth.

1. INTRODUCTION

Soil is a valuable natural resource on which human beings depend for agricultural stability and food security. However, soil is under the threat of numerous hazards, primarily contamination with oil products and by-products of oil manufacturing processes. Such pollutants render the soil less fertile and directly subject human existence and the agricultural environment to damage [1]. Among places contaminated with this type of pollution, the Dora refinery site in Baghdad is highly contaminated due to continuous emissions from refining activities and the invasion of fuel into the ground. To address this problem, various traditional methods have been devised to remediate oil-contaminated soil. These include physical methods (e.g., soil replacement or containment), chemical methods (e.g., oxidation or solvents), and biological methods on the basis of the use of microorganisms to biodegrade hydrocarbon compounds [2]. While effective to some extent, these methods are limited, for example, high cost and potential secondary environmental impacts.

In this context, biofuel is an eco-friendly and innovative means of treating soil contaminated with oil. Derived from plant biomass or waste oils, biofuel encourages microbial activity in soil, hence improving the biodegradation of contaminants and properties of soil and chemicals [3]. Therefore, it is also considered a sustainable alternative to chemical and physical treatment.

It was discovered in a 2019 study that biofuel from vegetable oils had more microbial activity and pollutant degradation significantly. It also reduced the level of polycyclic aromatic hydrocarbons (PAH) in the soil [4]. A study conducted in 2021 examined the use of biofuel with plants and bacteria. It showed that soil organic matter content and electrical conductivity increased, and polluted soils recovered their productive capacity [5].

A recent 2023 field experiment in a site with contamination that is equivalent to that of the Dora refinery showed that biofuel use led to enhanced plant growth, better soil physical and chemical characteristics, and a significant reduction in petroleum contaminant concentrations [6]. These results establish the potential use of biofuel as a highly efficient and sustainable approach to oil-contaminated soil treatment.

Based on these results, this study aims to evaluate the impact of biofuel on improving the qualities of oil-contaminated soil in the Dora Refinery area. Specifically, it aims to find out changes in the physical and chemical characteristics of the soil and how the treatment influenced plant growth.

2. MATERIALS AND METHODS

2.1 Soil sampling

Random soil samples were taken using different clean tools from different parts around the Daura refinery. The soil sampling is supposed to be taken from a reasonable depth (approximately 15-30cm) to better represent the contaminated soil, place them in sealed plastic bags, and record significant details such as location, date, and sample depth according to study [7].

2.2 Chemical tests

The degree of pollution was measured quantitatively by the aid of GC-MS spectroscopy to determine the concentration of oil impurities, along with the chemical parameters as per pH, organic material, and electric conductivity, according to studies [8-10].

1)-pH was determined in a pH meter after previously calibrating the device with known standard solutions before each measurement and then immersing the probe in the soil water mixture, awaiting stabilization of the reading [8].

2)-Organic content measurement was done by oven drying the sample at 105℃ for 24 hours, then weighing the sample after it had dried, and then burning in an oven at 550℃ for 4 hours, followed by weighing of the sample after burning. Organic content can be calculated from the formula given below [9]:

$$Organic\ Contents\% = \frac{Wt\ of\ Dry\ Sample - Wt\ of\ Ash\ Samples}{Wt\ of\ Dry\ Sample} \times 100$$

•Weight of Dry Sample: weight of the sample after it has been dried.

•Weight of Ash Sample: weight of the sample after it has been incinerated in a furnace at 550℃ for 4 hours.

3)-Electrical conductivity by means of an apparatus previously calibrated with standard known solutions, immersing the probe into the soil solution and letting it sit until it reaches a stable value, record the value of electrical conductivity [9, 10].

2.3 Measuring physical properties

Like density and moisture, including soil texture, according to studies [11-14]. Testing physical properties of soils, including measures of density and moisture content, and soil texture:

1)-Density Measurement: The sample of soil was oven-dried at 105℃ until it became completely dry, after which the sample was weighed on a balance to measure the volume of the sample. It was done by filling the graduated cylinder with water and recording the volume of the water while adding the dry sample of soil into the cylinder and recording the new volume of the water with the sample [12].

2)-Moisture Content Test: The weight of the soil sample, by balance, is measured after the sample has been completely dried in the oven at 105℃ for 24 hours; then, the sample is weighed after drying (W_2) to calculate the moisture content according to the following equation [13]:

$$Moisture\ Content\ \% = \frac{W_1 - W_2}{W_1} \times 100$$

3)-Measurement of Soil Texture: A soil sample was taken and put in a transparent container; water was added to the sample until it reached well over the top. The container was then shaken sideways, mixing the soil and water together for component determination purposes. Later, the container was left standing for 24 hours to allow the sand and clay particles to settle. Determination of the percentage of sand and clay in the sample was done based on the usage of the known database of the distribution of particle size after settling [14].

2.4 Preparing biodiesel from used cooking oil

According to Figure 1 and Figure 2, biodiesel preparation can be made from plant sources, including used cooking oil, ensuring decylglycerol is an agent to prepare biodiesel. The *Zea mays* was chosen because it had the ability to tolerate poor soil conditions, in addition to absorbing water and nutrients [15].

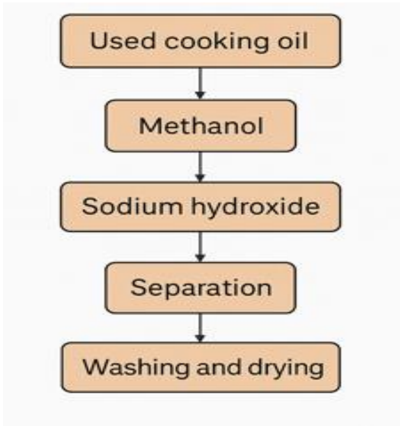

Figure 1. Schematic diagram of biodiesel preparation process

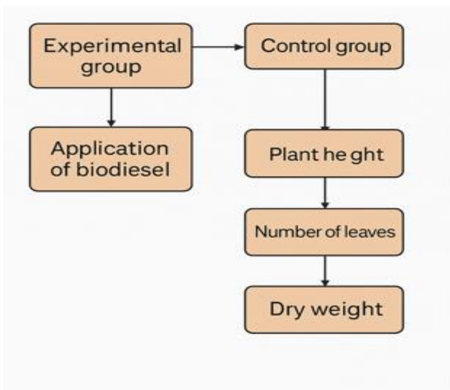

Figure 2. Schematic of the experimental setup

The mixture was prepared by measuring a quantity of used cooking oil (1 L), measuring a quantity of methanol (200 mL), and dissolving an appropriate quantity of sodium hydroxide in the methanol. Then, the cooking oil's temperature was raised between a range of 50-60 degrees Celsius by adding to the oil the methanol dissolved in sodium hydroxide, considering continuous stirring between a range of 30-60 minutes. After the stirring process is over, let it cool the mixture and we notice here the start of the separation of biodiesel from glycerin, have been used a strainer or bottle whereby separating the layers resulted in washing with water the resulting biodiesel to clean up possible contaminants or residues, then left to dry well before use [16].

Then the two groups were made from each of the contaminated samples: an experimental group, exposed to biodiesel, and a control group-untreated. To the experimental group, 10% of the soil weight of biodiesel was added; the soil was well mixed, taking into consideration that all samples were under similar conditions-such as temperature and humidity. Evaluate the impact of biodiesel on the plant by measuring the growth steps, as follows:

Measure the plant height by defining the base point: "Select a point from the bottom of the stem near the soil surface to the top of the plant-usually the top leaf." Measure the height by using a ruler or a tape measure for accurate height. Record the measurement for each plant in the log notes. Repeat the measurement. Count the number of leaves, taking into consideration removing dead or damaged leaves. Make sure to record the total number of damaged leaves.

Clean the samples extensively by rinsing to remove the adhering soil or impurities that could affect weighing. Leave them to dry for approximately 15-30 minutes to avoid too much weight because of surface wetness. Leave them in a low oven temperature, approximately 70-80 degrees Celsius, until completely dry, as shown in studies [17]. Subsequently, after the drying of the samples, the recording weight in a dry state was recorded.

The degree of contamination identified using the GC-MS technique is highly effective in detecting volatile organic compounds using solvent extraction, the Soxhlet extraction method, using appropriate solvents like hexane or chloroform that can extract the oil pollutant. It uses a purifying method on the sample to remove contaminants and dilutes extracts with the appropriate solvents like ethanol or water. Prepared samples are inserted into a gas chromatograph with an appropriate column for separating the compounds to find out the impurities. Impurities present in these samples include polyaromatic hydrocarbons (PAHs) like naphthalene, anthracene, and fluoranthene [18].

3. RESULTS AND DISCUSSION

Results showed that oil-contaminated soil has a different pH compared to uncontaminated soil. Contaminated soil was either more acidic or more alkaline, depending on the nature of the oil contaminants and their level of decomposition. Organic content reduction was noted to be associated with contaminated soil as a result of oil contamination, due to the fact that contaminants contribute to reducing available organic matter. This can be realized after thermal tests, which included burning of samples at 550°C. The same tests showed an increased electrical conductivity of the soil following contamination, indicating the accumulation of conductive chemical contaminants such as petroleum compounds and salts. An increase in conductivity could reveal an increased concentration of soluble contaminants in soil.

Results can be observed in Table 1, which includes an estimate of the magnitude of the effect of oil contamination on the chemical properties of the soil, to help understand environmental changes and the effects of contamination on the soil surrounding the area, in agreement with the study [19].

These results show the levels of pollution, especially oil pollution, on the soil's chemical properties. Soil pH ranges from 5.5 to 7.5; thus, this is an indication that the soil may be slightly acidic or neutral. Such variation in acidity could be due to the level of pollution in the soil. Oil-contaminated soils may indicate a change in pH as a result of chemicals leaked from the pollutants. Thus, the acidic soils may have a reduced capacity to support plant life, and the pH measure thus becomes an indication of soil quality. The organic contents were between 2 and 6%, although for oil-contaminated soil, it tended to be lower. This reduced organic content could be due to the decomposition of natural organic matter as a result of the presence of oil pollutants. Organic matter is one of the main factors responsible for improving fertility and supporting the activities of soil microorganisms; for this reason, its loss is considered a decrease in quality. This effect on contaminated soils impairs their capacity to be biodiverse. It is an indicative increase of conductivity due to the soluble pollutants, like petroleum hydrocarbons. High electrical conductivity means that the soil contains a higher percentage of dissolved salts or pollutants and may influence plant growth and stress. Such an increase is not welcome for soil and its suitability in agriculture [20]. Equal findings were also expressed by study [21] that petroleum pollution significantly alters the soil pH and the organic matter content, lowering soil biological activity as well as nutrient levels. From their work in oil-polluted soils around industrial establishments, they had a consistent drop in organic content up to 40%, affirming our finding of lowered organic matter in the contaminated regions. Furthermore, study [18] emphasized in recent studies the importance of monitoring organic degradation in oil-contaminated soils to predict long-term soil fertility loss [22].

Table 1. The chemical tests on oil-contaminated soils

Test No.	Chemical Test	Description	Approximate Results
1	pH Measurement	Using a pH meter to assess the acidity or alkalinity of the soil	5.5-7.5 (Ranges from slightly acidic to neutral, depending on contamination levels)
2	Organic Content	Determining organic matter by comparing the dry weight to the ash weight	2%-6% (Decreased organic content in soil affected by oil contamination)
3	Electrical Conductivity (EC)	Measuring soil solution conductivity with an EC meter	1-3dS/m (Increased EC due to the presence of soluble pollutants from oil)

Table 2. The physical tests on oil-contaminated soils

Test	Results	Percentage (%)
Density Measurement	1.2-1.6 g/cm³	-
Moisture Content	Varies between 10% and 25%	10%-25%
Clay Content	Around 30%	30%
Sand Content	Approximately 50%	50%
Silt Content	Estimated at 20%	20%

After drying in an oven at 105°C to complete dryness, the weight was measured on a precision balance. The dry sample was then put into a graduated cylinder full of water; this was used for volume measurement. The calculated soil density was recorded to range from 1.2 to 1.6 g/cm³, and the results from the measurement of the soil's moisture content gave a range of 10-25%, since clay soils are normally highly superior in moisture content compared to sandy soils. Regarding the analysis of soil texture, the test results indicated the presence of 30% clay, 50% sand, and 20% silt, thus making it a sandy clay textured soil, in accordance with study [21], as represented in Table 2.

The rise in electrical conductivity (EC) in oil-contaminated soils has been linked to the high concentration of dissolved ions like sodium (Na^+), chloride (Cl^-), and sulfate (SO_4^{2-}) that accompany petroleum products and their degradation products. Hydrocarbon degradation leaves various salts and organic acids in the soil solution, raising the ionic strength of the soil and thus its electrical conductivity. Study [17] also described the same, whereby soils that were exposed to petroleum for a long duration had elevated elevations in Na^+ and Cl^- concentrations, which led to sanitization and poor soil health [23].

The density test results ranged from 1.2 to 1.6 g/cm³ and are indicative of the soil cohesion strength. The more the density, the more cohesive the soil, hence this may affect the water retention and aeration of the soil. When the soil is less dense, it is more permeable to water and air; hence, this promotes root growth. The range given here is indicative of a rather balanced soil, but density may be affected by the moisture content of the soil and type of soil in question, as moisture content recorded between 10% and 25% is an important determining factor in the support capability of the soil for plant life. Soils with the right moisture content contribute to the provision of water to plants and help improve vital processes. With a too-low moisture content, drought would reach the plants, while with a too-high one, the lack of aeration, with water accumulation, may cause damage to the roots.

The average of clay in the soil was close to 30%. Clay retains water and nutrients inside the soil; besides that, it makes the soil difficult to aerate, and the speed of water drainage is reduced. With excess water, heavy clay content soils are heavy and difficult to handle. The sand content is about 50% of the soil; hence, it can be said that it is a well-aerated and fast-draining soil.

Generally, the sandy soils allow good drainage of the water and avoid waterlogging. However, they may be poor at retaining nutrients and moisture for long periods and, thus, require monitoring the moisture and feeding the plants regularly. It also constitutes about 20% of the soil are fine particles falling between sand and clay in size. Slightly earth has a moderate moisture-holding capacity, which adds proper balance between drainage and water retention, hence improving the quality of the agricultural soil. The soil in this study is balanced between clay, sand, and silt to an extent that it makes it suitable for agriculture, with good drainage combined with moderate water retention, the values of moisture content and density that fall in the range where plants can grow [24].

Initial contamination was consistent as both groups started with the same soil contamination level, ensuring that any observed differences could be attributed to the biodiesel treatment rather than the initial conditions. Biodiesel was applied at 10% by weight of soil consistently, demonstrating its potential role in improving soil and plant health. Improvements in soil chemistry were observed, with a slight increase in soil pH and higher moisture content in the biodiesel-treated soil indicating a more suitable environment for plant growth, leading to improved nutrient availability and uptake. Increased plant growth parameters in the experimental group showed significant increases in plant height, leaf number, and dry weight, suggesting that biodiesel positively affects plant physiology and biomass accumulation agrees with the study [25]. This is likely due to improved nutrient dynamics and soil conditions. This suggests an effective reduction in contamination, as biodiesel treatment significantly reduced contamination levels and polycyclic aromatic compounds (PAHs) concentrations, demonstrating its effectiveness as an environmental decontamination strategy. This suggests that biodiesel not only supports plant growth, but also contributes to the detoxification of contaminated soil (Table 3). The significant improvement in overall plant health assessments in the biodiesel-treated group further confirms the benefits of biodiesel application, suggesting its ability to enhance plant resilience to harsh environmental conditions [26].

Table 3. The biodiesel application and its effects on contaminated soil and plants

Parameter	Control Group (Untreated Soil)	Experimental Group (Biodiesel Treated Soil)
Initial Soil Contamination (mg/kg)	1500±100	1500±100
Biodiesel Added (10% of soil weight)	N/A	100 ml of biodiesel added per 1 kg of soil
pH Level of Soil	6.0±0.2	6.5±0.2
Moisture Content (%)	15±2	18±2
Plant Height (cm)	15±3	25±3
Number of Leaves	5±1	10±2
Dry Weight of Plants (g)	10±2	20±3
Contamination Level after Treatment (mg/kg)	1200±150	800±100
PAH Concentration (mg/kg)	300±50	150±30
Overall Plant Health Rating	3 (on a scale of 1 to 10)	8 (on a scale of 1 to 10)

Table 4. The experiment on determining contamination levels using Gas Chromatography-Mass Spectrometry (GC-MS)

Parameter	Result
Type of Contaminants Detected	Polycyclic Aromatic Hydrocarbons (PAHs)
Initial Contamination Level (mg/kg)	2500±300
Contamination Level After Treatment (mg/kg)	800±150
Extraction Efficiency	90%±5%
Solvent Used	Hexane/Chloroform
Dilution Ratio Used	1:10 (extract)
Analysis Accuracy	95%±2%
Total Analysis Time	90 minutes

Results presented in Table 4 confirm the efficiency of pollution analysis and treatment concerning soils contaminated with volatile organic compounds, especially polycyclic aromatic compounds. Naphthalene, anthracene, and fluoranthene were pointed out as the main components of the pollution. Such compounds are important indicators of soil pollution with organic matter, being mostly of burning fuel and oil origins.

The pollution degradation rate with biodiesel treatment, plant growth parameters in control with experimental groups, and comparison of soil chemical properties in untreated with biodiesel-treated soil, considering the initial pollution level of 2500±300 mg/kg, is serious pollution in the soil, calling for urgent measures regarding the solution of this environmental problem. After treatment, the level of pollution went down to 800±150 mg/kg. This is a large decline by about 68%, showing that indeed the method used was successful in cleaning up the pollution and improving the soil quality since the extraction efficiency had reached 90%±5%, proving that the Soxhlet method applied in the extraction of the pollutants was very effective. This is a ratio that reflects how the technique is able to acquire accurate samples of the pollutant. A mixture of hexane and chloroform solvents is appropriate for the experiment; this is useful in the extraction process of the VOCs and is one of the critical steps enhancing the results of the analysis.

Dilution used was 1:10, and this was appropriate to improve the precision of the measurements, hence contributing to obtaining reliable results, while the effect of any probable interference was also reduced. The high accuracy in the results using the GC-MS technology, of 95%±2%, is considered important for efficiency in the tools employed for analysis, plus the assurance that the extracted data are reliable. Even the time factor being only 90 minutes is ample time to ensure accuracy in the separation of the pollutants; this shows how efficient the analytical process is and eliminates any possibility of time pressure impacting the results. The application of proper techniques in analyzing and treating the pollutants will definitely go a long way toward ensuring that soil pollution is reduced. The results also indicate that reliable analysis methods can only give accurate results to make sound decisions in environmental protection. Based on the results, it's recommended that there is a need for continued monitoring and research in environmental treatment techniques to ensure the health and sustainability of soil, which agrees with studies [27].

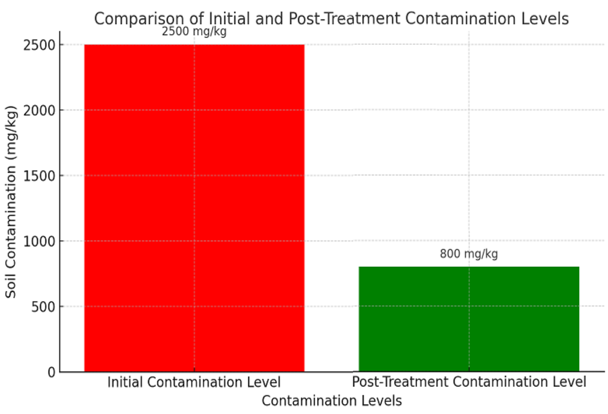

Figure 3. The initial contamination level compared to the post-treatment contamination

Figure 3 represents the initial contamination level, which is 2500 mg/kg, compared with the post-treatment contamination level, which is 800 mg/kg. The large reduction in contamination after the application of biodiesel treatment is exposed. It also represents the extraction efficiency, indicating a high rate of 90%. Justifying this, Soxhlet extraction will be very effective in the isolation of contaminants from soil samples. An analytic acumen obtained was 95%, outlining the reliability of a technique-GC-MS-for the correct detection of VOC and assessment of a contamination level [28].

4. CONCLUSION

1)-The acidity of the oil-contaminated soil can be different from that of the uncontaminated one, either more acidic or more alkaline, depending on the nature of the pollutants. The decrease in the organic content of contaminated soils is evidenced by a decrease in the available biomass. High electric conductivity of the soil shows the degree of conductive chemical pollutants, mainly petroleum compounds and salts that have built up in it. The water content of the soil remains between 10 to 25%, indicating that the very nature of the soil is affecting its water-retaining capacity.

2)-The treatment of soil with biodiesel had an ameliorating effect on acidity, improving the moisture content of the soil. This, in turn, improved the conditions for plant growth, as evidenced by the increase in plant height, the number of leaves, and dry weight observed within the biodiesel-treated group, thus evidencing positive effects on plant physiology.

3)-Pollutant levels were significantly reduced within the biodiesel-treated soil; hence, the levels of pollutants, including PAHs, decreased. GC-MS has, however, attained high efficiency in the extraction of pollutants, attaining even 90% extraction efficiency and an analysis accuracy of 95%. Therefore, the results hint at the use of effective strategies that could mitigate the effects of pollution through the use of effective means like biodiesel in cleaning the soil to improve environmental quality and thereby contribute to a sustainable environment.

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