

Investigating the role of nano in preserving the environment with new energy and preventing oil pollution

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Abstract. The escalating growth of industrial sectors has led to a pervasive global problem—oil pollution, particularly in industrial areas. The release of substantial volumes of oil and its by-products into the environment has resulted in extensive contamination. Multiple factors contribute to the entry of these substances into water bodies and soils, thereby inflicting irreparable consequences on ecosystems, natural resources, and human health. Consequently, it becomes imperative to comprehend the characteristics and behavior of oil pollution, anticipate its impacts, and develop effective mitigation strategies. Understanding this intricate issue requires considering the physicochemical properties of the environment, the interactions between oil and sediments, and biological factors such as evaporation and dissolution. Although the oil industry has brought about remarkable advancements, its activities have raised significant concerns regarding pollution from extraction and production processes. Oil-rich nations face a particularly challenging predicament of soil pollution caused by petroleum compounds. The areas surrounding oil exploration mines and refineries often endure contamination due to oil leakages from storage tanks and transmission lines resulting from deterioration and damage. Investigating the dispersion of such pollutants and devising methods to remediate petroleum-contaminated soil represent crucial and intricate issues within the realm of environmental geotechnics.

Keywords: contamination; environmental geotechnics; oil and derivatives; remediation; soil pollution

1. Introduction

Soil is one of nature's essential and valuable resources, from which about 95% of human food is obtained (Falandysz *et al.* 2022). Life on earth will not be possible without healthy soil, so planning to have healthy soil is necessary for human survival (Raimi *et al.* 2022). Having the power of self-healing, the soil is considered a purifier of nature, which, in addition to providing food, also has purifying properties (Luhar *et al.* 2022). This soil property is achieved due to its physical, chemical, and biological properties (Padalia *et al.* 2022). Therefore, soil pollution is one of the most important types of environmental pollution (Gavrilescu 2022). Any change in the characteristics of soil constituents in such a way that it is impossible to use it is called soil pollution (Shi *et al.* 2023). The discharge or leakage of organic matter causes most of the pollution caused in the soil (Xue *et al.* 2023). For a long time, petroleum products and their derivatives have caused soil pollution due to transportation or storage (Wang *et al.*

2023a). However, the deeper the oil penetrates the soil, the more difficult it will be to remove the pollution, and the cost will be several times higher (Nong *et al.* 2023). Types of soil pollutants are divided into four general categories according to the type of pollutant: organic compounds, minerals, radioactive elements, and microorganisms (Maqsood *et al.* 2023). High abundance and very high transferability in organic pollutants, very high stability in the environment and the ability to accumulate in the body of living organisms in inorganic pollutants, the ability to cause mutations in animal cells in radioactive elements, and the possibility of direct transmission of disease-causing organisms from the environment contaminated with living organisms from the environment contaminated with pathogenic microorganisms are the particular characteristics of each group and indicate the importance of different types of pollution in the environment (Cui *et al.* 2023). Based on their origin, pollutants are divided into two categories, human and terrestrial (Zhang *et al.* 2023). Human pollution results from human activities, and land pollution is caused by the natural accumulation of substances in some areas (Gautam *et al.* 2023). In examining the type of pollution in terms of the extent of the source, if the emission is from a specific place and a limited area, the pollution is a point

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source (Cazcarro *et al.* 2023). If the subsequent emission is from a wide area, the pollution has non-point pollution (Guo *et al.* 2023). It is difficult to control this type of pollution, and the amount of pollution entering the environment is much more (Liu *et al.* 2023). Petroleum fuel products are used in many applications, including ship fuel, jet fuel, gasoline, and many other things (Yusaf *et al.* 2023).

A refinery is an advanced industrial unit that distills and separates the components of crude oil using heat and produces valuable and practical materials such as liquid gas, kerosene, gasoline, diesel, and other petroleum products (Jing *et al.* 2022). The complexity of the refining process, the variety and multiplicity of facilities, equipment, and devices used, and the variety of materials consumed and produced in it have caused a wide range of contaminants to enter the environment in refineries and lead to environmental pollution (Hussain *et al.* 2022b).

1.1 Petroleum compounds

Hydrocarbons are a group of organic compounds and are the main components of crude oil, gas, and coal. These compounds are composed of carbon and hydrogen, and the type of bond between these atoms determines the type of hydrocarbon. Aromatic hydrocarbons are unsaturated cyclic compounds in crude oil with a high concentration (Dan *et al.* 2015, Turkeli *et al.* 2017, Zhai *et al.* 2018, Shakouri *et al.* 2021, Mekki *et al.* 2022, Oumedour and Lazzali 2022). In these compounds' structure, at least one ring containing three double bonds must be contained. Among aromatic hydrocarbons, compounds of benzene, toluene, ethylbenzene, and xylene (BTEX), raw materials of petrochemical industries, are more critical. BTEX compounds are the most crucial oil pollutants (Zhang *et al.* 2021, Ma *et al.* 2022, Yang *et al.* 2023, Yuan *et al.* 2023). In case of contact, inhalation, drinking, and eating foods contaminated with these compounds will harm humans and other living beings. These compounds are very volatile and have high mobility in the environment (Acter *et al.* 2022, Hussain *et al.* 2022b, Jabbar *et al.* 2022, Khademi *et al.* 2022).

1.2 Saturated aliphatic hydrocarbons (alkanes)

Alkanes consist of a chain of carbon atoms, each carbon atom in this group is bonded to four other atoms, and the bonded atoms can be carbon or hydrogen. The boiling points of these compounds increase with the number of carbon atoms (Lv *et al.* 2022, Ma *et al.* 2023).

1.3 Unsaturated aliphatic hydrocarbons (alkenes and alkynes)

In the structure of alkenes, carbon bonds with only three other atoms, indicating one or more double bonds between carbon atoms. The existence of a double bond in the structure of alkanes causes substitutions that make this family more complicated than alkanes. Alkynes have low polarity and are insoluble in water but soluble in solvents with low polarity (Faussone and Cecchi 2022, Srivastava *et al.* 2022).

1.4 Saturated cyclic hydrocarbons (cycloparaffins)

These hydrocarbons include a ring structure in their skeleton, and the number of carbon atoms in the ring varies. These compounds have a higher boiling point and density than alkanes and are primarily present as 5 or 6 carbons in crude oil (Gaur *et al.* 2022).

1.5 Soil pollution due to oil sources

The compounds in this group have atoms other than carbon and hydrogen in their structure. Sulfur is present in large quantities in crude oil. Oxygen in sulfur compounds is usually more than in crude oil (Esparham *et al.* 2021, Guo *et al.* 2021, Wang *et al.* 2021, Zhao and Yu 2021, Zhong and Liang 2022). Oxygenated compounds play an essential role in the composition of crude oil, despite their small amount, due to their acidity. The presence of nitrogen in crude oil is observed in sections with a boiling point above 250°C, especially in resins and asphalt compounds. Metal atoms such as nickel are found in the heavy fraction of crude oil and are placed in the center of the complex of molecules belonging to the porphyrin family. These compounds are similar to alkynes in solubility and dissolve in solvents with low polarity (Mozaffari *et al.* 2022, Tian *et al.* 2022, Zhu *et al.* 2022).

Oil and its derivatives are highly mobile, so soil and water pollution are possible. This pollution may be accidental, or the refinery may deliberately inject its oil effluent into the soil. Soil pollution with petroleum substances is significant, and even a tiny amount can affect the taste and smell of drinking water (Sarkar *et al.* 2022, Zhu *et al.* 2022). In the effective pollution of petroleum compounds, the pollutant concentration is usually more than the toxicity threshold for microorganisms. It is impossible to ignore the pollution in the hope of self-purification of the soil. When petroleum substances enter the soil environment after cutting off the source, the existing contamination must be removed from the environment to prevent its spread and spread (Wang *et al.* 2023c, Cao *et al.* 2022, Mohammadian *et al.* 2022). In non-cleaning, the pollutant will spread to greater depths, making improving and removing pollution from the soil more challenging (Xu *et al.* 2022). The expansion of oil through the soil and its downward movement from the spaces in the soil and rock is far more complicated and unpredictable. Contaminant movement speed in textured soils is highly permeable and less in soils with low permeability. Viscous compounds move at a lower speed than non-viscous compounds, especially in cold seasons (Jew *et al.* 2022, Hasnain *et al.* 2023). Soil is one of the most critical elements of the environment, and its non-contamination is vital in increasing the yield of agricultural products, the health of agricultural products, and the health of the human environment (Zhang *et al.* 2022b). Therefore, purifying and cleaning the soil from existing pollutants is an important issue. Nanotechnology has always been an efficient tool to help solve environmental challenges. The problem of contaminated soils is not an exception to this rule (Hussain *et al.* 2022a). Nanoscience and technology solve existing technological challenges by using materials

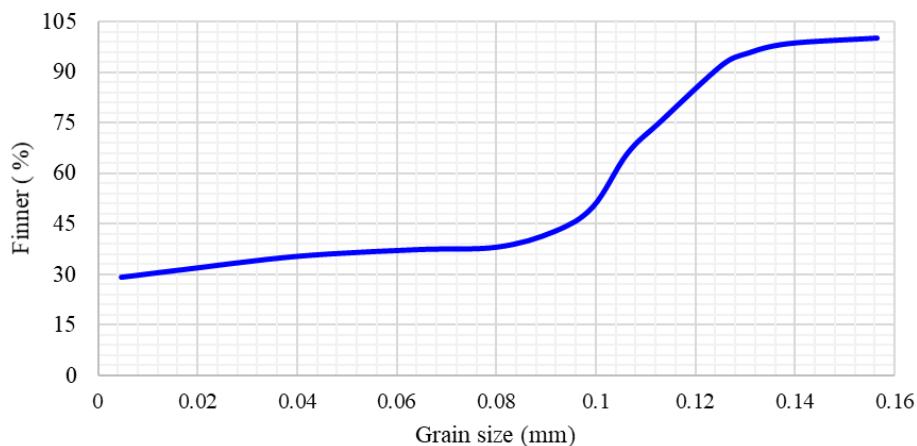


Fig. 1 Natural soil particle size distribution curve

Table 1 The list of materials and equipment

Materials and devices
Soil
Oil
Montmorillonite nanoclay
Cloisite 30B
Scanning electron microscopy (SEM)
X-ray diffraction analysis (XRD)

Table 2 Physical and mechanical properties of soil

Soil properties	The amount of
The specific weight of solid grains (kg/m ³)	1.2
Sand	47%
Silt	18%
Clay	22%
Amount of fluidity	22%
Optimal humidity (ω _{opt})	14%
Maximum dry density (γ _{d max} , KN/m ³)	17
Pushing resistance (kN/m ²)	281

in dimensions of 1 to 100 nanometers (Mamalis *et al.* 2004). Nanomaterials with small dimensions and diverse shapes have a large surface area and many reaction sites, which makes them highly prone to reaction, absorption, and catalytic activities (Ponce and Klabunde 2005). In recent years, nanotechnology has attracted the attention of scientists in the field of environment in order to purify water and sewage, air, and soil. Purification methods based on nanotechnology are effective and low-cost and do not harm the environment (Zhang *et al.* 2022a, Zhao *et al.* 2022, Cao *et al.* 2023). During the disinfection process, most interactions occur at the interface between nanomaterials and the pollutant (Ibrahim *et al.* 2016). Since the specific surface of nanomaterials is very high, these interactions occur at high speed. The presence of many active sites increases the purification rate and disinfection efficiency (Mohammadi *et al.* 2020, Wang *et al.* 2020,

2023b, Ugurlu and Ozturk 2021, Dehghanbanadaki *et al.* 2022). Also, the small size of nanoparticles helps them easily and quickly penetrate the infected areas (Yunus *et al.* 2012).

Nanoparticles, according to their application and function, can be surface or structurally modified and improve the efficiency and quality of disinfection. This category of nanomaterials is used not only in the purification of pollutants but also in their detection. All the mentioned properties have made nanomaterials a suitable option for treating pollutants (Yunus *et al.* 2012). If the oil pollution is not cleaned, its compounds can enter the underground water along with the deep-water flows, and finally, they can enter the human food chain and poison living organisms. According to what was said, studying and investigating oil pollution is necessary.

2. Materials and devices

The list of materials and equipment used to increase and improve the mechanical properties of oil-contaminated soils is shown in Table 1.

3. Method

The soil studied in the current research has proper granularity according to the Standard Test Method for Particle-Size Analysis of Soils Fig. 1. It has particles with an average diameter of 0.08 mm. The soil has particles with an average diameter of 0.08 mm. The soil has a specific density of 1.2 kg/m³ and a maximum dry density of 17.8 kN/m³. According to the X-ray diffraction test results, quartz mineral with an X-ray reflection angle of 25.8 is the main mineral, followed by albite, calcite, and montmorillonite with an X-ray reflection angle of 27.8, 29, and 10 are the minerals in solid soil (Fig. 2).

Also, the mechanical properties and constituent elements of the studied soil are given in Tables 2 and 3, respectively. In this research, oil with a specific gravity of 0.83 (kg/l) was used as a pollutant.

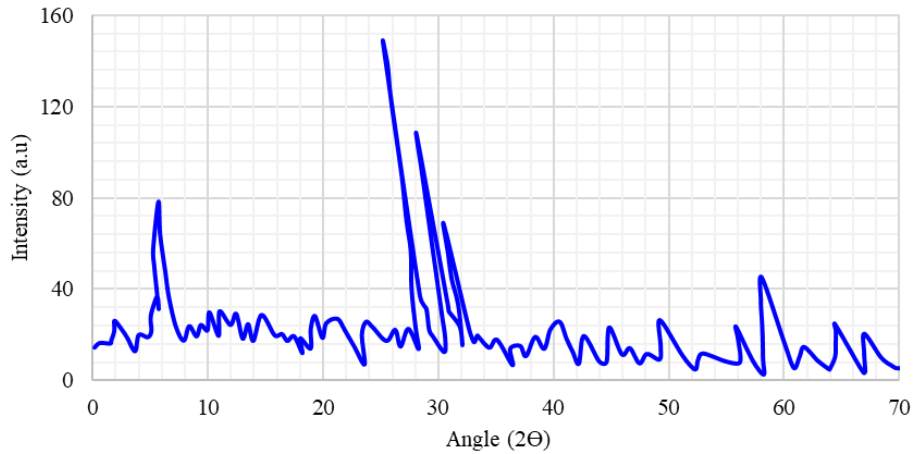


Fig. 2 The results of X-ray diffraction analysis of the studied soil

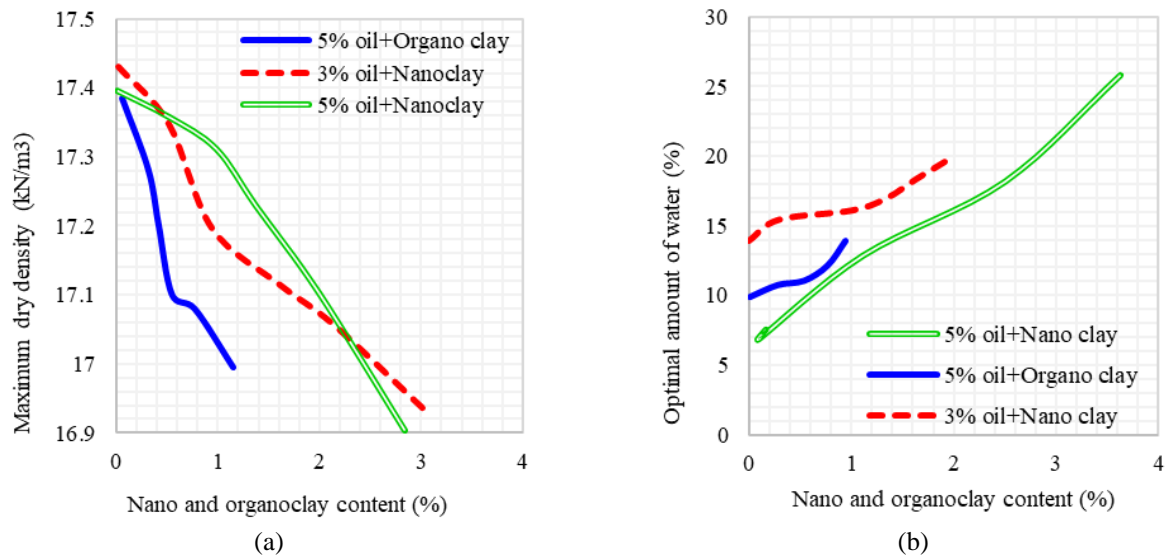


Fig. 3 Effect of nanoclay montmorillonite and cloisite 30B on maximum dry density (a) and optimal soil water (b)

Table 3 Chemical characteristics of the soil

Oxide type	The amount of (%)
SiO ₂	55
Al ₂ O ₃	16.1
CaO	13
Fe ₂ O ₃	4
MgO	3.2
K ₂ O	2

Table 4 Physical and chemical characteristics of nanoclay

Specification	Materials
Mineral type	Montmorillonite
Particle size (μm)	0.002-0.0025
Specific surface area (m ² /gr)	210-260
Space between pages (nm)	1
Humidity (%)	2

Table 5 Physical and chemical characteristics of nanoclay

Oxide type	The amount of (%)
SiO ₂	60
Fe ₂ O ₃	4.8
Al ₂ O ₃	20
CaO	2.3
MgO	3.5
K ₂ O	1
Na ₂ O	1.3
TiO ₂	0.8

This research used two types of nano clay in hydrophilic and organic states with the same primary mineral, montmorillonite, from Sigma Aldrich, Germany. Sodium montmorillonite nano clay with an average density of 3.35 and the characteristics presented in Tables 4 and 5 have been used to modulate contaminated samples.

Cloisite 30B brand organic clay with a density of 1.98 kN/m³, an apparent specific gravity of 0.354 gr/cm³, a distance between plates of 1.6 nm, and an average particle size of 5000 nm was used in oil-contaminated samples.

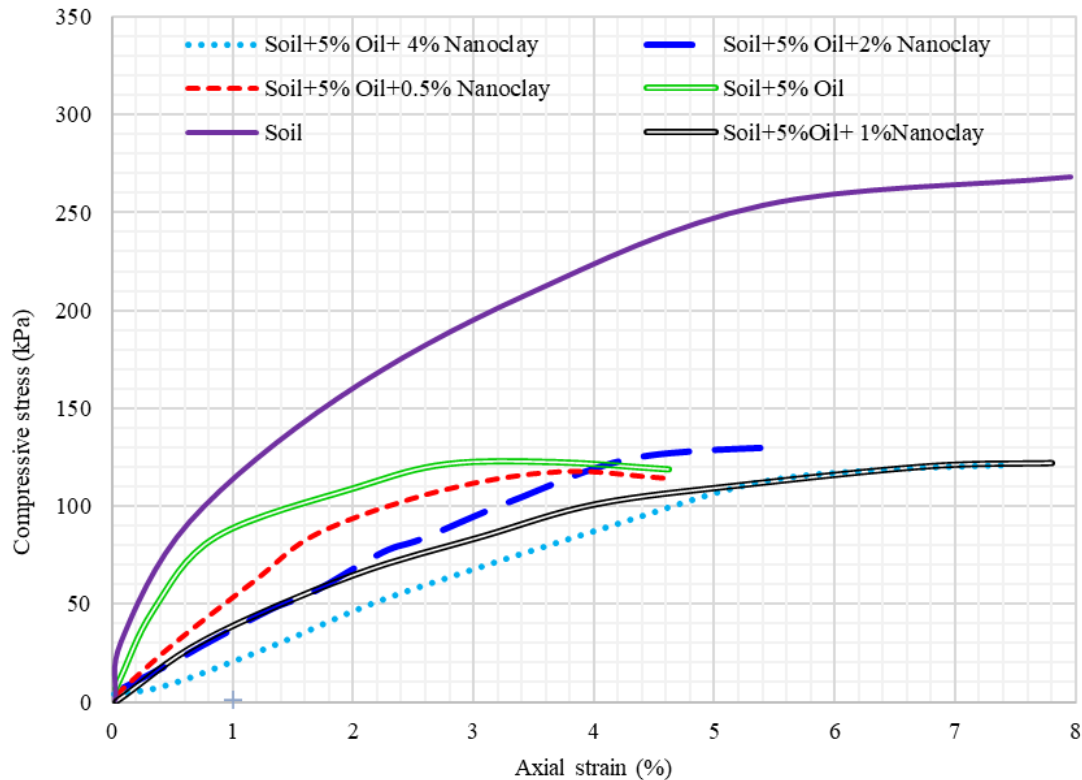


Fig. 4 Stress-strain curves of samples with 5% contamination during 10 days.

Table 6 Mechanical properties of soil with 3 and 5% contamination

Sample	Pushing resistance (Pa)	Average diameter (nm)	Liquid limit (%)	Doughy limit (%)	Density (kN/m ³)
3% oil	190000	150000	28	15	18
5% oil	188000	170000	25	12	17.5

In this research, first, the soil was contaminated with 1, 3, 5, 7, 10, and 15 percent oils to determine the critical percentage of oil. Tests were performed on grain size, Etterberg limit, standard density, and compressive strength. To create balance and carry out soil-oil reactions, contaminated soils with different amounts were stored in plastic cans at room temperature for 21 days. The initial investigation showed that the most unexpected drop in geotechnical properties was obtained in the samples contaminated with 3 and 5% oils. The properties of soil contaminated with 3 and 5% oil are presented in Table 6.

Adding pollutants to soil increases the average diameter of soil particles. In contaminated soils, due to the presence of oil, adhesion is created between soil particles, and the delicate grain part takes on a flocculated or complex structure. The reduction of the paste state can be attributed to the reduction of the dielectric constant caused by the presence of oil. The decrease in the dielectric constant due to the presence of oil causes a decrease in the thickness of the double layer and a decrease in the repulsive force between the particles. Since the attractive force between the particles is independent of the fluid properties, it ultimately causes the formation of a flocculation structure. Decreasing the dielectric constant and increasing the organic fluid-to-

water ratio reduces the flow limit (Liu *et al.* 2008, Shang and Luo 2021, Zhao *et al.* 2023).

The properties of clean soil and soil contaminated with 3 and 5% oil were used in the next stage of nanoclay in amounts of 0.5, 1, 2, and 4% of the dry weight of soil containing oil to correct the contaminated samples. Cloisite 30B was used in soil with 5% contamination in amounts of 0.4, 0.6, 0.8, and 1% by weight. By conducting standard compression tests (ASTM D896), unconfined compressive strength (ASTM D2166) during 10 and 30 days of processing and electron microscope photography, scanning electron microscopy (SEM) for virgin, contaminated, and contaminated soil samples modified with montmorillonite nano clay and Cloisite 30B, the effect of using unmodified and modified clay nanoparticles on the properties of oil-contaminated soil was investigated (He *et al.* 2021, Wu *et al.* 2022, Jiang and Xu 2023, Li *et al.* 2023).

4. Results and discussion

The degree of soil compaction on its engineering properties, including Compressibility, hardness, and compressive strength, are practical. The standard

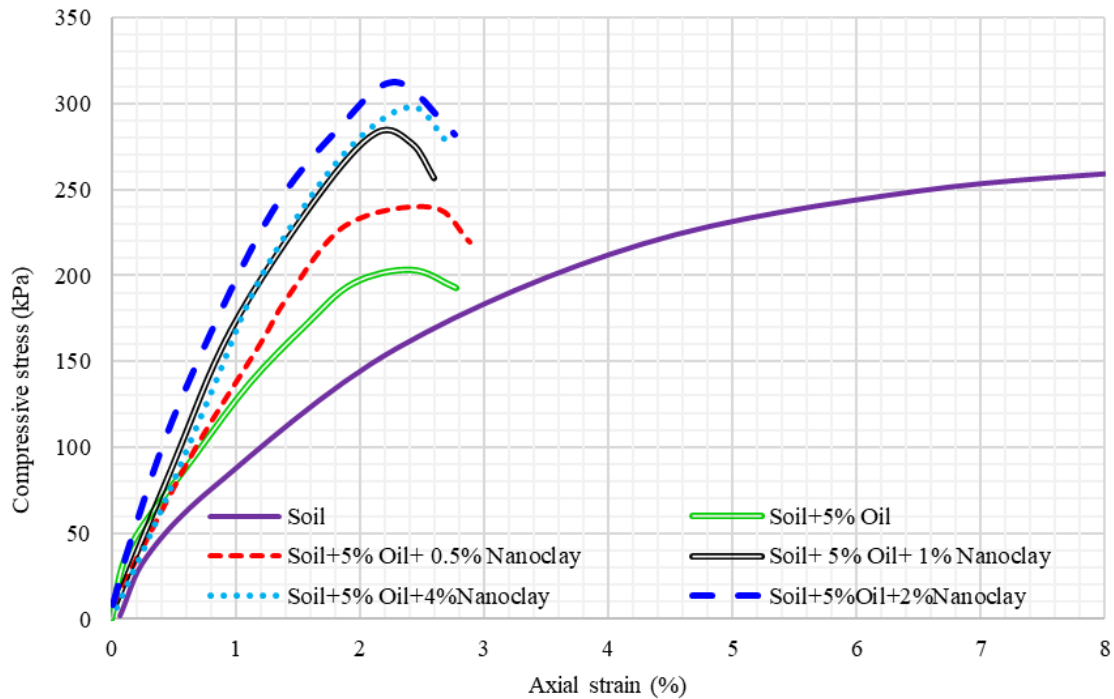


Fig. 5 Stress-strain curves of samples with 5% contamination during 30 days

Table 7 The unconfined compressive strength of soil with 3 and 5% contamination stabilized with montmorillonite nanoclay and organoclay during 10 and 30 days of processing

Sample	Amount of montmorillonite nanoclay (%)	Amount of organoclay (%)	Number of tests	10 days	30 days
Soil	0	0	3	253.5	-
Soil+ %3 Oil	0	0	3	115	186.9
Soil+ %3 Oil	0.5	0	3	117.98	207
Soil+ %3 Oil	1	0	3	141	281
Soil+ %3 Oil	2	0	3	164	296.1
Soil+ %3 Oil	4	0	3	178	277
Soil+ %5 Oil	0	0	3	112.9	184.87
Soil+ %5 Oil	0.5	0	3	116	225
Soil+ %5 Oil	1	0	3	129	264.2
Soil+ %5 Oil	2	0	3	128	289.45
Soil+ %5 Oil	4	0	3	129	271
Soil+ %5 Oil	0	0.4	3	142	195
Soil+ %5 Oil	0	0.6	3	149.8	202
Soil+ %5 Oil	0	0.8	3	210	254.89
Soil+ %5 Oil	0	1	3	200	238.1

compaction test was performed for the soil in its virgin state, with 3 and 5% contamination and contamination combined with different percentages of nano clay and organoclay based on standard ASTM. According to the results presented in Fig. 3, the maximum dry density decreased, and the optimum water content of the contaminated soil increased due to the addition of montmorillonite and Cloisite 30B nanoclays.

So that in the soil with 3% contamination containing the highest amount of montmorillonite nanoclay (4%), the dry

density and the maximum optimal amount of water decreased by 4.65% and increased by 36.71%, respectively. For soil with 3% pollution, adding 4% of montmorillonite nanoclay reduces density and increases the amount of optimal water. For soil with 5% contamination, adding 4% of montmorillonite nanoclay reduces the density and increases the optimal water content.

Soils with 3 and 5% contamination modified with montmorillonite nanoclay show that increasing the amount of contamination in the soil causes an increase in the

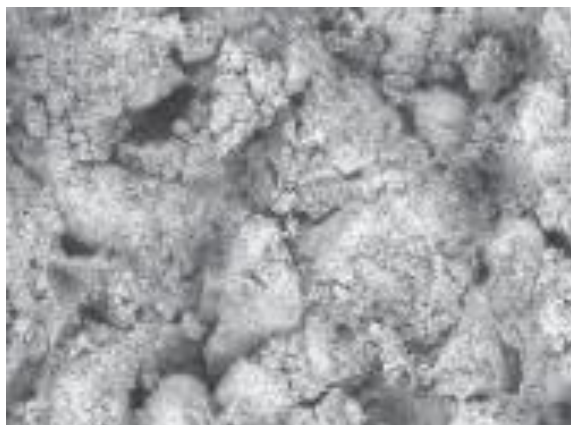


Fig. 6 SEM images of soil with 5% contamination stabilized with 0.8% organic matter during 30 days processing

optimal amount of water needed to achieve the maximum dry density. The results related to the contaminated soil amended with Cloisite 30B indicate a greater slope of changes compared to the case of using montmorillonite nanoclay. Compared to montmorillonite nanoclay, organoclay requires less water to reach maximum dry density. Due to the creation of a solid electrostatic bond of organometallics with hydrocarbon materials, unlike the samples modified with montmorillonite nanoclay, the pollutants are not easily separated from the soil texture and do not enter the pore fluid, which causes an increase in the dielectric constant and polarity in the soil and because the possibility of oil absorption by organic matter, the speed of increasing the optimal amount of water in contaminated soil containing Cloisite 30B is lower than in the case where montmorillonite nanoclay is used. The unconfined compressive strength test was performed on the samples molded in the optimal amount of water by a special hammer and Harvard scale compaction mold during 10 and 30 days of processing.

The results related to changes in unconfined compressive strength and ultimate strain of contaminated and contaminated samples modified by nanoclay are presented in Table 7.

The resistance of natural soil was found to be 253.5 kilopascals, and when it was contaminated with 3 and 5% of oil, the compressive strength for the 10-day and 30-day treatment period had a sudden drop of more than 30%. In order to use this type of soil as a base material, it is necessary to take measures to compensate for the loss of soil resistance caused by oil contamination. A suitable strategy is to use montmorillonite nanoclay and organoclay in different percentages. The highest unconfined compressive strength related to the addition of 2% of montmorillonite nanoclay. In fact, with the addition of 2% of montmorillonite nanoclay during the 30-day processing period, the soils with 3% and 5% of oil increased their resistance by 57.9% and 55.85%, respectively, compared to the contaminated soil without additives (Figs. 4 and 5).

The highest increase in compressive strength was obtained by adding 0.8% of organoclay during 30 days of

processing. The use of montmorillonite nanoclay and organoclay increases the resistance of oil-contaminated soils. The 30-day resistance of soil contaminated with hydrocarbons is higher than that of fewer days. The microscopic images prepared from the contaminated soil containing organoclay compared to the contaminated samples containing montmorillonite nanoclay indicate a better cohesion of the fine-grained part of the contaminated soil and a significant reduction in the floccule structure (Fig. 6). These observations can be attributed to its organic nature, organo-clay friendliness, and nanoporous properties. Nano montmorillonite nanoclay and modified nanoclay have caused a significant reduction in the space between the particles. Therefore, the flocculation of stabilized soils has been significantly reduced compared to contaminated and natural soil. Adding nanoclay montmorillonite and organoclay to oil-contaminated soil improves performance and restores reduced engineering properties due to changes in soil texture and structure.

5. Conclusions

The investigation conducted in this study examined the impact of montmorillonite nanoclay and organoclay additions on the mechanical properties of oil-contaminated soil through laboratory testing. The results highlight the crucial role played by these additives in restoring the lost resistance properties of oil-contaminated soil. The process of diffusion, or molecular diffusion, involves the movement of molecules, ions, or suspended particles from an environment with higher concentration to one with lower concentration. This phenomenon facilitates the distribution of pollutants while simultaneously reducing pollution concentration. Diffusion within a porous medium occurs at a slower rate compared to an aqueous medium due to the longer path that ions must traverse to pass through available pores. Pollution poses significant environmental challenges and represents a serious threat to human societies. Oil spills, accompanied by the release of oil vapors, result in inhalation of toxic substances, leading to burns, skin disorders, and even, at higher levels, cancer. Crude oil contains volatile and toxic chemical compounds, some of which can be inhaled by pregnant women, potentially causing premature birth, low birth weight, or miscarriage. Furthermore, babies exposed to ethylbenzene, a toxic substance found in crude oil, face a higher risk of congenital heart disease. Oil pollution in marine environments is primarily caused by accidental, general, or operational discharge and disposal of oil from ships, particularly oil tankers, oil transfer lines, and offshore platforms. Natural processes such as physical, chemical, and biological factors contribute to the release and discharge of oil into marine environments. The repercussions of oil release can have wide-ranging effects on the environment, economy, and society, resulting in significant changes at these levels. Marine and coastal habitats, wildlife species, restoration and recovery efforts, local industries, fishing, tourism, and water sports are critical areas and sectors susceptible to the detrimental

consequences of oil pollution. Contamination of soil by crude oil or its derivatives can inflict environmental harm, leading to the destruction of soil microbial and plant populations. Soil, a natural and dynamic entity formed through soil-forming processes and factors, consists of mineral and organic materials that cover the Earth's outer crust and support plant growth. Soil represents a valuable natural resource and plays a vital role in human life. Sustaining healthy soil is an indispensable environmental responsibility on par with addressing climate concerns.

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