scientific reports

OPEN

Effect of thermal treatment on stabilization and solidification of heavy metal contaminated clayey soil

Seyed Abolfazl Heidari[1], Mohammad Amiri[1]✉, Abbas Harifi[1] & Wei Wu[2]

Heavy metal pollution, particularly from copper, is a significant environmental challenge. This study investigates the impact of thermal treatment on the geotechnical and geo-environmental properties of copper-contaminated dispersive soil under temperatures ranging from 25 °C to 900 °C. The results demonstrate that temperature significantly alters soil properties, including pH, electrical conductivity (EC), unconfined compressive strength (UCS), thermal gravimetric, plasticity, and permeability. Among the factors influencing copper absorption and retention, cation exchange capacity (CEC), specific surface area (SSA), and carbonate content play critical roles, with carbonate content being the most influential. At 500 °C, despite a 56% reduction in CEC and a 37% decrease in SSA, the ability to absorb and retain copper increases significantly. Structural changes observed via SEM and XRD analyses reveal a transition from dispersed to flocculated, and ultimately to crystalline and porous structures, with the formation of new phases such as copper oxide (CuO) and mullite at higher temperatures. Notably, 300 °C shows the most effective pollutant retention, with a 13% increase in permeability and a fourfold increase in UCS, while 96% of the copper pollutant is absorbed. The soil remains classified in the CL range. This study highlights the potential of thermal treatment for improving the properties of copper-contaminated soil, reducing environmental risks, and enabling the stabilization and recycling of contaminated soils for use in construction materials.

Keywords Thermal treatment, Dispersive soil, Heavy metal, Microstructure, Permeability

The rapid expansion of mining and industrial activities has led to widespread contamination of soils, making it one of the foremost environmental concerns globally[1]. Heavy metals, such as copper, are particularly problematic, given their persistence and potential for leaching into the environment, posing risks to both ecosystems and human health[2]. As a transition metal, copper exists in various oxidation states (Cu (I) and Cu (II))[3], which contribute to its high mobility in soils and its detrimental effects on both terrestrial and aquatic ecosystems[4]. Excessive copper concentrations in soils can disrupt biological systems, leading to severe health issues, particularly liver damage and dysfunction of the digestive and nervous systems[5].

Among various soil remediation techniques, thermal treatment has garnered attention for its effectiveness in stabilizing and solidifying heavy metal-contaminated soils[3,6,7]. Thermal methods are often favored for their simplicity, speed, and ability to reduce the mobility of contaminants by turning them into more stable forms[8,9]. However, the effects of different thermal conditions on the behavior of dispersive soils, particularly those contaminated with copper, remain insufficiently explored. Previous studies have demonstrated that heating can significantly alter the physical, mechanical, and microstructural properties of soils, including pH, electrical conductivity, permeability, and unconfined compressive strength[10–12]. Furthermore, temperature has been shown to play a critical role in mineralogical transformations, which impact the retention and immobilization of heavy metals in contaminated soils[3,13].

In this context, dispersive clay soils are particularly relevant due to their structure and properties, such as high specific surface area and significant cation exchange capacity, which enhance their ability to act as buffers in pollutant containment[10,14]. The absorption and retention of heavy metals in these soils are governed by several factors, including cation exchange capacity, specific surface area, and the presence of carbonate content. Among these, carbonate content plays a decisive role, as it influences the solubility and adsorption capacity of heavy metals like copper[2,15,16]. Recent studies on the impact of heat on dispersive soils suggest that temperatures above

[1]Faculty of Engineering, University of Hormozgan, Bandar Abbas, Iran. [2]Institute of Geotechnical Engineering, University of Natural Resources and Life Sciences, Vienna, Austria. ✉email: amirii@hormozgan.ac.ir

300 °C lead to significant structural changes, which include the dehydration of soil moisture, as well as the formation of new minerals and the collapse of the soil's dispersed structure into a more flocculated and solid form[10,12,17]. These changes can enhance the retention capacity of the soil, particularly with regard to copper contaminants[18].

Despite the substantial body of research on the influence of thermal treatment on soil properties, much remains to be understood, especially concerning the combined effects of temperature and soil mineralogy on heavy metal stabilization. Most studies have focused on isolated factors such as chemical additives, irrigation practices, or the role of specific minerals[16,19], but there is a need for more comprehensive investigations that consider a wider range of thermal conditions. On the other hand, advancements in computational modeling, such as the development of unconstrained stress updating algorithms, offer valuable tools for simulating soil behavior under thermal stress[20,21]. By incorporating microscale details into macroscopic models, these approaches enhance our ability to predict soil response to changing thermal conditions, facilitating more accurate geotechnical analyses. Such research could provide valuable insights into the long-term environmental stability of thermally treated soils, especially in terms of their mechanical properties, pollutant retention, and potential applications in fields such as construction material development.

This study aims to address these gaps by exploring the effects of heat treatment on copper-contaminated dispersive soils across a wide range of temperatures (25 °C to 900 °C). Through the use of various analytical techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermal gravimetric, cation exchange capacity (CEC), carbonate percentage, specific surface area (SSA), this research investigates the thermal-induced changes in soil structure, pollutant absorption, and overall soil stability. Ultimately, the findings will contribute to the understanding of thermal treatment as a viable method for stabilizing contaminated soils and provide new avenues for utilizing such soils in the production of eco-friendly construction materials.

Materials and methods

Dispersive soil

In this study, natural dispersive soil was used to conduct behavioral experiments. All experiments were performed on a sample of natural dispersive soil collected from the city of Buyin-Zahra, located in the southern part of Qazvin province in the central plain of Iran, with geographical coordinates 36°10'78.01" N and 50°06'63" E (as shown in Fig. 1). For soil sampling, approximately fifty centimeters of the weathered surface soil was removed to minimize the effects of weathering. The soil was then collected from the designated location using manual excavation in an undisturbed state and transported to the laboratory in 10 kg plastic bags for further analysis, including mechanical and microstructural tests to identify and stabilize the soil properties.

The purpose of this selection was to investigate the factors of morphology, dispersive potential, carbonate content, cation exchange capacity (CEC), and specific surface area (SSA) of dispersive soil. Each of these factors was analyzed to determine geotechnical and geo-environmental characteristics in heat treatment on dispersive soil containing copper heavy metal pollutant. According to the Unified Soil Classification System (USCS), the dispersive soil under study is classified as clay with low plasticity (CL), and 95% of its weight has passed through the No. 200 sieve. The characteristics of this soil include the presence of 11.5% carbonate, the SSA of 36.28 m^2/g, CEC of 28.36 cmol/kg-soil, high dispersive potential (PD) of 84%, a liquid limit (LL) of 36, a plasticity limit (PL) of 18, and an unconfined compressive strength (UCS) of 0.43 MPa. The full specifications of the sample are presented in Table 1.

Sample preparation

In Fig. 2, the soil sampling and sample preparation methods used in this study at different thermal levels are presented. This figure provides a visual overview of the various stages of the process, including soil collection from the study area, preparation of copper-contaminated samples, curing of the samples, and conducting thermal treatment operations.

Aqueous copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) with a purity of 99.9% (CAS: 1.02735.1000, Mw: 241.60 g/mol) from Merck Chemical Company was used to prepare the metal ion pollutant. To model the effect of heat on copper-contaminated soil, the soil was initially artificially contaminated with a concentration of 25 cmol/kg-soil. For this purpose, 100 g of sieved natural divergent soil (Figs. 2A and B) was mixed with one liter of contaminant solution (at a 1:10 ratio) in 1.5-liter bottles. The resulting suspension was placed on an electric shaker for 3 h daily over a period of 3 days to homogenize and allow the soil to absorb the contaminant (Fig. 2-C). Finally, the samples were stored at room temperature for one week to allow the system to fully homogenize and ensure the necessary cation exchange. The resulting soil-contaminant suspension was poured into glass dishes for drying (Fig. 2D) and dried in an oven at 60 °C (Fig. 2E and F).

The amount of the selected pollutant was determined based on the reported pollutant range and around the cation exchange capacity (CEC) of the soil, to assess the role of CEC in the pollutant retention phases[2,15]. The amount of copper nitrate contamination was obtained using Eqs. (1) and (2), and then the calculated amount was weighed using a digital balance with an accuracy of 0.0001 g place[15].

$$M = \frac{P}{1000} \quad (\text{with a ratio of } 1:10) \tag{1}$$

$$\mathrm{Cu} = \mathrm{M} \times \mathrm{V} \times 241.6 \tag{2}$$

In this equation, P represents the desired pollutant amount in (cmol/kg-soil), V represents the volume of the pollutant solution in liters (here V is equal to 1 L), Cu is the amount of copper nitrate obtained in (g), and 6.241 is the molar mass of the consumed copper nitrate.

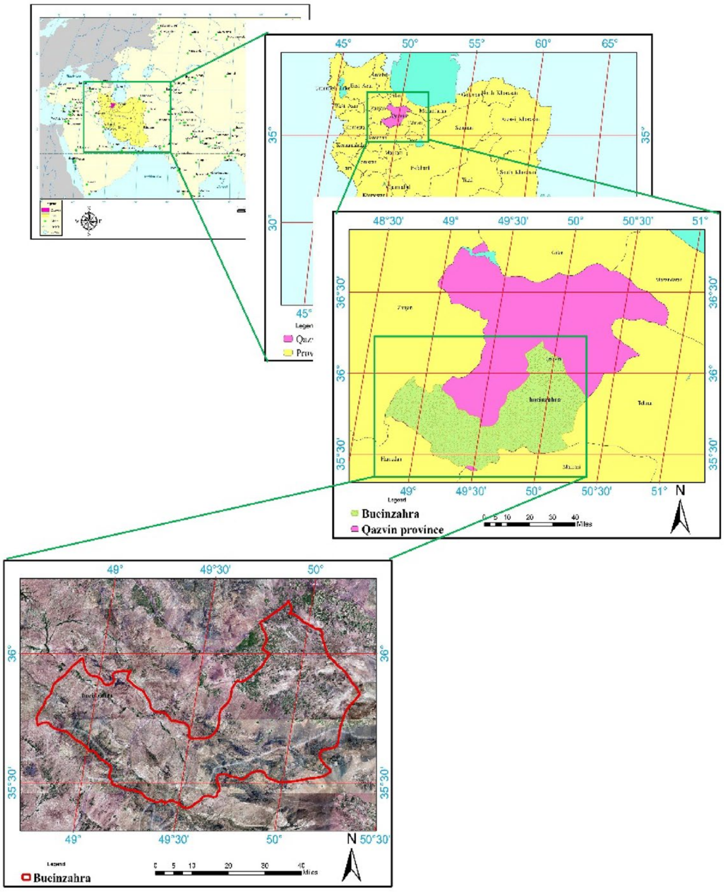

Fig. 1. Geographical location of the study area in Buin Zahra, Qazvin Province, Iran. The base map imagery was sourced from Bing Maps and processed in ArcGIS 10.4.1 (https://www.esri.com/en-us/about/about-esri/overview).

Properties	Measured values	Methods
Clay fraction < 2 µm (%)	51	ASTM D422
pH (1:10; soil: water)	10.8	ASTM D4972
EC (1:10; soil: water)	1.66	ASTM D4972
Carbonate content (%)	11.5	Hesse, 1971
CEC (cmol/kg-soil)	28.36	Hendershot and Duquette, 1986
ESP (%)	72	Sherard et al.,1977
SSA (m^2/g)	36.28	Eltantawy and Arnold, 1973
Strength Parameters		ASTM D3080
C (kPa)	25	
Friction angle φ°	15	
UCS (kPa)	410	ASTM D2166
Liquid limit (%)	36	ASTM D4318
Plastic limit (%)	18	ASTM D4318
Plasticity index (%)	18	ASTM D4318
Optimum water content (%)	18.4	ASTM D698
Maximum dry density (g/cm^3)	1.78	ASTM D698
Percent Dispersion (%)	84	ASTM D4224
Crumb (Final Grade)	4	ASTM D6572
USCS classification	CL	ASTM D422-87
Mineral composition using XRD analysis	Kaolinite, Illite, Calcite, Quartz, Dolomite, Feldspar	ASTM D2216

Table 1. Geotechnical and environmental geotechnical characteristics of the studied dispersive soil.

Fig. 2. Demonstration of soil sampling and sample preparation methods at different temperature levels.

In this study, to prepare 100 g of polluted divergent soil with an impurity amount of cmol/kg-soil 25, the required amount of copper nitrate was calculated as follows:

$$M = \frac{25}{1000} = 0.025\,mol/L$$

$$Cu = 0.025\left(\frac{mol}{L}\right) \times 1(L) \times 241.6\left(\frac{gr}{mol}\right) = 6.04(gr)$$

For the experiments, the dry copper-contaminated samples were crushed using a plastic hammer and passed through a 40-mesh sieve. The samples were then exposed evenly to temperatures ranging from 100 °C to 900 °C for 2 h. The furnace temperature was automatically increased at a rate of 5 °C per minute until the desired temperature was reached. Once the desired temperature was attained, the samples were held at that temperature for 2 h. Afterward, the furnace was turned off, and the samples were kept at a constant temperature for 2 h. After reaching the desired temperature, the samples were placed in a sealed container and allowed to cool down to room temperature[10].

Methodology

In this study, to determine the geotechnical and geo-environmental characteristics of natural dispersive soil at 25 °C, the following tests were performed: Double Hydrometer Tests (ASTM D4224), Determination of Crumb Dispersive Percentage (ASTM D6572), Standard Density (ASTM D698), Atterberg Limits (ASTM D4318), Direct Shear Test (ASTM D3080), Unconfined Compressive Strength (ASTM D2166), and Determination of pH and Electrical Conductivity (EC) (ASTM D4972). The results are presented in Table 1.

To investigate the effect of heat on the physical and chemical characteristics of the samples, cation exchange capacity (CEC) tests, determination of carbonate percentage, and specific surface area (SSA) were performed on natural dispersive soil at temperatures of 25 °C, 100 °C, 300 °C, 500 °C, 700 °C, and 900 °C. These experiments were conducted to explain and evaluate the role of each factor in the ability to absorb and retain the heavy metal pollutant copper (Cu^{2+}) in the thermal stabilization process.

Additionally, to investigate the effect of heat treatment on the stabilization process of dispersive soil containing heavy metal copper, the following tests were performed on soil containing 25 cmol/kg-soil of heavy metal copper (Cu^{2+}) pollutant at temperature levels from 25 °C to 900 °C: Atomic Absorption Spectrometry (AAS), X-ray Diffraction Analysis (XRD), Scanning Electron Microscope (SEM) Imaging, Determination of pH and Electrical Conductivity (EC), Thermal Gravimetry, Atterberg Limits, Permeability Coefficient, and Unconfined Compressive Strength (UCS). Figure 3 shows the experiments conducted on copper-contaminated soil samples under various thermal conditions. The figure includes images of the following tests: double hydrometer test (A), crumb dispersion test (B), Atterberg limits (C), unconfined compressive strength (D), permeability coefficient determination (E), pH and electrical conductivity measurements (F), cation exchange capacity (G), and atomic absorption spectroscopy (H). These tests were performed on copper-contaminated samples that were heat-treated at temperatures ranging from 25 °C to 900 °C to assess their physical and chemical properties.

The measurement of CEC of dispersive soil at thermal levels was obtained using the $BaCl_2$ substitution method[22]. The titration method was also used to measure the amount of carbonate in dispersive soil at thermal levels[23]. Soil SSA measurement was performed using BET analysis by the Belsorp mini II device with the help of nitrogen absorption. Sample preparation for this test included drying the samples at room temperature and grinding them to pass through the No. 40 sieve. Before the BET test, each sample was degassed for 15 h at 120 °C under vacuum suction and its mass was recorded[24].

The permeability test was performed by the falling head method based on ASTM D2434-19 to measure the permeability coefficient. For this purpose, the samples with optimal moisture and maximum dry density were compacted in 5×10 centimeters molds in 5 layers. Then, the samples with distilled water were subjected to the UCS test under controlled strain conditions according to ASTM D2166 with a constant loading rate (strain rate 0.1 mm/s). Cylindrical samples with a diameter of 48 mm and a height-to-diameter ratio of 2 were made in three equal layers with optimal moisture and maximum dry density. To prevent significant changes in water content, the samples were wrapped in plastic foil and kept at an ambient temperature of 24 ± 2 degrees Celsius for seven days to ensure moisture balance. The samples were saturated with distilled water as the permeable liquid, and the permeability test was performed[25].

To investigate the effect of heat treatment on the stabilization process of dispersive soil containing heavy metal copper, the soil suspension equilibrium test was used. For this purpose, a series of heavy metal retention tests were conducted using the soil suspension equilibrium method at a concentration of 25 cmol/kg-soil[26]. One gram of the soil-electrolyte suspension dried at temperatures of 25 °C to 900 °C was weighed with an accuracy of 0.001 g and poured into a 50 ml centrifuge tube. Then, 50 ml of distilled water was added. This soil-electrolyte suspension was thoroughly stirred by an electric shaker for three hours. After keeping the samples for 24 h to

Fig. 3. Demonstration of various experimental tests on contaminated soil at different thermal levels.

establish equilibrium conditions, this process was repeated again for three hours using an electric shaker. This process was repeated for seven days to ensure complete cation exchange. After this step, the liquid phase of the sample was separated from the solid phase of the soil by a centrifuge at a speed of 3000 rpm. The concentration of copper ions in the separated liquid phase was analyzed using an atomic absorption spectrometer (AAS) model GBC 932 AB Plus.

pH values of the soil-electrolyte suspension for all samples were measured according to the ASTM D49721-13 standard. The EC of the samples was also measured using a Lovi Bond device. To prepare X-ray samples (XRD), 5 to 7 drops of the suspension from all samples were poured onto a glass slide using a micropipette. After drying, the samples were tested with a Siemens-Diffractometer D8 Advance X-ray diffraction machine. To examine the structure and morphology, the samples were analyzed using a TESCAN-Vega3 scanning electron microscope after gold plating[10,27].

Discussion and investigation

The effect of heat on the durability of the microstructure characteristics of dispersive soil contaminated with copper

The effect of thermal treatment on changes in pH and EC of dispersive soil containing copper pollutant

The changes in pH and EC of the dispersive soil containing copper pollutant at thermal levels of 25 °C to 900 °C after 14 days are shown in Fig. 4. The pH of the normal soil is about 10.8, which has been reduced to 8.4 by adding 25 cmol/kg-soil of copper pollutant to the soil. By increasing the temperature to 100 °C, the pH value decreased by about 0.02 units, which is not a significant change. The activation of heavy metal pollutant maintenance mechanisms depends on the pH value of the environment[28–30]. The presence of copper heavy metal lowers the pH of the system for two reasons. First, when the metal pollution is dissolved in water, hydrated ion is produced, and the metal cation in the solution is hydrolyzed and converted into the form of metal string complexes, resulting in a decrease in pH. On the other hand, the release of H^+ ions due to the adsorption of Cu^{2+} metal ions on the clay surface leads to a decrease in pH. Equation 3 is related to hydrolysis, and the result of this reaction is the precipitation of copper hydroxide in the soil and a decrease in pH[15,28,31].

$$M^{2+} + nH_2O \leftrightarrow M\,(OH)_n{}^{2-n} + nH^+ \tag{3}$$

By applying heat to 300 °C, the pH increased by 2.7 units and reached 11.1 units. Meanwhile, the pH of the sample did not change significantly at the thermal range of 300 °C to 500 °C. In this range, copper nitrate undergoes thermal decomposition, releasing nitrogen dioxide and oxygen gases. The decomposition reaction can be shown as Eq. (4) [32].

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2 \tag{4}$$

In the thermal range of 300 °C to 500 °C, the formation of copper oxide (CuO), which is a basic oxide, leads to an increase in pH. In addition, the emission of nitrogen dioxide (NO_2) and oxygen (O_2) gases can contribute to the pH change by altering the balance of dissolved gases in the suspension[31]. Therefore, the increase in pH is due to two reasons: the burning and thermal decomposition of copper nitrate destroy the acidity and increase

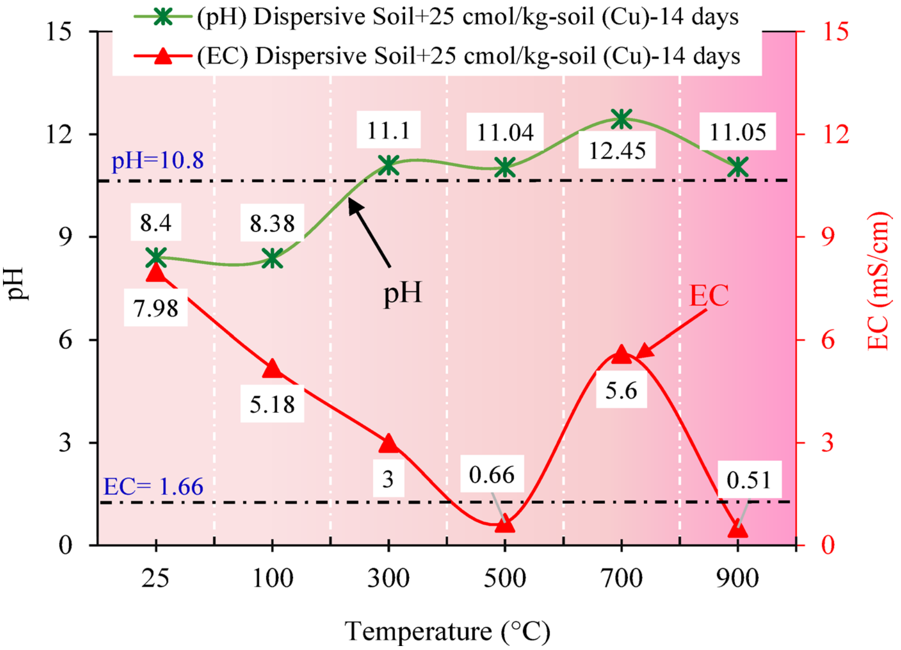

Fig. 4. The effect of heat treatment on pH changes and EC of heterogeneous soil containing copper pollutant.

the pH. The decrease in soil acidity in this range is due to the beginning of the dehydroxylation process of clay minerals in contaminated soil, including kaolinite, which leads to the release of cations and the reduction of OH^- groups[32].

According to Eq. 5 [34], with the increase in temperature and the decomposition of calcium carbonate in the dispersive soil, CaO and CO_2 are released at temperatures higher than 700 °C. Two mechanisms occur: (1) CO_2 reacts with water (H_2O) and forms a weak acid (H_2CO_3); (2) Quicklime (CaO) reacts with water and forms hydrated lime (Ca $(OH)_2$).

The first reaction increases the acidity of the soil, while the second reaction increases the pH due to lime hydration and pozzolanic reactions. According to the results of Fig. 5, at 700 °C, with the release of 4.68% carbonate content and the formation of primary cement compounds at this temperature and some pozzolanic reactions during dehydroxylation, the pH of the sample increased by 1.41 units to 12.45. By applying heat of 900 °C, calcium-containing compounds lead to the creation of crystalline structures, and the amount of calcium oxide in the soil decreases. As a result, the pH of the sample decreased by 1.4 units and reached 11.05 [10,35,36].

$$\mathrm{CaO} + \mathrm{H_2O} \rightarrow \mathrm{Ca(OH)_2} \tag{5}$$

The results of Fig. 4 show that the EC of the natural dispersive soil is about 1.66 mS/cm, which has reached a maximum of 7.98 mS/cm by adding 25 cmol/kg-soil of copper pollutant to the soil. Electric current is carried by ions (cations or anions) in solutions, and EC is determined by the contribution of all ions present in the solution. Cu^{2+} changes the ionic composition of the soil solution and increases the concentration of charged particles (ions). H^+ ions are among the most mobile cations and can lead to a decrease in pH[31]. According to the relationship between pH and EC, a decrease in pH means an increase in the concentration of H^+ ions, which causes an increase in EC[15].

By increasing the temperature up to 100 °C, the EC value decreased to 5.18 mS/cm. At this temperature, some chemical changes occur, such as the formation of solid sediments, the formation of new complexes, and the adsorption of ions on the surfaces of solid soil particles. These changes reduce the number of free ions in the solution and, consequently, decrease the EC[31]. At the temperature of 300 °C, the value of EC decreased by about 62% to 3 mS/cm. The evaporation of pore water, which is a source of H^+ and OH^- ions, leads to a decrease in EC[33]. By applying heat of 500 °C and starting the dehydroxylation process, the EC value decreased by 92% to 0.66 mS/cm. This temperature range leads to the thermal decomposition of copper nitrate, breaking the molecular structure and creating materials with low conductivity properties. Additionally, some compounds of copper nitrate are removed in the form of vapor, which reduces the concentration of ions in the solid phase and further decreases EC[34].

After the dehydroxylation process, the mobility of Na^+, K^+, and to some extent Ca^{2+} ions carrying the electrical charge increases simultaneously with the expansion of the amorphous phase. This has led to a significant increase in EC at 700 °C, reaching 5.6 mS/cm[35]. At 900 °C, due to the destruction of clay minerals, the

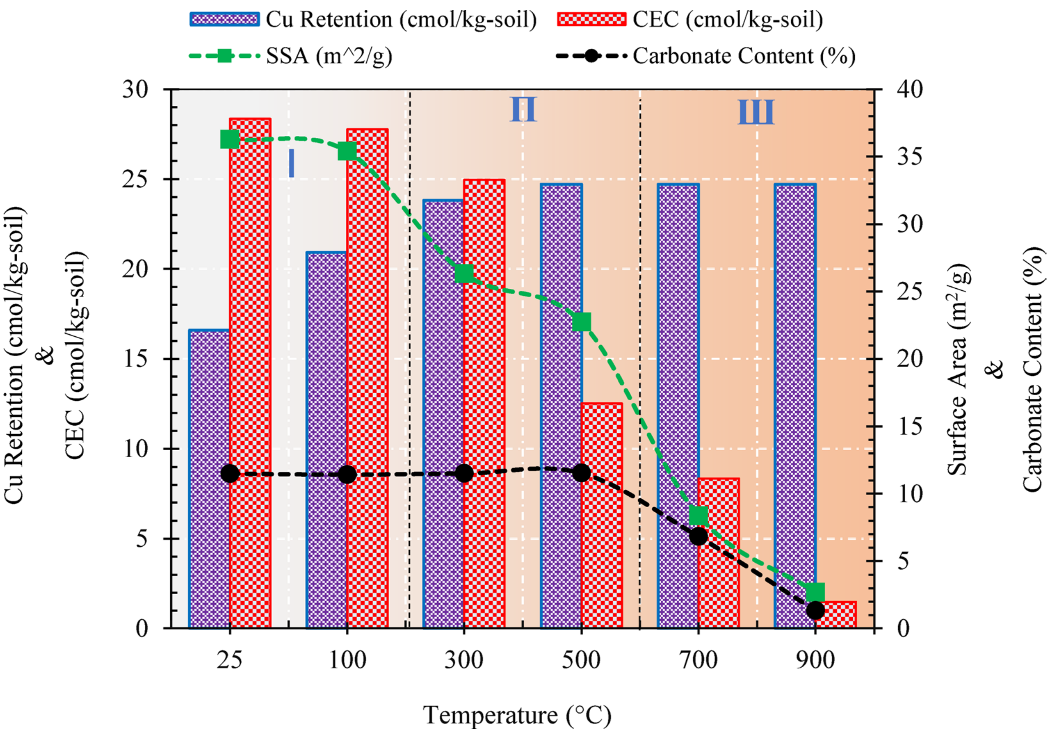

Fig. 5. The curve of the effect of heat treatment on changes in CEC, SSA, carbonate content, and Cu^{2+} absorption in dispersive soil.

formation of oxides, the formation of coarse particles, and the creation of a glassy structure, EC has decreased, reaching 0.51 mS/cm[10].

The effect of heat treatment on the absorption characteristics and storage capacity of dispersive soil containing copper pollution

Based on the results of the double hydrometric test, the natural dispersive soil under study has a dispersive percentage of approximately 84%. In the crumb dispersive test, it falls into category 4. Dispersive potential is directly related to the presence of sodium ion as the main exchangeable cation[10]. Due to the large presence of Na^+ cations, the exchangeable sodium percentage (dispersive potential) in the clay part of the studied sample is about 72% (Table 1).

The absorption and retention characteristics of dispersive soil containing heavy copper metal at thermal levels of 25 °C to 900 °C are presented in Fig. 5. Dispersive soil with a concentration of 25 cmol/kg-soil of copper pollutant has the ability to retain about 66% of the pollutant. The three factors CEC, SSA, and carbonate content play significant roles in the soil's ability to retain pollutants[36].

According to the presented results, the CEC of the dispersive soil is 28.36 cmol/kg-soil, the SSA of the sample is 36.28 m^2/g, and the carbonate content is 11.5%. The dispersed structure of the dispersive soil due to the effect of Na^+ cation has resulted in significant pollutant retention capacity. Since the type and amount of exchangeable cations in the soil are functions of cation capacity and its hydrated radius, Cu^{2+} cations, which have a higher capacity, are absorbed more strongly than cations with lower capacity. The valence difference between the two cations Cu^{2+} and Na^+ and the greater absorption of Cu^{2+} have led to a reduction in the thickness of the double layer and a decrease in the specific surface area of the soil. The release of a higher amount of H^+ ions has caused the pH to decrease[37,38].

By applying heat at 100 °C, the absorption capacity of copper pollutant has reached about 20.9 cmol/kg-soil. The first thermal reaction occurred by increasing the temperature to 100 °C, resulting in the removal of free pore water from the soil texture. This caused a 2.11% decrease in CEC to 27.76 cmol/kg-soil and a 2.42% decrease in SSA to 35.4 m^2/g. The changes in carbonate content at this temperature are not significant. In this temperature range, the anions in the double layer of dispersive soil and heavy metal copper bind together to form composite complexes as ligands. These complexes can significantly impact the biological activity and transport of heavy metals in the environment[38,39].

Applying heat at 300 °C increased the Cu^{2+} absorption capacity by 29% compared to the initial sample. At this temperature, due to the dehydration process, the amount of interlayer water decreased, resulting in a 27% reduction in SSA and a 12% reduction in CEC compared to the initial sample[37]. The carbonate content did not show significant changes at this temperature. At 500 °C, the Cu^{2+} absorption capacity at a concentration of 25 cmol/kg-soil reached 100%. The reaction between two hydroxyls in the octahedral sheet, the removal of water from the clay crystalline sheet, and the reduction of the interlayer distance due to the onset of the dehydroxylation process at this temperature caused the CEC to decrease by 56% to 12.53 cmol/kg-soil and the SSA to decrease by 37% to 22.71 m^2/g. The carbonate content changes were also not significant at this temperature[37,39]. Comparing the results presented in Fig. 4, it can be concluded that the pH change at 500 °C is not the only factor affecting the measured EC, but the severe reduction in EC by more than 92% was also influenced by the decrease in SSA and the presence of fewer active clay surfaces[18,33]. According to AAS test results, since the dispersive soil under study cannot fully retain Cu^{2+}, the pollutant precipitates as copper nitrate compounds. The presence of highly soluble copper nitrate precipitates cannot be considered a stable mechanism for retaining copper pollutants, as such precipitates can dissolve and transfer with slight changes in acidity when moisture is added to the sample. Therefore, as expected, the pollutant absorption rate in soil samples exposed to temperatures of 300 °C to 500 °C is significantly high[40,41].

The Cu^{2+} absorption capacity at a concentration of 25 cmol/kg-soil did not change significantly in the thermal range of 700 °C to 900 °C and reached a constant value. At 700 °C, the carbonate content of the soil decreased by 4.68% to about 6.82%, and at 900 °C, it decreased to 1.33%. The trend of decreasing CEC in the thermal range of 700 °C to 900 °C continued due to the gradual phase change of the soil and the reduction of charge on the clay surfaces, reaching 8.36 cmol/kg-soil and 1.48 cmol/kg-soil, respectively[42]. At 700 °C, SSA decreased by 77% to 8.36 m^2/g. At this temperature, dehydroxylation leads to the destruction of the clay mineral structure in dispersive soil, resulting in the breaking of the crystalline structure and their joining together through electrochemical bonding, leading to a reduction in SSA and CEC. At 900 °C, with the completion of the dehydroxylation process and the decomposition of calcium carbonate at temperatures of 830 °C to 870 °C, the replacement of the clay part with carbonate leads to recrystallization and the formation of new minerals with a glassy texture. This, in addition to reducing CEC, causes SSA to decrease by 92.6% to 2.69 m^2/g[43].

By examining three influencing factors, namely CEC, SSA, and carbonate amount, the changes in copper storage at different temperatures can be divided into three stages.

Between 25 °C and 100 °C, the decrease of about 2.11% CEC compared to 2.42% SSA due to the increase in temperature up to 100 °C could not prevent the increase in the ability to absorb and retain the copper heavy metal pollutant.

Between 100 °C and 500 °C, the reduction of about 56% CEC and 37% SSA in this stage still could not prevent the increase in the ability to absorb and retain copper pollutants.

Between 500 °C and 900 °C, the thermal decomposition of copper and the decomposition of carbonates into CO_2 and CaO lead to structural and chemical changes in the soil. In fact, Cu^{2+} in the dispersive soil under study is primarily concentrated in the carbonate and residual part, while the exchangeable part and specific surface have the lowest contribution[15,38]. Based on the obtained results, it can be stated that the role of carbonate is greater than the other two factors, so the retention of Cu^{2+} by different parts of dispersive soil under thermal levels is as follows:

$$\text{Exchange phase} < \text{Specific surface} < \text{Residual part} < \text{Carbonate}$$

Changes in pH are recognized as a fundamental criterion in evaluating the ability to absorb and retain pollution in soil. The presence of cations with a low ionic radius such as Cu^{2+} in the interlayer space of clay flakes intensifies the behavioral change of dispersive clay, compared to the presence of Na^+ and Ca^{2+} cations[38]. As evident from the CEC results, the increase in temperature leads to a reduction of cations in the dispersive soil. The small ionic radius of the Cu^{2+} cation in the interlayer space of the clay plates causes this cation to migrate to the pre-empty spaces of the octahedral structure during heat exposure. Consequently, the amount of charge on the clay plates is significantly reduced and the pH of the environment increases[44,45].

The important point is the growth trend of the pH of the suspension environment with increasing the temperature to 700 °C, which shows that the pH growth rate was the highest with the dissolution of 4.68% of the carbonate content. In fact, the complete thermal decomposition of Cu^{2+} after the dehydroxylation process at this temperature leads to the destruction of the clay mineral structure of dispersive soil. As a result, the crystal structure is broken, and they start to join each other by electrochemical bonding. The formation of primary cement compounds at this temperature, as well as the release of carbonate at 700 °C and some pozzolanic reactions in the presence of water, and the release of cations and the reduction of OH groups during dehydroxylation, have led to the growth of the pH of the suspension environment[31,44].

The data provided in Table 2 show the impact of thermal treatment on various characteristics of dispersive soil contaminated with copper. The changes observed in pH and EC indicate that heat treatment can modify the soil's acidity and ion concentration, which can affect its overall stability and pollutant retention capacity[38]. The significant decrease in CEC and SSA at higher temperatures suggests that thermal treatment leads to a breakdown of the soil structure, which can influence its ability to retain contaminants. Comparing the results across the different temperature ranges reveals that the most significant improvements in pollutant retention occur between 300 °C and 500 °C, where the soil reaches its maximum Cu^{2+} absorption capacity. However, the subsequent reduction in CEC and SSA at higher temperatures (700 °C and 900 °C) indicates that while the soil may initially retain pollutants effectively, the long-term stability of these pollutants could be compromised at extremely high temperatures[37].

The effect of thermal treatment on XRD changes of dispersive soil containing copper pollution

Evaluation of XRD is known as a measure in determining the microstructure of soils. In order to interpret the observed behavior from a microstructural point of view, Fig. 6a shows the XRD of natural dispersive soil and a dispersive soil sample containing a concentration of 25 cmol/kg-soil of the heavy metal copper pollutant under temperature levels of 25 °C to 900 °C.

In Fig. 6a and b, it can be seen that the characteristics of the X-ray spectrum of dispersive soil, including peak intensity and peak position, change significantly when interacting with Cu^{2+} in the thermal range of 25 °C to 900 °C. According to the XRD pattern of clay minerals with the main peaks of illite (10.04 Å), kaolinite (3.01 Å), and non-clay minerals dolomite (3.67 Å), quartz (3.34 Å), feldspar (3.21 Å), and calcite (2.28 Å) in natural dispersive soil[10,12,27]. The results show that by adding 25 cmol/kg-soil of copper pollutant to natural dispersive soil, the carbonate present in the soil reacts with the Cu^{2+} ion and forms new compounds called azurite with the chemical formula $Cu_3(CO_3)_2(OH)_2$. At a distance of 3.52 Å with an intensity of 465 CpS, it has reduced the intensity of the spectrum of all clay and non-clay minerals[46]. The X-ray diffraction peak intensity of clay samples with dispersed structure is higher than that of contaminated clay samples with tangled structure. This confirms that the increase in pore fluid salt concentration caused the formation of a complex structure in the samples, resulting in the intensity reduction of the main peak and other mineral peaks[38,47]. It is noteworthy that increasing the salt concentration of the pore fluid did not change the position of the peaks. Also, based on the results of Fig. 5, it is concluded that the changes are due to two separate mechanisms: I- the effect of interlayer cation change and Π- the effect of heat in changing the concentration of solutes between clay particles, causing changes in the soil microstructure and consequently changing the engineering properties of the soil.

Another issue is the stability of calcium carbonate and dolomite sediments after adding 25 cmol/kg-soil of copper pollutant to the dispersive soil, so that they remain stable and do not decompose at a pH of about 8.4. On the other hand, with the addition of Cu^{2+} to the soil, the intensity of the quartz peak at a distance of 3.34 Å in natural soil has decreased from 818 CpS to 710 CpS, indicating that one of the reasons for the decrease in pH is due to dissolution processes and the release of silica in the sample to the solution phase[44]. With the start of thermal treatment on the soil contaminated with copper, the intensity of the main peak of the illite mineral at a distance of 10.4 Å is equal to 124 CpS, decreasing by about 5% up to 500 °C. This reduction continues up to

Temperature (°C)	pH	EC (mS/cm)	CEC (cmol/kg)	SSA (m^2/g)	Carbonate Content (%)	Cu^{2+} Retention (%)
25	8.4	7.98	28.36	36.28	11.5	66.4
100	8.38	5.18	27.76	35.4	11.43	83.6
300	11.1	3	24.96	26.31	11.51	95.2
500	11.04	0.66	12.53	22.71	11.54	100
700	12.45	5.6	8.36	8.36	6.82	100
900	11.05	0.51	1.48	2.69	1.33	100

Table 2. Effect of thermal treatment on key soil properties and copper pollutant retention in dispersive soil.

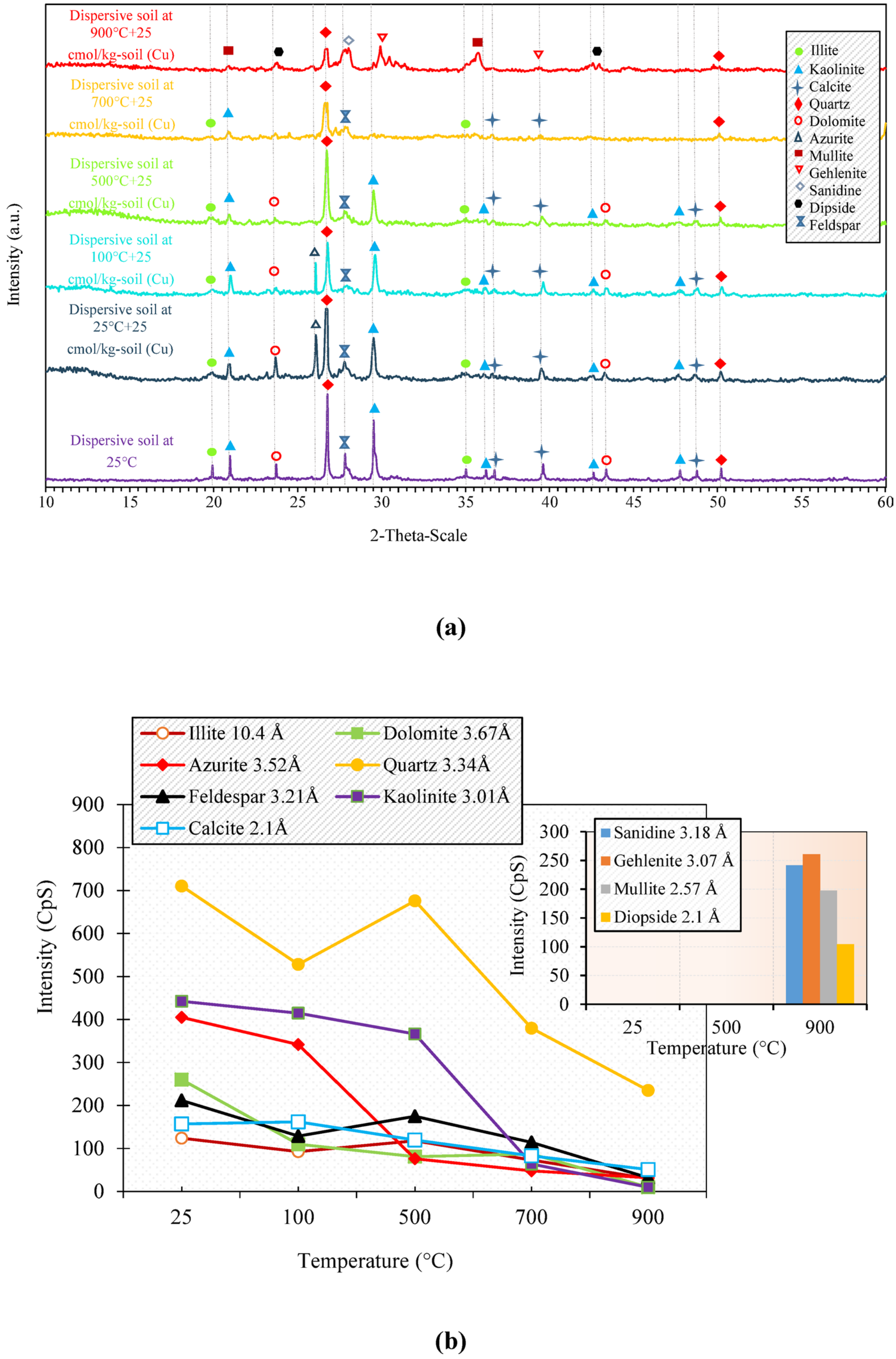

Fig. 6. (**a**) The effect of heat treatment on the X-ray diffraction pattern of natural dispersive soil and soil containing copper pollutant. (**b**) The intensity change plot of the main peaks of dispersive soil containing copper pollutant under thermal levels.

900 °C, at which point the illite peak is completely removed. Illite is dihydroxylated in the temperature range of 350 °C to 600 °C, but the remaining illite structure is destroyed and a liquid phase is formed in the temperature range of 700 °C to 850 °C[48].

The intensity of the main peak of the kaolinite mineral at a distance of 3.01 Å in soil contaminated with Cu^{2+} is equal to 442 CpS, which experiences a sharp drop by increasing the temperature up to 500 °C, and the peak corresponding to this clay mineral is completely removed at 700 °C. This trend also applies to other kaolinite mineral peaks, such as those at distances of 4.46 Å, 2.49 Å, 2.06 Å, and 1.9 Å, which are also completely eliminated at this temperature. Kaolinite is stable up to 500 °C, after which it loses its stability[49]. Dihydroxylation of kaolinite occurs in the thermal range of 300 °C to 600 °C, and after the removal of hydroxyl from the mineral structure of kaolinite, metakaolin (the amorphous form of kaolinite) is formed[48].

In contaminated soil, the distance of 3.21 Å corresponding to the feldspar mineral with intensity of 212 CpS is observed, and by applying heat up to 500 °C, the intensity of this peak has decreased by 17% to 175 CpS. Feldspar loses its stability in the temperature range of 500 °C to 800 °C and turns into sanidine at 900 °C to 950 °C. At the temperature of 900 °C, the peak related to sanidine is observed at a distance of 3.34 Å with the intensity of 242 CpS, which is formed by the phase change of the feldspar mineral[50].

The results show that the intensity of the Azurite peak at a distance of 3.52 Å from 465 CpS was created by adding Cu^{2+}, which decreased to 342 CpS by applying heat at 100 °C. This reduction can be due to the dehydration and precipitation of part of Cu^{2+} after exposure to this temperature, but no major chemical changes occur. By applying heat of 500 °C, the intensity of the Azurite peak has experienced a sharp drop and has reached 76 CpS. These results confirm that all the deposits formed from the copper pollutant were decomposed after being subjected to 500 °C heat. Azurite is transformed into malachite in the thermal range of 200 °C to 400 °C according to Eq. 6, and then malachite is converted into copper (II) oxide (CuO), carbon dioxide (CO_2), and water (H_2O) in the thermal range of 400 °C to 500 °C according to Eq. 7 [52,53].

$$\mathrm{Cu_3(CO_3)_2(OH)_2 \rightarrow 2Cu_2\,(CO_3)\,(OH)_2 + CO_2} \tag{6}$$

$$\mathrm{Cu_2\,(CO_3)\,(OH)\,2 \rightarrow 2CuO + CO_2 + H_2O} \tag{7}$$

These compounds are formed and decomposed at temperatures below 500 °C, so a weak peak of these compounds is observed at a temperature of 500 °C. The results of Fig. 5 confirm that the temperature of 500 °C can be effective in stabilizing the copper pollutant and increase the rate of pollutant absorption from the sample. In the temperature range of 700 °C to 900 °C, all the peaks related to copper impurity disappeared, indicating the vaporization of copper impurity at this temperature[51]. The main peak of calcite in contaminated soil is observed at a distance of 2.28 Å with an intensity of 157 CpS. The decrease in the intensity of the peaks related to carbonate under the application of 500 °C heat has reached 120 CpS with a decrease of 23%. The results of the pH test and Fig. 5 confirm that the carbonate in the soil is at the threshold of decomposition at a temperature of 500 °C. This issue confirms the role of the carbonate decomposition mechanism in increasing the pH level of heated samples at different temperatures. As mentioned before, the pH level of the system plays a very important role in contaminant retention. As the pH level increases, the amount of pollutant retention and absorption increases. This trend of reducing the intensity of the peaks shows that at 700 °C most of the carbonate in the soil is decomposed and at 900 °C the peaks related to carbonate are completely removed. This trend also exists for other calcite mineral peaks at distances of 2.48 Å and 1.88 Å. Calcium carbonate is completely decomposed at 700 °C to 870 °C. In fact, calcium carbonate is decomposed by heat and carbon dioxide is released according to the reaction of Eq. 5 and turns into calcium oxide or quicklime[43]. Based on this, it can be stated that one of the main reasons for the increase in pH at 700 °C is the combination of released calcium oxide and water and the formation of calcium hydroxide or slaked lime ($Ca(OH)_2$)[52].

The dolomite peak at a distance of 3.67 Å at a temperature of 500 °C has decreased from 260 CpS to 111 CpS. Dolomite ($CaMg(CO_3)_2$) is decomposed by heat in the temperature range of 350 °C to 400 °C and finally it is completely destroyed at 700 °C and according to Eq. 8 with the release of carbon dioxide (CO_2) into oxide Magnesium (MgO) and calcium oxide (CaO) are converted[53].

$$\mathrm{CaMg(CO_3)_2 + Heat \rightarrow CaO + MgO + 2CO_2} \tag{8}$$

The main peak of soil-contaminated quartz mineral is observed at the distance of 3.34 Å with the intensity of 710 CpS. By increasing the temperature to 100 °C, the intensity of the peak has decreased to 528 CpS. At 500 °C, the intensity of the peak has reached 676 CpS, which can be due to the increase in the volume of grains. Quartz mineral transforms from alpha phase to beta phase (α→β) in the temperature range of 573 °C. This phase change leads to an increase in volume equivalent to 21% in the sample. By increasing the temperature up to 900 °C, the intensity of the quartz peaks decreases but is not eliminated. Although at 573 °C, after the decomposition of kaolinite, alpha quartz turns into beta quartz (α→β), this leads to changes in some soil engineering properties[10,54].

By increasing the temperature to 900 °C, a new peak related to mullite, which is a silicate mineral, is observed at the distances of 3.84 Å and 2.57 Å. In fact, by applying heat of 850 °C, the mineral illite ($KAl_2(Si_3Al)O_{10}(OH)_2$) according to Eq. 9 has led to the formation of mullite ($Al_6Si_2O_{13}$)[50]. It is worth mentioning that the amorphous phase of kaolinite (metakaolin) after destruction and passing through the spinel phase at a temperature of about 900 °C leads to the formation of mullite[10,48].

$$\mathrm{3KAl_2\,(Si_3Al)\,O_{10}(OH)_2 + \ 2SiO_2 \rightarrow \ 3KAlSi_3O_8 + Al_6Si_2O_{13} + 3H_2O} \tag{9}$$

At the temperature of 900 °C, the peaks of gelenite compounds are observed at distances of 3.07 Å and 2.29 Å. In fact, when the temperature reaches 800 °C, calcite is decomposed into calcium oxide and semi-stable gelinite appears. As the temperature increases, the amount of gelinite decreases. Also, at the temperature of 900 °C, the peaks of 3.62 Å and 2.1 Å corresponding to the diopside mineral are observed, which are formed by the reaction of materials obtained from the decomposition of dolomite with amorphous materials and aluminosilicates in the temperature range of 800 °C to 900 °C. With the formation of glassy phases, the movement of alkaline ions has increased and the electrical conductivity has increased, which is also observed in the X-ray diffraction results[10,55].

The effect of thermal treatment on the morphology (SEM) of dispersive soil containing copper pollution

The SEM images in Fig. 7 illustrate changes in the microstructure of dispersive soil due to interaction with heavy metal copper pollutant at temperatures from 25 °C to 900 °C. Figure 7a shows the image of natural soil without the heavy metal copper pollutant. This image shows the dispersed structure of the natural soil texture, which is observed as completely dispersed and almost crystalline. Based on the presented image, the thickness of the clay

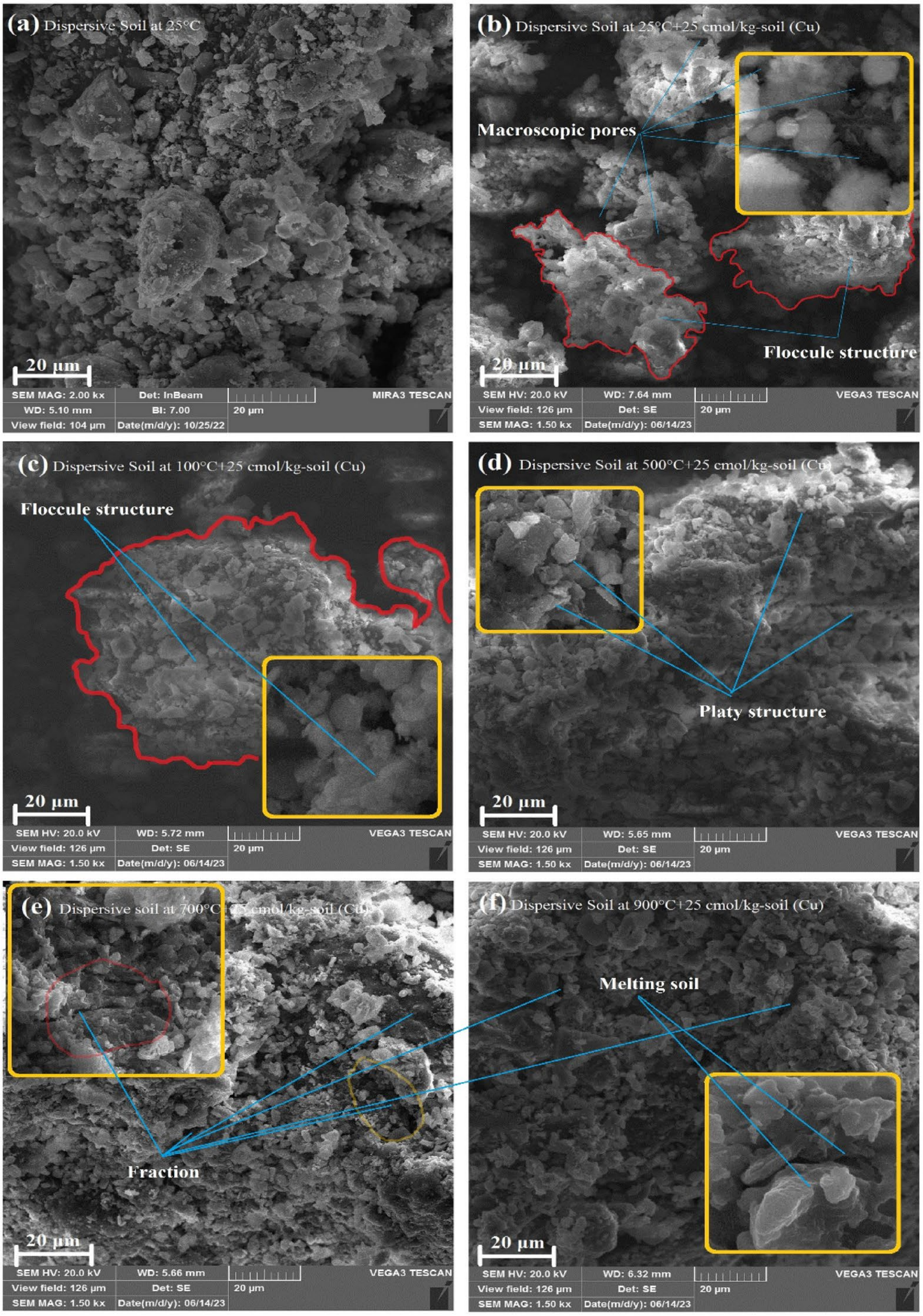

Fig. 7. Scanning Electron Microscope (SEM) images of dispersive soil containing copper pollutant under different thermal levels.

compound plates is in nano dimensions. In other words, one of the main reasons for the dispersiveness of the studied natural soil sample is the size of the particles, which are mostly in the nano scale[10].

Adding 25 cmol/kg-soil of copper pollutant changes the initially dispersed structure of the soil to a flocculated one. Figure 7b shows changes in the internal structure of the soil and an increase in macroscopic pores due to the aggregation of clay flakes, as compared to Fig. 7a. This is due to the stronger effect of the divalent cation Cu^{2+} on the soil behavior mechanisms compared to the monovalent cation Na^{+} in the soil environment. Based on the XRD results, the cause of the microstructural changes observed in Fig. 7b is the occurrence of mechanism I[38]. According to Chapman's sphere theory, reducing the thickness of the double layer and the repulsive force leads to the flocculation of soil clay particles. Additionally, considering the capacity of low pH to facilitate the formation of complex structures and clay clusters, a part of the severe microstructural changes in the soil in the presence of copper pollutant can be attributed to low soil pH[31,56].

Figure 7c shows the structure of Cu^{2+} contaminated soil at 100 °C in a completely flocculated state, with no significant morphological and physical changes compared to those in Fig. 7b. According to the results obtained from XRD analysis, new Azurite compounds, formed as a result of the combination of Cu^{2+} with $CaCO_3$, as well as the calcium carbonate phase, are visible as white masses at approximately 11.5% [53].

As shown in Fig. 7d, heating up to 500 °C causes the soil particles to lose their initial cohesion, and the sheet structure associated with the kaolinite mineral is rarely observed. This is due to the initiation of the dehydroxylation process and the destruction of this mineral's structure, which was also observed in the X-ray diffraction pattern. Additionally, at this temperature, the new Azurite compounds are not distinctly observed, and heating has led to the decomposition of this mineral. The calcite mineral is still observed at 500 °C[37,44].

Figure 7e shows an image of the sample heated to 700 °C. The gray grains represent the quartz mineral or silicate phase. Considering the XRD results, one of the reasons for the creation of cracks is the phase and volume change of quartz at 573 °C. With quartz exposed to 700 °C and the phase transformation of quartz from alpha to beta ($\alpha \rightarrow \beta$), volume changes occur in the quartz, leading to the creation of cracks in this thermal range. Additionally, kaolinite in this thermal range is completely destroyed, and crystalline and flaky particles are not observed in the images[10,43,54].

Figure 7f shows a significant change in the soil texture upon heating to 900 °C. The melting of the soil, the decomposition of calcium carbonate, and the release of CO_2 from the soil structure result in the formation of porosity and free spaces between soil particles and a crystalline texture (indicating phase changes in minerals and the initial melting of materials). The crystalline and porous mineral gehlenite, formed from the reaction of alumina and silica phases and the decomposition products of calcite, is also observed. Additionally, the mineral mullite is also somewhat visible. Although the glassy structure of gehlenite weakens the soil's strength, the more prominent role of mullite may explain the increased soil strength at 900 °C due to the presence of mullite[50,55].

The effect of thermal treatment on weight changes of dispersive soil containing copper pollutant

Since changes in the absorption and retention rates of pollutants impact the physical properties of dispersive soil, including its weight, to further ensure the accuracy of the aforementioned results, Fig. 8 presents the weight change curve of a sample containing 25 cmol/kg-soil of heavy metal copper pollutant under thermal levels ranging from 25 °C to 900 °C. The application of heat results in an increased weight loss in copper-contaminated soil, which can be divided into three stages. This is consistent with the trends observed in changes in carbonate percentage, SSA, and the XRD spectrum of the soil.

Stage 1: Between 25 °C and 100 °C, the thermal gravimetric curve shows that with increasing temperature, the weight of the sample gradually decreases. Evaporation of free pore water and dehydration of the copper pollutant within the sample pores primarily occur between 25 °C and 100 °C. Therefore, this results in a gradual decrease in the weight of the copper-contaminated soil. At this stage, no chemical decomposition occurs, and it only results in a 1.9% reduction in the weight of the copper-contaminated soil[44,39].

Stage 2: Between 100 °C and 500 °C, the thermal gravimetric curve shows that when the temperature exceeds 100 °C, the sample's rate of weight loss increases. At 300 °C, due to the dehydration process and partial removal of organic materials, it experiences a weight loss of 6.4%. The weight loss rate in stage 2 reaches 13.4%, which is an increase of about 11.5% compared to stage 1 [35]. At 500 °C, the sudden weight loss serves as a suitable indicator for detecting the dehydroxylation temperature and indicates the beginning of the dehydroxylation process and the destruction of the clay mineral structure of the dispersive soil contaminated with copper. Also, as shown in relations (6), (7), and XRD results, all the deposits formed from copper impurity start to decompose at temperatures below 500 °C, converting into copper (II) oxide (CuO), carbon dioxide (CO_2), and water (H_2O)[57,58].

Stage 3: Between 500 °C and 900 °C, the thermal gravimetric curve shows that by applying heat up to 700 °C, the weight loss rate rapidly increases, reaching a peak weight loss rate of 24%. As shown in Eqs. 10 and 11, the dehydroxylation reactions of kaolinite between 455 °C and 700 °C lead to the crystallization of mullite and cristobalite, and the H_2O produced from the decomposition is released as gas through endothermic and exothermic reactions[59]. According to Eq. 12, when the temperature exceeds 700 °C, kaolinite, feldspar, and calcite undergo endothermic chemical decomposition in sequence. By 900 °C, the weight loss at this stage reaches 23.4%. This occurs due to the decomposition of calcium carbonate at around 830 °C to 870 °C and the formation of a new glassy structure[43,57,59].

$$\mathrm{Al_2O_3SiO_22H_2O} \xrightarrow{455^\circ\mathrm{C}\text{-}520^\circ\mathrm{C}} \mathrm{Al_2O_32SiO_20.5H_2O} \ + \ 1.5\mathrm{H_2O}\uparrow \tag{10}$$

$$\mathrm{Al_2O_3SiO_20.5H_2O} \xrightarrow{>540^\circ\mathrm{C}} \mathrm{Al_2O_32SiO_20.5H_2O}\uparrow \tag{11}$$

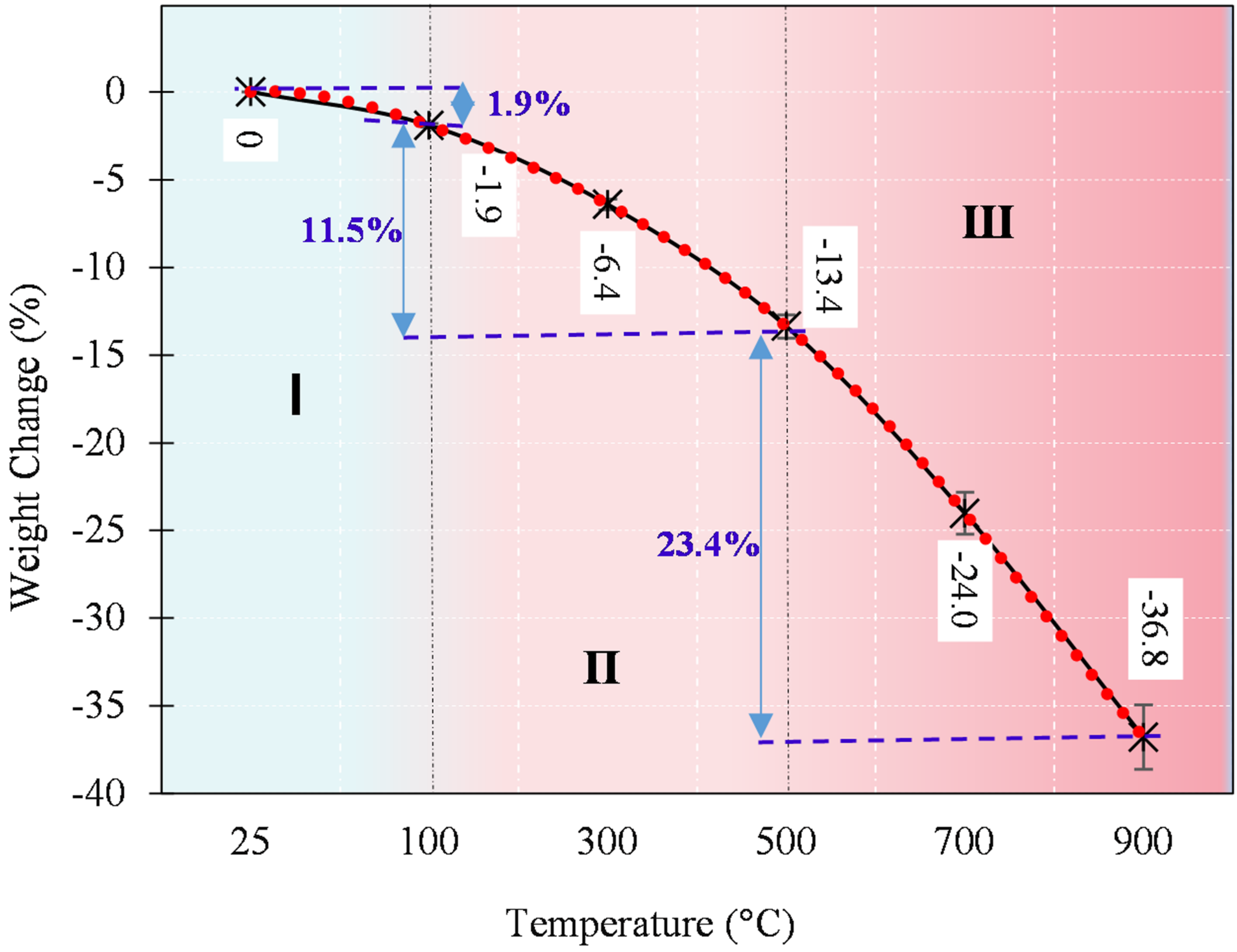

Fig. 8. Weight change curve of copper-contaminated soil against heat.

Stage	Temperature range (°C)	Weight loss (%)	Key processes
Stage 1	25 °C to 100 °C	1.9%	Evaporation of free pore water and dehydration of copper pollutant
Stage 2	100 °C to 500 °C	13.4%	Dehydration, removal of organic materials, and initiation of dehydroxylation
Stage 3	500 °C to 900 °C	23.4%	Crystallization of mullite and cristobalite, decomposition of calcium carbonate

Table 3. Weight loss and thermal stages of copper-contaminated dispersive soil.

$$\mathrm{CaCO_3} \xrightarrow{700^\circ \mathrm{C}\text{-}830^\circ \mathrm{C}} \mathrm{CaCO_3} + \mathrm{CO_2}\uparrow \quad (12)$$

The data presented in Table 3 summarize the weight loss of copper-contaminated dispersive soil at various thermal stages, providing insight into the physical transformations that occur as a result of heat treatment. The weight loss occurs in three distinct stages. In Stage 1 (25 °C to 100 °C), the weight decreases by 1.9%, primarily due to the evaporation of free pore water and dehydration of the copper pollutant within the sample pores. There are no significant chemical changes at this stage, and the weight reduction is gradual[39].

In Stage 2 (100 °C to 500 °C), the weight loss increases to 13.4%. This stage is marked by dehydration, the removal of organic materials, and the initiation of the dehydroxylation process in the clay minerals. At temperatures above 300 °C, copper pollutants start to decompose into copper oxide (CuO), and this contributes to the observed weight loss[57,58]. Finally, in Stage 3 (500 °C to 900 °C), the weight loss reaches 23.4%, with significant changes occurring due to the crystallization of minerals such as mullite and cristobalite and the decomposition of calcium carbonate[59]. These processes result in the formation of a new glassy structure, contributing to the final weight reduction[43].

The effect of heat on the durability of macrostructural properties of dispersive soil contaminated with copper

The effect of heavy metal copper pollutant on the grain size distribution of dispersive soil

Changes in the size distribution of clay particles (< 2 μm) of dispersive soil and the sample containing heavy copper metal pollutant are shown in Fig. 9. It can be seen that the addition of 25 cmol/kg-soil copper pollutant to the dispersive soil has increased the size of the particles. In naturally dispersive soil, the percentage of particles smaller than 0.01 mm passing through was about 54% initially, but it decreased to about 26% after adding Cu^{2+} to the soil.

Therefore, based on the results obtained in XRD analysis and SEM images, it is evident that the size of soil particles has increased and the structure has changed from dispersed to flocculated. This issue is due to the decrease in the repulsive forces between clay plates in dispersive soil in the presence of divalent cation Cu^{2+} compared to the presence of monovalent cation Na^+ and as a result of the decrease in the thickness of the hydrated layer around the clay flakes and the shrinkage of the soil structure[15,38,47].

The impact of the type of exchangeable cation on the formation and growth of dispersive soil particle size is consistent with the results of other microstructural tests, particularly the XRD analysis results, confirming the internal structural changes of dispersive soil contaminated with Cu^{2+}. By adding 25 cmol/kg-soil copper pollutant to the dispersive soil, due to the higher valence and smaller hydrated radius of the polyvalent Cu^{2+} cation, this cation replaces the monovalent Na^+ cation in the interlayer space of the particles (mechanism I). The trend of changes in the intensity of the spectra has completely changed, and the intensity of the XRD spectrum peaks has decreased. After the completion of mechanism I, with the application of heat and the occurrence of mechanism Π, the peak intensity starts to decrease again.

To validate the hypothesis regarding soil dispersion changes, Fig. 10 shows the results of the Crumb test over a 6-hour period and the comparison of changes in the percentage of soil dispersion in the presence of 25 cmol/kg-soil copper pollutants. In the Crumb test, the dispersive category of natural soil is 4, indicating a fully dispersive soil, but with the addition of copper pollutant, the soil's dispersive category changes to 1 (non-dispersive). This is due to the reduced hydration tendency of the Cu^{2+} interlayer cation and decreased dispersibility of the structure compared to the presence of sodium as the interlayer cation, which is consistent with other obtained results[38].

The effect of heat treatment on the changes of Atterberg limits of dispersive soil containing copper pollution

Figure 11a shows the changes in the liquid limit and plasticity index of dispersive soil with a concentration of 25 cmol/kg-soil copper heavy metal pollutant. The liquid and plastic limits of natural dispersive soil are 36.1 and 18 units, respectively. After the interaction of the soil with solutions containing 25 cmol/kg-soil copper heavy metal, based on the results presented in Fig. 4, the pH of the soil decreases significantly. The decrease in pH causes a reduction in the repulsive force between the clay plates of the dispersive soil, bringing them closer together, so that the liquid limit decreased to 31.16 units, and the plastic limit decreased to 14.16 units[37,44].

Due to the increased concentration of solutes in the fluid surrounding the soil, with the increase in cation valence from monovalent (Na^+) to divalent (Cu^{2+}), the clay surfaces are compressed together, reducing the ability to absorb water between the layers. As a result, the engineering properties of dispersive soil, including its Atterberg limits, change[44,38]. Upon applying heat, the Atterberg limits of copper-contaminated soil decrease, which can be categorized into three stages. This is in good agreement with the trend in weight changes, SSA, and XRD spectrum of the soil.

Stage 1: By applying heat up to 100 °C, the liquid limit decreased by 6.16 units, reaching 28 units, and the plastic limit decreased by 0.91 units, reaching 13.58 units at this temperature. During heating from ambient

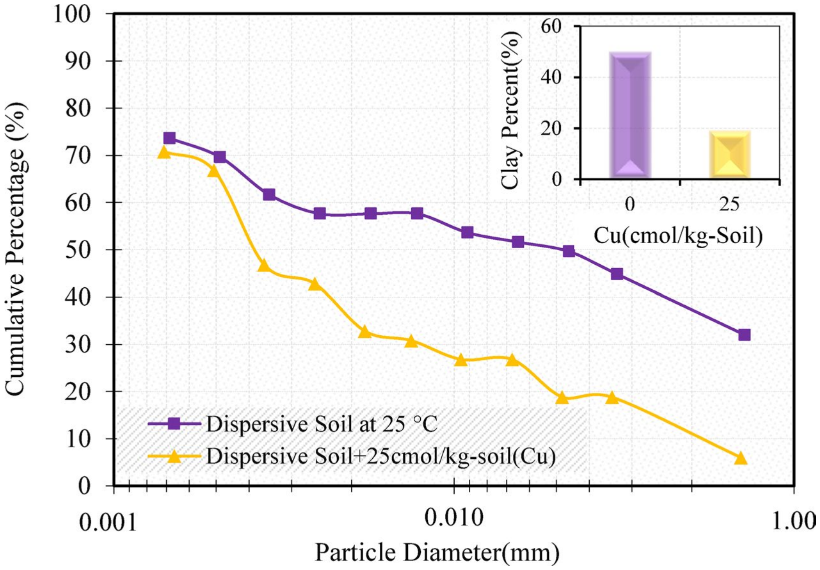

Fig. 9. Hydrometric curve of dispersive soil contaminated with copper heavy metal.

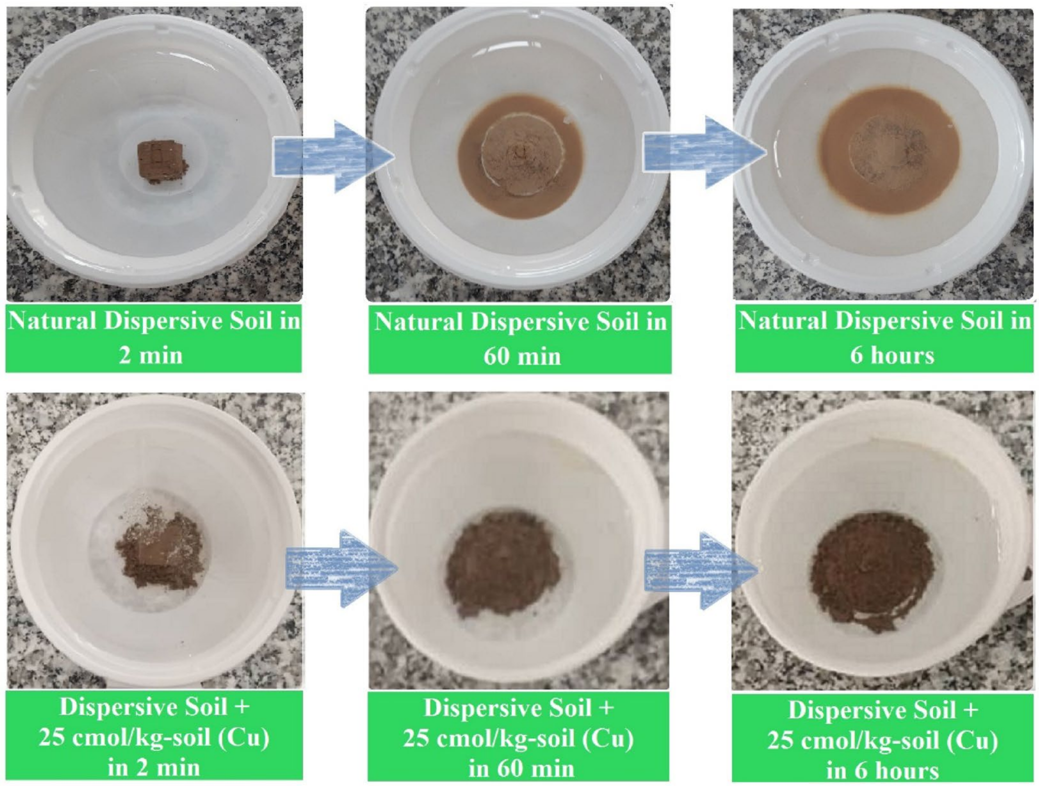

Fig. 10. Crumb test results in a period of 6 h and changes in dispersive of natural clay in interaction with copper pollutant.

temperature to 100 °C, free pore water is removed from the soil texture. These changes at this stage can be directly related to the SSA of the dispersive soil. Clays with a high SSA, and consequently more interparticle contact, are highly sensitive to temperature changes[17].

Stage 2: By applying heat up to 300 °C, due to the dehydration process, the water between the silicate layers of the clay is removed from the electrostatic field of the flakes, and the liquid limit is reduced to 24.9 units and the plastic limit is reduced to 12.8 units[10]. When the temperature is increased to 500 °C, the clay particles form larger particles through electrochemical bonding, which causes an irreversible structural change. Additionally, the initiation of the dehydroxylation process in this thermal range leads to the removal of interlayer water and consolidates the soil structure. As a result, the liquid limit reaches 19.1 units and the plastic limit reaches 11.3 units[44].

Stage 3: Based on the results from Fig. 5 and the XRD analysis, when heat is applied from 700 °C to 900 °C, the crystal structure of the samples breaks and the SSA of the samples significantly decreases. As a result, the soil no longer exhibits plastic behavior[10].

In Fig. 11b, based on the Atterberg limits results, the dispersive soil is classified as clay with low plasticity (CL). By adding 25 cmol/kg-soil of copper pollutant to the dispersive soil, this classification did not change and remained in the CL range. It can be concluded that soil contamination with this concentration cannot disrupt the classification and place the soil in another category. The behavior of the soil did not change in the thermal range of 100 °C to 400 °C, and the soil classification remained in the clay with low plasticity (CL) range.

This classification changes from CL to CL-ML (clay with low plasticity to silt with low plasticity) by applying heat of 500 °C. Based on the results of XRD analysis and the thermal gravimetric curve, this change is due to the removal of water in the clay crystal plate and the reduction of the interlayer distance of clay flakes due to the start of the dehydroxylation process at this temperature. This issue has resulted in less water absorption and reduced the plasticity properties of the soil. By increasing the temperature to 700 °C, the soil loses its plasticity and becomes non-plastic. The occurrence of dehydroxylation has caused the destruction of the clay mineral structure of the dispersed soil and has affected the Atterberg limits of the soil. The decrease in the Atterberg limits is due to structural changes under the influence of applied heat and changes in soil behavior[10,12].

Table 4 demonstrates the significant changes in the Atterberg limits of copper-contaminated dispersive soil as the temperature increases. The results show that with rising temperatures, both the liquid limit and plastic limit decrease, indicating a reduction in the soil's plasticity and its ability to absorb water. For temperatures ranging from 25 °C to 100 °C, there is a modest reduction, primarily due to the removal of free pore water[17]. This trend continues as temperatures increase from 100 °C to 300 °C, where further decreases are linked to dehydration and the formation of electrochemical bonds[10]. At higher temperatures, from 300 °C to 500 °C, the loss of plasticity becomes more pronounced, a result of the dehydroxylation of clay minerals, which consolidates

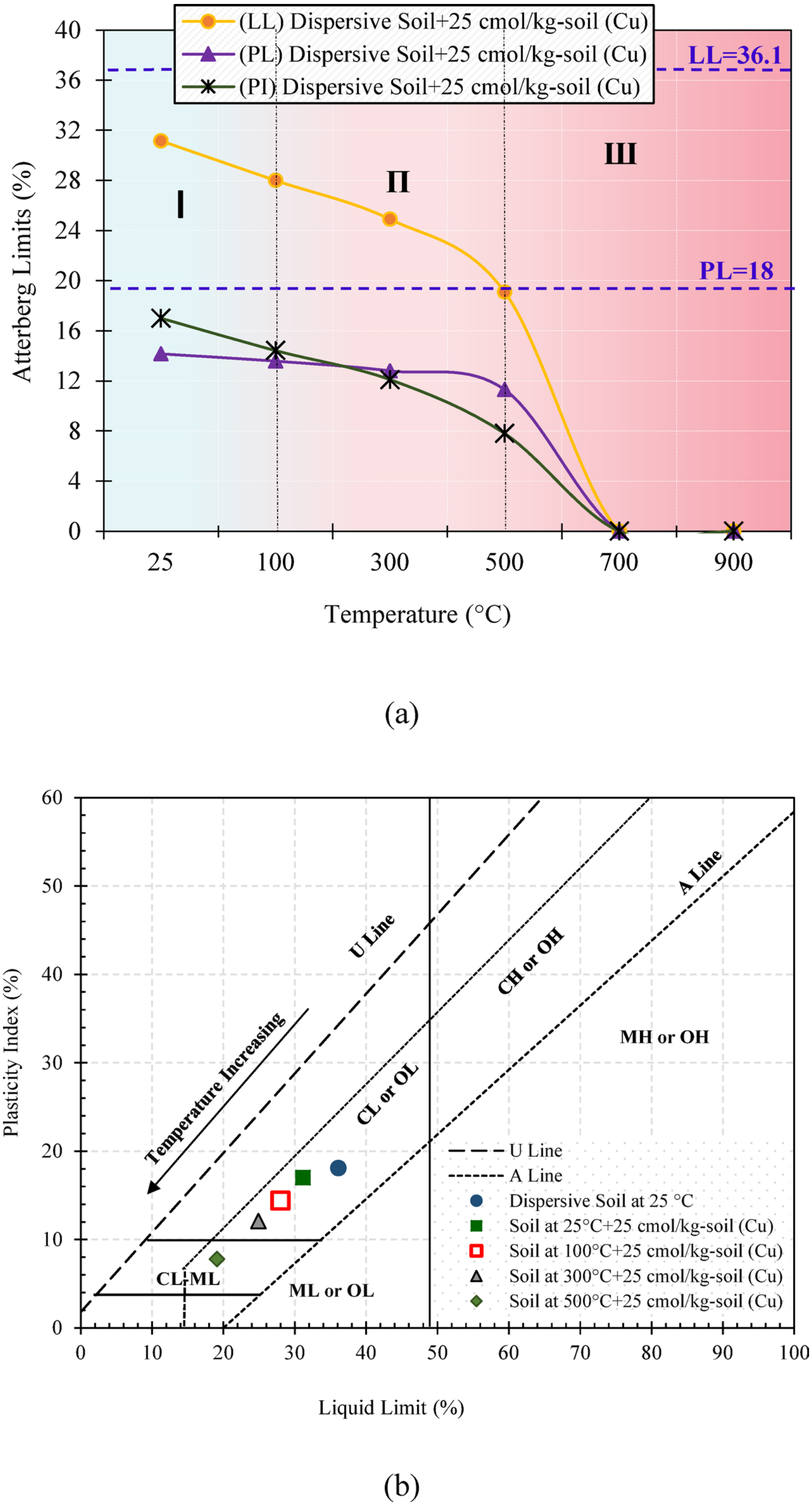

Fig. 11. (**a**) Shows the Atterberg limits curve of dispersive soil contaminated with heavy metal copper under thermal levels. (**b**) Plasticity curve of natural dispersive soil and copper-contaminated samples under thermal levels.

the soil structure. By 500 °C to 700 °C, the soil transitions to non-plastic, as observed in the XRD and SEM analyses, signaling the complete breakdown of the clay mineral structure. Finally, at 700 °C to 900 °C, the soil maintains its non-plastic state, as the clay minerals are fully destroyed, significantly altering the soil's engineering properties[44].

Temperature range (°C)	LL	PL	Behavioral change
25 °C to 100 °C	28.00	13.58	Removal of free pore water, minor changes in structure
100 °C to 300 °C	24.90	12.80	Dehydration and electrochemical bonding, irreversible changes
300 °C to 500 °C	19.10	11.30	Dehydroxylation of clay minerals, further consolidation
500 °C to 700 °C	Non-plastic	Non-plastic	Complete dehydroxylation and structural breakdown
700 °C to 900 °C	Non-plastic	Non-plastic	Complete destruction of clay minerals, loss of plasticity

Table 4. Atterberg limits of copper-contaminated dispersive soil at different temperatures.

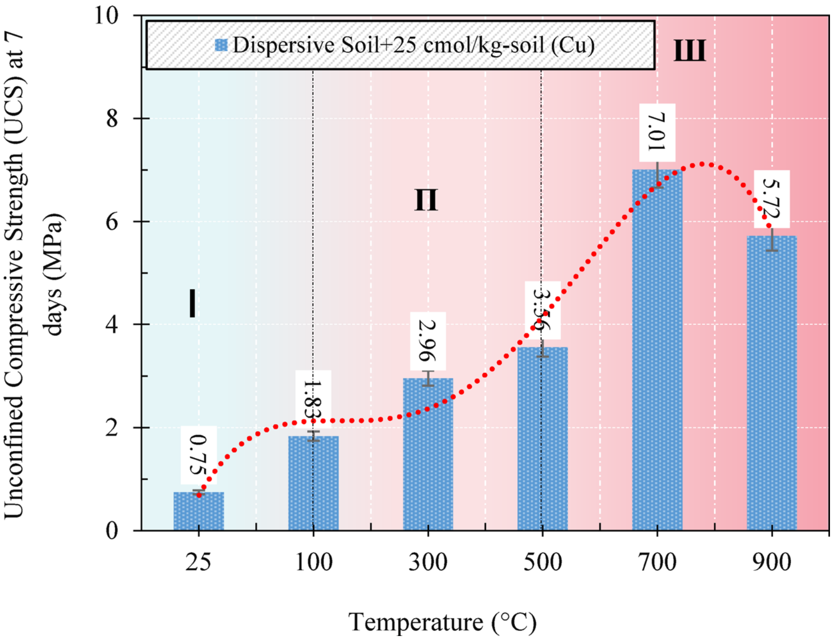

Fig. 12. Shows the effect of thermal levels on the UCS of dispersive soil contaminated with heavy metal copper.

The effect of thermal treatment on the UCS of dispersive soil containing copper pollutants

The unconfined compressive strength (UCS) characteristics of dispersive soil containing 25 cmol/kg-soil of heavy metal copper after various thermal treatments from 25 °C to 900 °C are shown in Fig. 12. The UCS of natural dispersive soil is 0.43 MPa based on Table 1. With the addition of 25 cmol/kg-soil of heavy metal copper, this strength has increased to 0.75 MPa. The reason for this increase in strength is the reduction of repulsive forces between clay plates due to the presence of divalent copper cation (Cu^{2+}) and the reduction of the thickness of the hydrated layer around the clay flakes, resulting in the transformation of the dispersed structure into a flocculated one[15].

By applying heat of 100 °C, the unconfined compressive strength of the soil increased approximately 2.5 times to 1.83 MPa. The reason for this increase in strength could be the loss of moisture from the sample, which leads to the removal of free water from the soil structure. This phenomenon confirms the significant difference in compressive strength of soil in wet and dry conditions[12].

By increasing the temperature to 300 °C, the unconfined compressive strength of the soil increased 4 times compared to the dispersive soil containing copper pollutants, reaching approximately 2.96 MPa. At this stage, dehydration occurs, leading to the removal of adsorbed water and double layer water from the soil structure. This phenomenon reduces the electric repulsion and the distance between clay flakes, resulting in an increase in soil strength. Additionally, according to SEM and XRD results, the decomposition of copper nitrate and the formation of copper oxide (CuO) at 300 °C also contribute to the increase in compressive strength[12,37].

The trend of increasing compressive strength at 500 °C, considering the occurrence of dehydroxylation and the complete decomposition of copper nitrate to copper oxide, leads to approximately a 1.2-fold increase in compressive strength compared to 300 °C and about a 4.8-fold increase compared to the compressive strength of dispersive soil containing copper pollutants, reaching 3.56 MPa at this temperature. At this temperature, new bonds between soil particles are strengthened, and the compressive strength increases[37].

Upon reaching 700 °C, a significant increase in the compressive strength of the soil is observed. The compressive strength has increased by 9.4 times compared to the dispersive soil containing copper pollutant, reaching 7.01 MPa. In the thermal range of 500 °C to 700 °C, clay minerals undergo dehydroxylation, leading to changes in soil structure and the formation of new cementitious compounds. The dispersed structure of the particles and clay flakes transforms into adhered and homogeneous particles, which results in an increase in compressive strength.

With the increase in temperature to 900 °C, due to the decomposition of calcium carbonate and its transformation into calcium oxide, the compressive strength decreases by approximately 18.5% compared to 700 °C, reaching 5.72 MPa. The decrease in compressive strength at this temperature is due to the formation of a porous and glassy structure and the formation of compounds such as gehlenite, diopside, and anorthite[12]. These results indicate that microstructural changes and thermal effects on the compressive strength of dispersive soil in the presence of copper have significant impacts, leading to a considerable improvement in its mechanical properties.

The effect of thermal treatment on the permeability coefficient of dispersive soil containing copper pollutant

Based on the results of microstructural tests including XRD analyses and SEM images, due to the formation of a complex structure and structural changes in the dispersive soil after interaction with heavy metal copper at thermal levels of 25 °C to 900 °C, the importance of hydraulic conductivity of the soil as a determining factor in the optimal performance of clay buffer materials and possible changes in permeability coefficient at thermal levels of 25 °C to 900 °C have been studied. The changes in this coefficient and its results are presented in Fig. 13.

The permeability coefficient of natural dispersive soil is 0.039×10^{-8} m/s based on the results in Table 1. In fact, based on XRD analyses and SEM images, the presence of multivalent cations Cu^{2+} in the interlayer space causes the reduction of the opening of clay flakes (occurrence of mechanism I). Considering the formation of a complex structure in the dispersive soil containing 25 cmol/kg – soil heavy metal copper after interaction with the Cu^{2+} cation, the permeability coefficient has increased by about 90% to approximately 0.074×10^{-8} m/s[38]. With the initiation of heat treatment at 100 °C, the permeability coefficient of dispersive soil containing heavy metal copper has not changed significantly and has reached approximately 0.075×10^{-8} m/s. In the thermal range of 300 °C, the permeability coefficient of dispersive soil containing heavy metal copper increases due to the approach of clay particles to each other as a result of the decomposition of copper nitrate and the formation of copper oxide (occurrence of mechanism Π). Under such conditions, with saturation and the beginning of water flow in the soil due to the presence of macroscopic pores in the soil structure, the movement of water in the void space between clay particles becomes possible. As a result, the soil permeability has increased by approximately 10% to about 0.084×10^{-8} m/s[60,34].

By applying heat at 700 °C, the agglomeration of soil particles results in an increase in permeability at this temperature, reaching 1340×10^{-8} m/s. Heating at 900 °C leads to the destruction of clays and the complete decomposition of carbonates at 850 °C, causing porosity in the soil structure and creating channels for water flow, increasing permeability to about 4120×10^{-8} m/s. According to XRD analysis results, the phase change of quartz leads to porosity in the soil structure, and the formation of crystalline silicates such as gelenite and diopside, due to their porous nature, contributes to increased permeability[12].

Table 5 illustrates the significant changes in UCS and permeability of copper-contaminated dispersive soil under varying temperature conditions. As the temperature increases, UCS shows a steady rise due to the transformation from a dispersed to a flocculated structure and the loss of moisture. The permeability follows a similar trend, with a sharp increase beyond 500 °C, as structural changes, such as macropore formation and the breakdown of minerals like calcite, allow easier water flow[10].

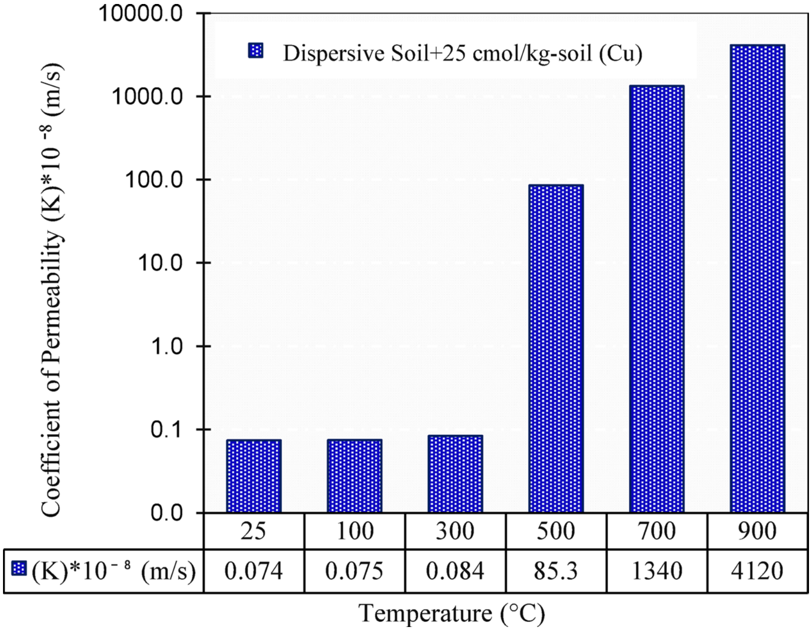

Fig. 13. Graph of the effect of thermal levels on the permeability coefficient of dispersive soil contaminated with heavy metal copper.

Temperature range (°C)	UCS (MPa)	Permeability coefficient ($\times10^{-8}$ m/s)	Behavioral changes
25 °C to 100 °C	0.75	0.039	Initial increase in UCS due to Cu^{2+} presence and moisture loss
100 °C to 300 °C	1.83	0.074	UCS increases due to removal of free water and copper oxide formation
300 °C to 500 °C	2.96	0.084	Further UCS increase from dehydration, dehydroxylation, and consolidation
500 °C to 700 °C	3.56	1340	Significant UCS increase due to clay mineral dehydroxylation and cement formation
700 °C to 900 °C	7.01	4120	UCS decreases due to porous structure and glassy phase formation, but permeability rises significantly

Table 5. UCS and permeability changes in copper-contaminated dispersive soil at different temperatures.

Practically, these results indicate that while UCS improves at high temperatures, the permeability increase could reduce the soil's effectiveness in contaminant containment, especially in applications like thermal remediation of polluted soils. The enhanced permeability at temperatures above 500 °C is crucial when considering environmental impacts, as it could lead to greater migration of pollutants, thus compromising the barrier function of the soil. Therefore, understanding these temperature-induced changes is essential when designing treatments for contaminated soils, ensuring that both strength and hydraulic conductivity are optimized[37].

Conclusion

Based on our experimental results the following conclusions can be drawn.

Thermal treatment has a significant impact on the chemical and physical properties of soil. Specifically, heating leads to significant changes in pH levels, electrical conductivity, X-ray diffraction, morphology, and the permeability coefficient.

Increasing the temperature to about 300 °C leads to an increase in soil pH from 8.4 to 11.1, indicating a reduction in acidity and an improvement in heavy metal retention conditions. These changes are due to the decomposition of copper nitrate and the formation of copper oxide (CuO), which acts as a basic oxide and alters the chemical balance of the soil. Therefore, thermal treatment can effectively reduce the acidity of contaminated soils and create better conditions for the stabilization of heavy metals.

By applying heat up to 500 °C, the ability of the soil to absorb copper pollutants increases to about 100%. This is due to the onset of the dehydroxylation process and the destruction of the clay mineral structure, leading to a reduction in cation exchange capacity (CEC) and specific surface area (SSA) of the soil. These changes indicate that heating can effectively stabilize metal pollutants in the soil and prevent their spread into the environment.

The XRD results showed that with increasing temperature up to 700 °C, the clay minerals such as kaolinite are completely decomposed, and new compounds such as mullite and gelenite are formed. These structural changes indicate improved soil stability and reduced likelihood of pollutant release into the environment. These findings emphasize that heat treatment can create more resilient structures in contaminated soils and prevent the decomposition and transfer of pollutants.

The permeability coefficient of the dispersive soil containing copper increased by about 4120 times at a temperature of 900 °C compared to its initial state. These changes are due to the complete destruction of clay minerals and the decomposition of carbonates, which leads to the formation of pores and water flow channels within the soil structure. This finding indicates that high-temperature heat treatment can result in the creation and formation of a new structure in the contaminated heterogeneous soil, significantly increasing its permeability.

The results of this study provide valuable insights into the potential of thermal treatment for stabilizing and recycling contaminated soils, offering a promising approach for reducing the environmental impact of heavy metal pollutants. The ability to reuse thermally treated soils in the production of construction materials, such as bricks and aggregates, not only addresses soil contamination but also contributes to resource efficiency and sustainability. While large-scale implementation of this method requires consideration of energy consumption and emission control, the economic benefits from reduced material costs and the potential for widespread soil reuse make it an attractive solution for environmental remediation. Further research is necessary to assess the long-term performance of thermally treated soils in real-world applications and to explore the broader applicability of this method across various soil types and contaminants.

Data availability

All data supporting the findings of this study are included within the manuscript.

Received: 2 December 2024; Accepted: 5 May 2025

References

1. Zhou, R. et al. Enhanced capacitive Deionization for cr (VI) removal from electroplating wastewater: Efficacy, mechanisms, and high-voltage flow electrodes. *J. Environ. Chem. Eng.*, 113178 (2024).
2. Amiri, M. & Ouhadi, V. R. Comparison of impact of carbonate content, cation exchange capacity and specific surface area in the retention of heavy metal contaminant by bentonite, kaolinite, and Nano-Clay. (2019).
3. Li, B., Jian, S., Zhu, J., Gao, X. & Gao, W. Effect of sintering temperature on lightweight aggregates manufacturing from copper contaminated soil. *Ceram. Int.* **47**, 31319–31328 (2021).

4. Hsu, C. Y. et al. Adsorption of heavy metal ions use chitosan/graphene nanocomposites: A review study. *Results Chem.*, 101332 (2024).
5. Lytle, D. A. et al. Georgeite: a rare copper mineral with important drinking water implications. *Chem. Eng. J.* **355**, 1–10 (2019).
6. Cheng, Y. et al. Distribution and bioaccessibility of polycyclic aromatic hydrocarbons in industrially contaminated site soils as affected by thermal treatment. *J. Hazard. Mater.* **411**, 125129 (2021).
7. El-eswed, B. I. Chemical evaluation of immobilization of wastes containing Pb, cd, Cu and Zn in alkali-activated materials: A critical review. *J. Environ. Chem. Eng.* **8**, 104194 (2020).
8. Samaksaman, U., Peng, T. H., Kuo, J. H., Lu, C. H. & Wey, M. Y. Thermal treatment of soil co-contaminated with lube oil and heavy metals in a low-temperature two-stage fluidized bed incinerator. *Appl. Therm. Eng.* **93**, 131–138 (2016).
9. Wei, Y. L., Yang, Y. W. & Cheng, N. Study of thermally immobilized Cu in analogue minerals of contaminated soils. *Environ. Sci. Technol.* **35**, 416–421 (2001).
10. Heidari, S. A., Amiri, M. & Harifi, A. The effect of thermal regimes on the dispersive behavior of natural soils from the perspective of microstructure and morphology. *Arab. J. Sci. Eng.*, 1–14 (2024).
11. Wang, X. L., Wang, M. H., Quan, S. X., Yan, B. & Xiao, X. M. Influence of thermal treatment on fixation rate and leaching behavior of heavy metals in soils from a typical e-waste processing site. *J. Environ. Chem. Eng.* **4**, 82–88 (2016).
12. Amiri, M., Kalantari, B. & Porhonar, F. The effect of thermal stabilization process on mineralogy, morphology and engineering properties of red soil in Southern Iran. *Case Stud. Constr. Mater.* **19**, e02454 (2023).
13. Yu, J. et al. Removal of toxic and alkali/alkaline Earth metals during co-thermal treatment of two types of MSWI fly ashes in China. *Waste Manage.* **46**, 287–297 (2015).
14. Amiri, M. & Zare, R. An experimental study on the effects of Pore-Fluid parameters on microstructural behavior of clay core materials in embankment dams. *J. Civil Environ. Eng.* **52**, 13–24 (2023).
15. Amiri, M., Dehghani, M., Javadzadeh, T. & Taheri, S. Effects of lead contaminants on engineering properties of Iranian marl soil from the microstructural perspective. *Miner. Eng.* **176**, 107310 (2022).
16. Gadouri, H. Behavior of natural pozzolana-lime-stabilized clayey soils artificially contaminated by sulfates. *Jordan J. Civil Eng.* **17** (2023).
17. Morris, P. H. & Wong, L. Modification of dredged sediments to produce useful product by heating to high temperatures. *Sustainable Tourism CRC* (2005).
18. Chun, Y. Y. et al. Effect of high temperatures (100–600° C) on the soil particle composition and its Micro-Mechanisms. *Eurasian Soil. Sci.* **54**, 1599–1607 (2021).
19. Yi, J. et al. Assessing soil water balance to optimize irrigation schedules of flood-irrigated maize fields with different cultivation histories in the arid region. *Agric. Water Manage.* **265**, 107543 (2022).
20. Heidari, S. A. & Kalantari, B. Case study: method artificial neural network for earthfill dams seepage analysis: Shahrchay dam in Iran. *Electron. J. Geotech. Eng.* **22**, 1387–1396 (2017).
21. Chen, J. et al. Metallogenic prediction based on fractal theory and machine learning in Duobaoshan area, Heilongjiang Province. *Ore Geol. Rev.*, 106030 (2024).
22. Hendershot, W. H. & Duquette, M. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci. Soc. Am. J.* **50**, 605–608 (1986).
23. Hesse, P. R. & Hesse, P. A textbook of soil chemical analysis. (1971).
24. Meegoda, J. N. & Martin, L. In-situ determination of specific surface area of clays. *Geotech. Geol. Eng.* **37**, 465–474 (2019).
25. ASTM, D. 2166. *Standard Test Method for Unconfined Compressive Strength of Cohesive Soil*. (ASTM International, 2016).
26. EPA. (Center for Environmental Research Information Cincinnati, 1983).
27. Ouhadi, V. & Yong, R. Impact of clay microstructure and mass absorption coefficient on the quantitative mineral identification by XRD analysis. *Appl. Clay Sci.* **23**, 141–148 (2003).
28. Mohajeri, P., Smith, C. & Selamat, M. Abdul Aziz, H. Enhancing the adsorption of lead (II) by bentonite enriched with pH-adjusted meranti sawdust. *Water* **10**, 1875 (2018).
29. Shi, M. et al. Recent progress in Understanding the mechanism of heavy metals retention by iron (oxyhydr) oxides. *Sci. Total Environ.* **752**, 141930 (2021).
30. 30 Kumar, P., Nawaz, T. & Singh, S. P. Optimization of electrocoagulation process parameters for the treatment of oil industry drill site wastewater. *Environ. Sci. Pollut. Res.* **31**, 47101–47115 (2024).
31. Żołnowski, A. C. & Wyszkowski, M. Mineral neutralizers as a tool for improving the properties of soil contaminated with copper. *Minerals* **12**, 895 (2022).
32. Han, Q., Sun, T., Zhang, X., Li, S. & Zhu, Y. Degradation of Polyvinyl alcohol (PVA) in neutral conditions based on copper-manganese bimetallic catalyst. *Environ. Sci. Pollut. Res.* **30**, 97990–98003 (2023).
33. Hasan, M. F. & Abuel-Naga, H. Effect of temperature and water salinity on electrical surface conduction of clay particles. *Minerals* **13**, 1110 (2023).
34. Dubinsky, S., Grader, G. S., Shter, G. E. & Silverstein, M. S. Thermal degradation of Poly (acrylic acid) containing copper nitrate. *Polym. Degrad. Stab.* **86**, 171–178 (2004).
35. Csáki, Š. et al. Temperature dependence of the AC conductivity of illitic clay. *Appl. Clay Sci.* **157**, 19–23 (2018).
36. Hassan, W. et al. Incorporating potassium-rich waste material in a sustainable way to stabilize dispersive clay: A novel practical approach for the construction industry. *Constr. Build. Mater.* **400**, 132717 (2023).
37. Ouhadi, V. R. & Vejdani Vahid, A. Impact of temperature and type of clay double layer cation on adsorption of copper heavy metal contaminant. *J. Civil Environ. Eng.* **53**, 1–12 (2024).
38. Yong, R. N., Ouhadi, V. R. & Goodarzi, A. R. Effect of Cu 2 + ions and buffering capacity on smectite microstructure and performance. *J. Geotech. GeoEnviron. Eng.* **135**, 1981–1985 (2009).
39. Liu, W., McPhail, D. & Brugger, J. An experimental study of copper (I)-chloride and copper (I)-acetate complexing in hydrothermal solutions between 50 C and 250 C and vapor-saturated pressure. *Geochim. Cosmochim. Acta*. **65**, 2937–2948 (2001).
40. Mhalla, B. et al. Solubility relationship of metals in acid soils of Kumaon himalaya region of India. *Commun. Soil Sci. Plant Anal.* **52**, 2373–2387 (2021).
41. Wang, H., Xia, W. & Lu, P. Study on adsorption characteristics of Biochar on heavy metals in soil. *Korean J. Chem. Eng.* **34**, 1867–1873 (2017).
42. Giovannini, C., Lucchesi, S. & Giachetti, M. Effects of heating on some chemical parameters related to soil fertility and plant growth. *Soil Sci.* **149**, 344–350 (1990).
43. Cultrone, G., Rodriguez-Navarro, C., Sebastian, E. & Cazalla, O. De La Torre, M. J. Carbonate and silicate phase reactions during ceramic firing. *Eur. J. MINERALOGY-STUTTGART-*. **13**, 621–634 (2001).
44. Ouhadi, V. R., Yong, R., Hejazifar, H. & Bahadorinezhad, O. Effect of temperature on buffering capacity of carbonated and decarbonated kaolinite in copper contaminated soil. *Environ. Eng. Manage. J. (EEMJ)*, **19** (2020).
45. Fernández-Calviño, D., Pérez-Novo, C., Nóvoa-Muñoz, J. & Arias-Estévez, M. Copper fractionation and release from soils devoted to different crops. *J. Hazard. Mater.* **167**, 797–802 (2009).
46. Jalali, M. & Zinli, N. A. M. Effect of common ions on copper sorption behavior in dryland calcareous soils in Iran. *Arch. Agron. Soil. Sci.* **59**, 197–212 (2013).
47. Ouhadi, V. & Goodarzi, A. Assessment of the stability of a dispersive soil treated by alum. *Eng. Geol.* **85**, 91–101 (2006).

48. McConville, C. J. & Lee, W. E. Microstructural development on firing illite and smectite clays compared with that in kaolinite. *J. Am. Ceram. Soc.* **88**, 2267–2276 (2005).
49. Muñoz, P., Letelier, V., Bustamante, M., Marcos-Ortega, J. & Sepúlveda, J. Assessment of mechanical, thermal, mineral and physical properties of fired clay brick made by mixing kaolinitic red clay and paper pulp residues. *Appl. Clay Sci.* **198**, 105847 (2020).
50. Cultrone, G. & Rosua, F. J. C. Growth of metastable phases during brick firing: mineralogical and microtextural changes induced by the composition of the Raw material and the presence of additives. *Appl. Clay Sci.* **185**, 105419 (2020).
51. Frost, R., Ding, Z., Kloprogge, J. & Martens, W. Thermal stability of azurite and malachite in relation to the formation of mediaeval glass and glazes. *Thermochim. Acta*. **390**, 133–144 (2002).
52. Rodriguez-Navarro, C., Ruiz-Agudo, E., Luque, A., Rodriguez-Navarro, A. B. & Ortega-Huertas, M. Thermal decomposition of calcite: mechanisms of formation and textural evolution of CaO nanocrystals. *Am. Mineral.* **94**, 578–593 (2009).
53. Rodriguez-Navarro, C., Kudlacz, K. & Ruiz-Agudo, E. The mechanism of thermal decomposition of dolomite: new insights from 2D-XRD and TEM analyses. *Am. Mineral.* **97**, 38–51 (2012).
54. Štubňa, I., Húlan, T., Kaljuvee, T. & Vozár, L. Investigation of dynamic mechanical properties of Estonian clay Arumetsa during firing. *Appl. Clay Sci.* **153**, 23–28 (2018).
55. Trindade, M. J., Dias, M., Coroado, J. & Rocha, F. Mineralogical transformations of calcareous rich clays with firing: A comparative study between calcite and dolomite rich clays from Algarve, Portugal. *Appl. Clay Sci.* **42**, 345–355 (2009).
56. Kant, R. & Singh, M. B. Generalization of the Gouy-Chapman-Stern model of an electric double layer for a morphologically complex electrode: deterministic and stochastic morphologies. *Phys. Rev. E*. **88**, 052303 (2013).
57. Brown, I., Mackenzie, K. & Gainsford, G. Thermal decomposition of the basic copper carbonates malachite and azurite. *Thermochim. Acta*. **75**, 23–32 (1984).
58. Kiseleva, I., Ogorodova, L., Melchakova, L., Bisengalieva, M. & Becturganov, N. Thermodynamic properties of copper carbonates—malachite Cu 2 (OH) 2 CO 3 and azurite Cu 3 (OH) 2 (CO 3) 2. *Phys. Chem. Miner.* **19**, 322–333 (1992).
59. Xiao, W., Zhang, D., Li, S. & Wu, M. Microstructural and thermal properties of coal measure sandstone subjected to high temperatures. *J. Rock Mech. Geotech. Eng.* (2023).
60. Lokh, B. Effect of temperature on structural, morphological and electrochemical properties of the spray pyrolysed CuO@ stainless-steel electrodes via non-aqueous route: supercapacitive approach. *ES Energy Environ.* **16**, 59–66 (2022).

Acknowledgements

The authors would like to thank the University of Hormozgan, which supported the expenses for all the tests conducted in this study.

Author contributions

S.H. Investigation, Resources, Investigation, Formal analysis, Methodology, Visualization, Writing. M.A. Conceptualization, Methodology, Validation, Formal analysis, Writing - Review & Editing, Supervision, Writing. A.H. Review & Editing. W.W. Writing - Review & Editing, Supervision.

Declarations

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to M.A.