Influence of Lead Nitrate Contamination on the Geo-environmental Behavior of Sand–Bentonite–Zeolite Mixtures

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Abstract

Heavy metal contamination can significantly alter both the environmental performance and mechanical stability of engineered soil systems. Previous studies have rarely considered the effects of extremely high contaminant concentrations, which can simulate long-term accumulation over years in real structures containing adsorbent materials. This study aims to investigate the pH-controlled influence of lead nitrate contamination on the adsorption capacity, consistency limits, and unconfined compressive strength of sand–bentonite and sand–bentonite–zeolite mixtures. Bentonite and zeolite were exposed to lead nitrate solutions at pH 3, 4, and 6, representing extremely high to low contaminant concentrations. Temporal changes in pH and Atterberg limits were evaluated, and lead adsorption capacity was quantified. Subsequently, unconfined compressive strength tests were conducted on sand mixtures containing 20% fines (20% bentonite or 10% bentonite + 10% zeolite) after curing periods up to 28 days. The results show that both adsorbents exhibit mildly alkaline behavior in their natural state but shift toward acidic conditions upon contamination. Lead exposure reduced the plasticity of bentonite due to compression of the diffuse double layer, whereas zeolite exhibited comparatively stable consistency, reflecting its rigid three-dimensional framework. Adsorption efficiency decreased with decreasing pH for both materials; however, bentonite consistently outperformed zeolite, particularly under extreme contamination levels. At low contamination (pH = 6), lead presence enhanced the compressive strength of both sand–adsorbent systems, while severe acidity (pH = 3) resulted in strength degradation, especially in zeolite-containing mixtures. Overall, sand–bentonite mixtures exhibited higher strength gains than sand–bentonite–zeolite mixtures, and all specimens showed pronounced time-dependent strength evolution. The findings highlight the critical role of pH in governing the efficiency of heavy metal adsorption and the mechanical stability of engineered soil systems under extreme contamination conditions.

Keywords: lead, heavy-metal adsorbent, bentonite, zeolite

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1. Introduction

The introduction of heavy metal contaminants into soils can significantly alter their biological and geotechnical properties [1-5]. These contaminants may also modify soil pH, a parameter of critical importance from both environmental and geotechnical perspectives [6-9]. Numerous studies have demonstrated that the adsorption capacity of fine-grained materials for heavy metals depends on several factors, including soil or adsorbent type, contact time, fine particle content, temperature, and ambient pH. Among these factors, pH plays a dominant role, as it directly governs the mobility of metal ions. Several researchers have reported an increase in adsorption efficiency with increasing pH [10, 11]. Similarly, adsorption efficiency generally increases with higher clay content [12, 13] and longer contact time until equilibrium is reached [14]. Although no universal guideline exists regarding the optimum adsorbent content, many studies have shown that even small amounts of clayey materials can effectively remove heavy metals from contaminated environments [13, 15-17]. The optimal temperature for heavy metal adsorption has generally been reported to be close to room temperature [14].

The presence of heavy metal contaminants can alter the geotechnical properties of soils due to adsorption on mineral surfaces. Karkush and Ali (2019) reported that soil contamination originating from an oil field with copper sulfate resulted in a reduction in fine particle content, Atterberg limits, permeability, and optimum moisture content, while the maximum dry density increased. In addition, increasing contaminant concentration led to a decrease in the unconfined compressive strength of the soil [1]. Similarly, Zhang et al. (2019) reported that copper chloride contamination reduced the shear strength, cohesion, and internal friction angle of kaolinite[18]. With increasing copper concentration, the liquid limit and plasticity index increased, whereas the plastic limit and effective shear strength decreased. Resmi and Thampi (2011) showed that increasing lead concentration reduced the Atterberg limits and unconfined compressive strength, while increasing the compaction coefficient and permeability of contaminated soils [19]. Li et al. (2015) reported that in silty clay soils, higher lead concentrations led to reductions in liquid limit, plasticity index, and optimum moisture content, accompanied by increases in silt content, maximum dry density, equilibrium time, hydraulic conductivity, and shear strength; these effects were attributed to a reduction in diffuse double layer thickness [20].

Ouhadi et al. (2017) attributed changes in the plastic limit and permeability of bentonite contaminated with organic pollutants and heavy metals such as lead and zinc to increased electrolyte concentration and compression of the diffuse double layer, resulting in increased permeability and reduced plasticity[4]. Other researchers have also related the altered behavior of contaminated fine-grained soils to changes in diffuse double layer thickness [21, 22]. Sivapullaiah (2009) demonstrated that the mechanical and fabric changes of contaminated fine-grained soils can be explained by diffuse double-layer theory, provided that no severe mineralogical alterations occur [23].

Hassanlourad et al. (2021) reported a reduction in shear strength and internal friction angle and an increase in cohesion for lead-contaminated sand–kaolinite mixtures, while the strength increase observed in sand–bentonite mixtures was attributed to the development of a flocculated structure induced by contamination [24]. Hosseinzade et al. (2022) observed that lead contamination reduced shear strength and elastic modulus in soils containing low-plasticity adsorbents (kaolinite), whereas the same contamination increased these parameters in mixtures containing high-plasticity adsorbents (bentonite) [16]. In that study, the unconfined compressive strength decreased with increasing zeolite content and zinc concentration in sand samples containing 15% kaolinite and varying proportions of zeolite and bentonite. The results showed that at copper nitrate concentrations up to 20,000 ppm, strength increased in bentonite-containing samples but decreased in zeolite-containing samples.

Gori (1994) reported that the liquid limit of kaolinite is not affected by pore water pH, whereas studies on smectite have shown that its liquid limit is strongly pH-dependent [7, 25]. Sunil et al. (2006) investigated compacted soil blocks at pH values of 5, 7, and 8 and observed that unconfined compressive strength decreased with increasing curing time up to 90 days [26]. The plastic limit increased at pH values of 5 and 7, but decreased at pH = 8. In another study, Hassanlourad et al. (2017) reported that the shear strength of sand–bentonite mixtures increased at pH = 3 but decreased at pH=1 [27]. Similarly, Torabi and Hassanlourad (2019) showed that increasing acidity leads to a reduction in the shear strength of clayey soils [28]. Karimdad et al. (2021) proposed an optimal bentonite–zeolite combination as an effective adsorbent and barrier material for landfill liners [29]. Furthermore, Huang et al. (2022) demonstrated that acidic conditions in Sichuan soils enhance moisture absorption and promote the self-healing of cracks induced by wetting [8].

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As indicated by the reviewed literature, the geotechnical behavior of fine-grained soils contaminated with heavy metals is governed by multiple interacting factors, including soil type, type and concentration of contaminants, ambient pH, contact time, temperature, and environmental conditions. Nevertheless, substantial inconsistencies among reported results highlight the need for further systematic experimental investigations. Accordingly, the present study aims to examine the effects of lead nitrate contamination, as a commonly encountered heavy metal in industrial wastes, on the geotechnical and environmental properties of bentonite and zeolite as fine-grained adsorbents. In this framework, the influence of lead nitrate on soil pH, Atterberg limits, and adsorption capacity is evaluated. Furthermore, the unconfined compressive strength of sand mixtures containing 20% fines (either 20% bentonite or 10% bentonite + 10% zeolite) is assessed under lead nitrate contamination. In this study, the lowest pH values correspond to extremely high contaminant concentrations, a condition that has received limited attention in previous research. Investigation under such severe contamination levels not only simulates long-term contaminant accumulation but also provides insight into the effective adsorption capacity and service life of the adsorbents. Moreover, examining soils under extreme chemical conditions enables clearer identification of physicochemical and geotechnical changes induced by heavy metal contamination.

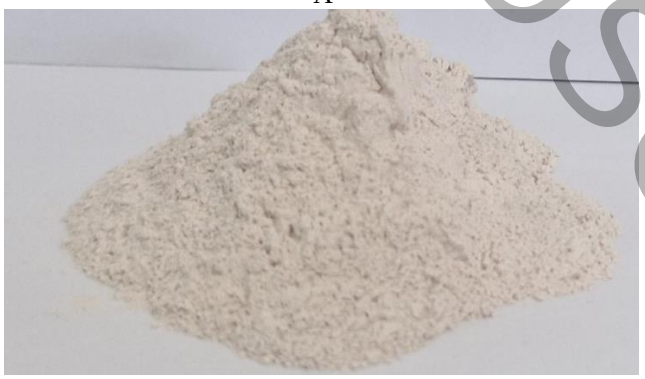
2. Materials and Methods

The bentonite used in this study was pinkish in color and supplied by *Poudersazan Company* (Qazvin, Iran). The zeolite, with a pale-yellow appearance, was obtained from *Kanipowder Mining Industries* (Semnan, Iran). The sand employed in this research was a golden-colored sand (Code 101) sourced from the Firuzkuh mine. The physical appearance of the materials is shown in Figure 1, and their particle size distributions, determined in accordance with ASTM D422-63 (2007), are presented in Figure 2[30].

The material properties, including specific gravity (Gs) measured according to ASTM D854-23[31], Atterberg limits comprising liquid limit (LL), plastic limit (PL), and plasticity index (PI) determined following ASTM D4318-17[32], pH measured based on BS 1377-3:2021[33], and soil classification according to the Unified Soil Classification System (USCS), are summarized in Table 1. Based on these results, the sand was classified as poorly graded sand (SP), the bentonite as high-plasticity clay (CH), and the zeolite as low-plasticity silt (ML).



A



B

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c

Figure 1. Physical appearance of the tested soil materials: a) sand, b) bentonite, and c) zeolite.

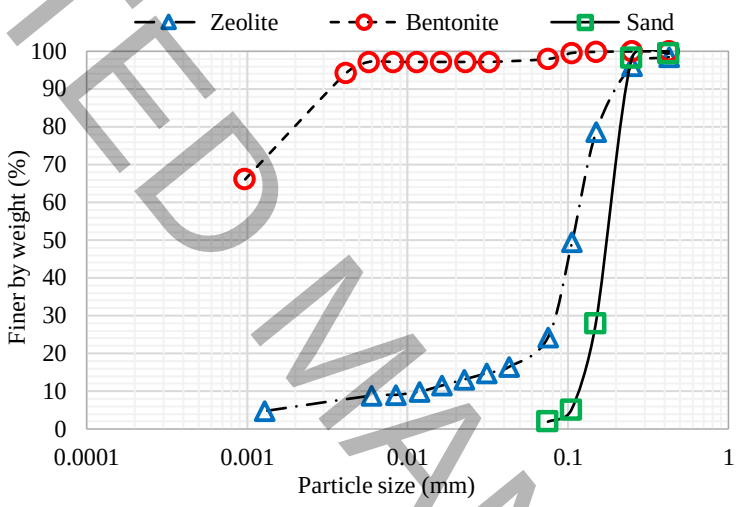


Figure 2. Grain size distribution curves of the tested soil materials.

Table 1. Properties of the soil materials.

Material	G_s	LL	PL	PI	pH	Soil Classification
Sand	2.69	–	–	–	–	SP
Bentonite	2.83	144.9	64.3	80.6	8.23	CH
Zeolite	2.45	46.8	38.3	8.5	8.27	ML

3. Experimental Procedure

In this study, the effects of different lead nitrate contaminant concentrations on pH, Atterberg limits, adsorption capacity, and unconfined compressive strength (UCS) [34]were investigated. Initially, the pH of uncontaminated bentonite and zeolite was measured over 28 days to determine both the natural pH of the adsorbents and the influence of time on their inherent pH variations. Subsequently, pH measurements were performed on each adsorbent contaminated with a specific concentration of the contaminant over 28 days to evaluate the temporal effect of contamination on pH changes.

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To examine the influence of the contaminant and its concentration on the properties of the samples, contaminant solutions were prepared with pH values of 3, 4, and 6. Each pH value corresponds to a specific contaminant concentration: pH 6 corresponds to 598 ppm, pH 4 to approximately 127,000 ppm, and pH 3 to approximately 497,000 ppm. Following this, the liquid and plastic limits of uncontaminated and contaminated bentonite and zeolite samples at the specified concentrations were measured over 28 days to assess the effects of contaminant concentration and contact time on the Atterberg limits. Atomic absorption spectroscopy (AAS) tests were then conducted on bentonite and zeolite samples contaminated with all three concentrations.

After evaluating the fine-grained fraction (adsorbents), standard compaction tests were carried out on sand mixtures containing 20% adsorbent (either 20% bentonite or 10% zeolite + 10% bentonite) in accordance with ASTM D698-07 to determine the maximum dry density and optimum moisture content for the preparation of samples for UCS testing. The compaction results are presented in Figure 3. For the sand–bentonite mixture, the maximum dry density was 17.3 kN/m³ with an optimum moisture content of 16%, whereas for the sand–bentonite–zeolite mixture, the maximum dry density was 16.3 kN/m³ with an optimum moisture content of 16.7%.

Based on the standard compaction test results[35], sand+ 20% adsorbent samples were prepared for unconfined compressive strength testing and cured for periods ranging from 0 to 28 days. The samples were labeled using two or three letters representing the soil and adsorbent (B for bentonite, Z for zeolite, S for sand), L for lead nitrate contaminant, and a number indicating pH. For instance, BL3 denotes bentonite contaminated with lead nitrate at pH 3. To evaluate the repeatability and reliability of the experimental results, selected key laboratory tests were conducted in a repeated manner under identical experimental conditions. Due to the extensive scope of the experimental program, it was not feasible to repeat all tests; therefore, representative tests, including Atterberg limit and unconfined compressive strength (UCS) tests, were repeated to confirm the reliability of the measurements. As an illustrative example, the repeatability of the Atterberg limit tests was assessed for a seven-day cured, uncontaminated zeolite sample. The measured values of the liquid limit (LL) were 45.9% and 44.85%, corresponding to a coefficient of variation (CV) of approximately 1.6%, while the plastic limit (PL) was 43.8% in both repetitions, resulting in a CV of 0%. These results demonstrate the high repeatability and reliability of the experimental procedure.

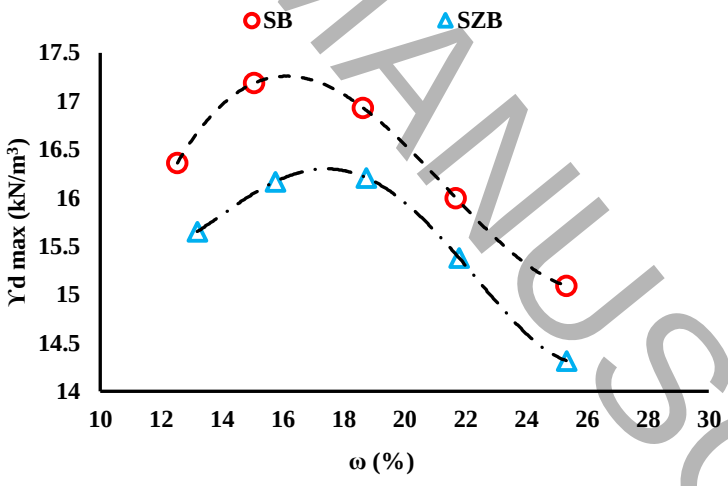


Figure 3. Standard compaction curves of the sand–adsorbent mixtures.

4. Results and Discussion

4.1. Effect of Contamination and Contact Time on the pH

The natural pH of bentonite and zeolite was determined following the BS 1377-3 standard. In each test, 30 g of the adsorbent was mixed with 75 mL of solution (either distilled water or a 20000-ppm lead nitrate solution), and the pH

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was measured after 24 hours. Measurements were subsequently repeated on days 1, 7, 14, and 28. The temporal variations are presented in Figure 4.

Uncontaminated samples exhibited a nearly constant pH over the 28 days. The mean pH of the uncontaminated bentonite was 8.22, with only a 0.8% difference between the minimum and maximum recorded values. For uncontaminated zeolite, the mean pH was 8.27, with the same 0.8% variation. These findings indicate a mildly alkaline nature and high chemical stability of both adsorbents when in contact with distilled water.

Exposure to lead nitrate resulted in a significant pH reduction for both adsorbents, indicating acidification. The mean pH of bentonite contaminated with lead nitrate was 6.89, while zeolite exhibited a mean pH of 6.46, corresponding to relative decreases of 16.1% and 21.9%, respectively, compared to their uncontaminated counterparts. Over the 28 days, the pH of the bentonite sample increased by 7.5% relative to day 1, whereas the pH of the zeolite slightly decreased by 1.5%. These trends suggest that zeolite demonstrates greater pH stability than bentonite during prolonged exposure to the contaminant.

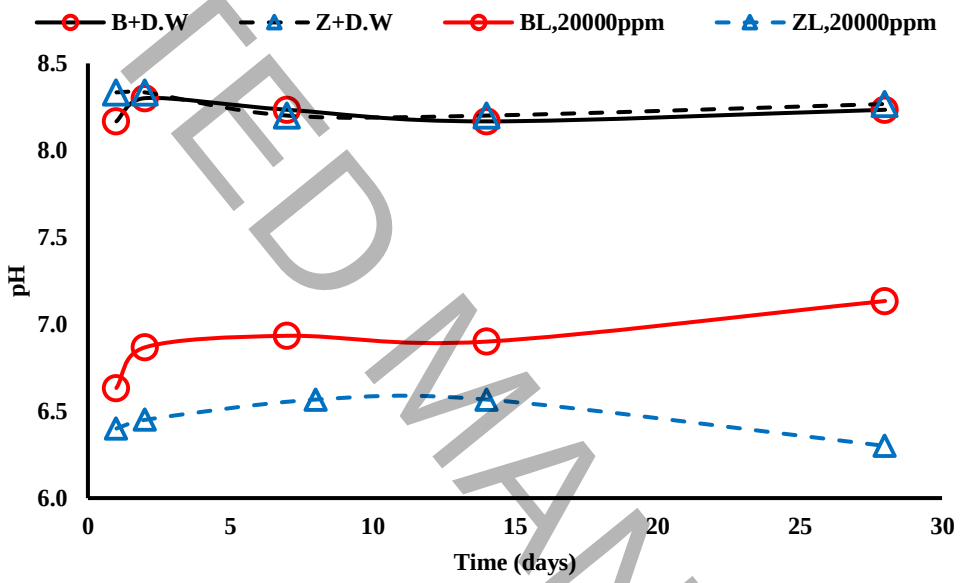


Figure 4. Temporal variations of adsorbent pH in contact with distilled water and 20000-ppm lead nitrate solution over 28 days.

4.2. Effect of Contamination and Contact Time on the Atterberg Limits

In the Atterberg limits tests, the adsorbents were exposed to lead nitrate solutions with pH values of 3, 4, and 6. After contamination, the samples were stored in sealed containers to maintain moisture and allow for secondary reactions. The tests were conducted after 24 hours of storage and repeated on days 7, 14, and 28. The variations in liquid limit, plastic limit, and plasticity index of bentonite and zeolite, both uncontaminated and contaminated with lead nitrate at pH 3, 4, and 6 over 28 days, are summarized in Table 2.

As shown in Table 2, the liquid limit of both uncontaminated adsorbents decreased slightly over time, with bentonite exhibiting a larger reduction of approximately 9%, while zeolite showed a minor decrease of about 2%. Contamination with lead nitrate further reduced the liquid limit of all samples. The lowest liquid limit was observed for the BL3 bentonite sample on day 28, which represents a 20% decrease compared to the initial liquid limit of uncontaminated bentonite and a 7% decrease relative to BL3 on day 1. For zeolite, the reduction in liquid limit over time was modest; the ZL3 sample on day 28 showed a 4% decrease relative to the initial liquid limit of the uncontaminated sample and a 5% decrease compared to ZL3 on day 1. The plastic limits of uncontaminated and contaminated bentonite samples at pH 3 and 4 decreased over time. For zeolite samples, the plastic limit increased for the uncontaminated and contaminated samples at pH 6, whereas for ZL4 and ZL3 samples, it decreased over the 28 days.

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Table 2. Variations in the Atterberg limits of uncontaminated and lead nitrate-contaminated bentonite and zeolite at different pH values over 28 days.

Adsorbent	LL (%)	PL (%)	PI (%)	Time(days)	Adsorbent	LL (%)	PL (%)	PI (%)
	144.9	64.3	80.6	1		46.8	38.3	8.5
B+D.W.	137.0	52.3	84.7	14	Z+ D.W.	48.2	41.7	6.6
	131.7	49.0	82.7	28		45.9	43.8	2.2
	128.2	46.3	81.9	1		47.6	36.5	11.1
BL6	134.1	50.1	84.0	14	ZL6	45.5	36.1	9.4
	128.6	59.5	69.1	28		46.5	44.5	2.0
	134.8	69.1	65.7	1		47.5	40.5	7.1
BL4	133.6	66.5	67.2	14	ZL4	46.8	41.4	5.4
	126.3	63.6	62.7	28		44.0	35.7	8.3
	124.5	83.5	41.0	1		47.5	37.8	9.7
BL3	122.7	71.2	51.5	14	ZL3	47.1	37.7	9.4
	115.2	62.5	52.7	28		44.9	36.5	8.4

The reduction in the liquid and plastic limits of bentonite can be attributed to particle rearrangement and reorganization of hydrogen bonding, which slightly decreases the soil's water retention capacity. When bentonite was in contact with distilled water, a slight increase in the plasticity index was observed during the first seven days, which is consistent with the findings of Bharat et al. (2020) [36]. The temporal variations in soil consistency can be interpreted using the dual-porosity concept, which assumes that soils consist of two hydraulically connected pore systems: macropores and micropores, allowing water transfer between them [37]. Micropores play a dominant role in water retention, as the absorbed water remains strongly bound within these regions. Under natural conditions, the presence of monovalent and divalent cations (such as Na^{+} and Ca^{2+}) increases the thickness of the diffuse double layer (DDL) and enhances interlayer water adsorption, which explains the high Atterberg limits of uncontaminated bentonite.

Upon contamination with multivalent heavy metal cations such as Pb^{2+}, these ions replace the naturally exchangeable cations. Due to their higher charge and smaller hydrated radius, Pb^{2+} ions intensify interlayer attractive forces, leading to compression of the diffuse double layer and a reduction in interlayer spacing. Consequently, the water retention capacity within micropores decreases. Part of the released water migrates to macropores, which contribute less to Atterberg limits. Therefore, the overall reduction in water trapped within the clay structure accounts for the observed decrease in the liquid and plastic limits of lead-contaminated bentonite compared with uncontaminated samples.

In contrast, contaminated zeolite exhibited considerably smaller variations, confirming the structural stability of this mineral in the presence of heavy metal ions. Overall, lead nitrate contamination had a more pronounced effect on the plasticity characteristics of bentonite than zeolite, owing to the expandable layered structure of bentonite. The relatively minor influence of curing time further suggests that chemical interactions, rather than time-dependent processes, were the primary drivers of changes in plasticity behavior.

Similar trends have been reported in previous studies. Hassanlourad et al. (2024) observed reductions in the liquid limit, plastic limit, and plasticity index of bentonite contaminated with heavy metals such as lead and zinc, while these parameters increased in kaolinite [38]. Nosrati et al. (2021) reported decreases in Atterberg limits of sand–bentonite mixtures containing zeolite following contamination with lead and zinc nitrates, attributing this behavior to flocculated structure formation and DDL compression [39]. Nartowska et al. (2019) documented reductions in liquid limit and

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increases in plastic limit for three bentonites contaminated with divalent copper and zinc ions [40], whereas Ray et al. (2022) reported decreases in the liquid limit of two bentonites exposed to lead, copper, and zinc solutions [41]. Conversely, Bharat et al. (2020) observed an increase in the liquid limit of bentonite during curing with distilled water, particularly up to the fourth day, which was attributed to the gradual development of the diffuse double layer around clay particles [36].

Figures 5 and 6 illustrate the temporal variations in the plasticity index of bentonite and zeolite under different levels of lead nitrate contamination. As shown in Figure 5, the plasticity index of uncontaminated bentonite (B+DW) increased slightly from 80.6 on day 1 to 82.7 on day 28, indicating relatively stable behavior with minor fluctuations. In contrast, contaminated samples exhibited more pronounced changes depending on contaminant concentration. A greater reduction in plasticity index was observed with decreasing pH (i.e., increasing contaminant concentration). With increasing contact time, the plasticity index of sample BL6 decreased from 81.6 on day 1 to 69.1 on day 28 (a 15.3% reduction). Corresponding values for sample BL4 decreased from 65.7 to 62.7 (a 4.5% reduction), while for sample BL3, the plasticity index increased from 41.0 to 52.7 (a 28.5% increase).

Overall, lead contamination leads to a general reduction in the plasticity of bentonite, while the effect of contact time may either intensify or mitigate this behavior depending on contaminant concentration (or pH).

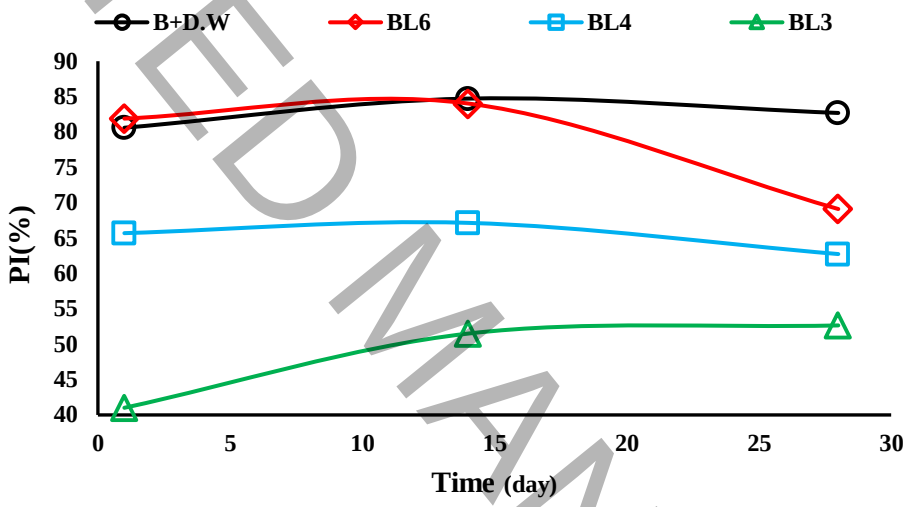


Figure 5. Temporal variations of the plasticity index of uncontaminated and lead nitrate–contaminated bentonite.

According to Figure 6, zeolite samples exhibit substantially lower plasticity index (PI) values than bentonite samples, which is consistent with the granular structure of zeolite characterized by a three-dimensional crystalline framework with interconnected channels [42]. The plasticity index of uncontaminated zeolite (Z+DW) gradually decreased over the 28-day period from approximately 8.5% to 2.2%, corresponding to a 73% reduction.

For zeolite samples contaminated with lead nitrate, different behaviors were observed. The initial PI of sample ZL6, corresponding to the lowest contaminant concentration, was approximately 30% higher than that of the uncontaminated sample. Similarly, the initial PI of sample ZL3 (the highest contaminant concentration) was about 14% higher than the corresponding value of the uncontaminated sample, whereas the initial PI of ZL4 was approximately 16% lower than that of the uncontaminated sample. Among the three contaminated samples, ZL3 exhibited the smallest temporal variation, and on day 28, the PI values of both ZL3 and ZL4 were higher than that of Z+DW.

Overall, considering the relatively narrow range of plasticity index values in zeolite, it can be concluded that zeolite is less sensitive to lead nitrate contamination than bentonite.

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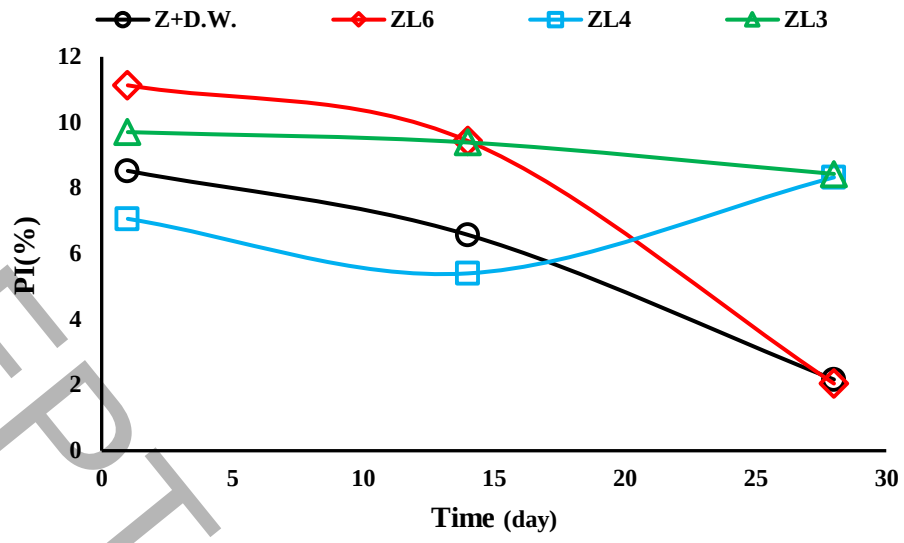


Figure 6. Temporal variations of the plasticity index of uncontaminated and lead nitrate–contaminated zeolite.

Figure 7 illustrates the variation of the plasticity index (PI) of 28-day bentonite and zeolite samples at different pH levels. In addition, the PI values of uncontaminated samples are plotted using a distinct black marker for comparison. As shown in the figure, zeolite samples clearly exhibit lower PI values than bentonite samples. With decreasing pH (i.e., increasing contaminant concentration), the PI of bentonite samples decreases, whereas an opposite trend is observed for zeolite, where PI increases with decreasing pH, indicating a slight increase in plasticity under more acidic conditions. Overall, these results further confirm that zeolite exhibits lower sensitivity to lead contamination and greater behavioral stability compared to bentonite.

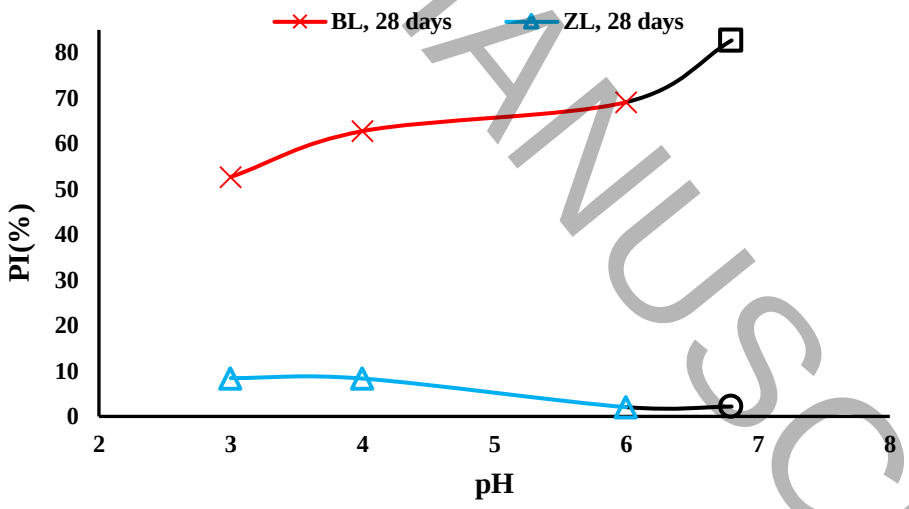


Figure 7. Variations of the plasticity index of the adsorbents as a function of contaminant pH after 28 days of contact.
Note: The black-colored portion of the plot, indicated by a distinct marker, corresponds to the uncontaminated (clean) samples.

At a pH of approximately 6, the effective concentration of Pb^{2+} ions in the vicinity of clay particles is relatively low. Partial hydrolysis of these ions occurs, leading to the formation of hydroxyl-containing species with lower charge density and weaker affinity for clay surfaces. This process promotes the expansion of the diffuse double layer (DDL),

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allowing more water to be retained between clay layers and resulting in an increase in the plasticity index (PI). As pH decreases to around 4, the concentration of Pb^{2+} ions increase, providing a sufficient number of divalent cations to replace naturally occurring monovalent clay cations such as sodium and potassium. Owing to their higher charge and smaller hydrated radius, these metal ions generate stronger electrostatic attraction between particles, leading to compression of the diffuse double layer and a consequent reduction in PI. With a further decrease in pH to approximately 3, although the contaminant concentration increases, the number of available adsorption sites becomes limited. As a result, a portion of the metal ions remains in the pore water without being adsorbed onto clay surfaces. These free ions exhibit weaker interactions with clay particles and are more easily released upon contact with water. Their presence in the pore fluid enhances interparticle repulsion and increases void spaces, thereby allowing greater water uptake and leading to an increase in PI. Similar behavior was reported by Li et al. [20], who observed that the swelling potential of clay increased as Pb concentration rose from 1,000 to 10,000 ppm, followed by a sharp decrease at 20,000 ppm.

In the case of zeolite samples, the most pronounced behavior is the relative stability of their response to contamination, increasing contaminant concentration, and contact time.

4.3. Effect of Contaminant pH on the Adsorption Capacity of the Adsorbents

To conduct the adsorption tests, 10 mL of contaminant solution at the selected pH values was added to 1 g of adsorbent in test tubes. The selected adsorbent mass (1 g) is consistent with values commonly adopted in previous adsorption studies [for instance: Ouhadi et al., 2016], while the solution volume was determined considering the capacity of the available laboratory equipment. Moreover, the adsorbent mass and solution volume are inherently accounted for in the equilibrium concentration relationships used to evaluate adsorption capacity; therefore, the selected solid-to-liquid ratio does not affect the validity of the adsorption analysis. The samples were agitated for four days, with stirring performed once every 24 hours for a duration of 2 hours, and following the procedure proposed by Ouhadi and Zarei [43]. Subsequently, the suspensions were centrifuged at 300 rpm for 15 minutes and filtered through filter paper. Atomic absorption spectroscopy (AAS) was then performed on the resulting solutions. Figure 8 presents the adsorption percentages of the adsorbents at different pH levels of the lead nitrate solution.

According to the results, at pH 6, both adsorbents achieved 100% removal of the contaminant. When pH decreased to 4, the adsorption capacity of bentonite decreased to 90%, while that of zeolite declined to 85%. With a further increase in contaminant concentration at pH=3, the adsorption capacity of bentonite slightly decreased to 86% and remained relatively high; however, the adsorption performance of zeolite deteriorated significantly, with approximately 41% of the contaminant remaining unabsorbed. Overall, at higher pH levels, both adsorbents exhibit satisfactory adsorption performance. In contrast, at pH=3, zeolite shows limited efficiency for lead removal, indicating an approach to saturation under highly acidic conditions.

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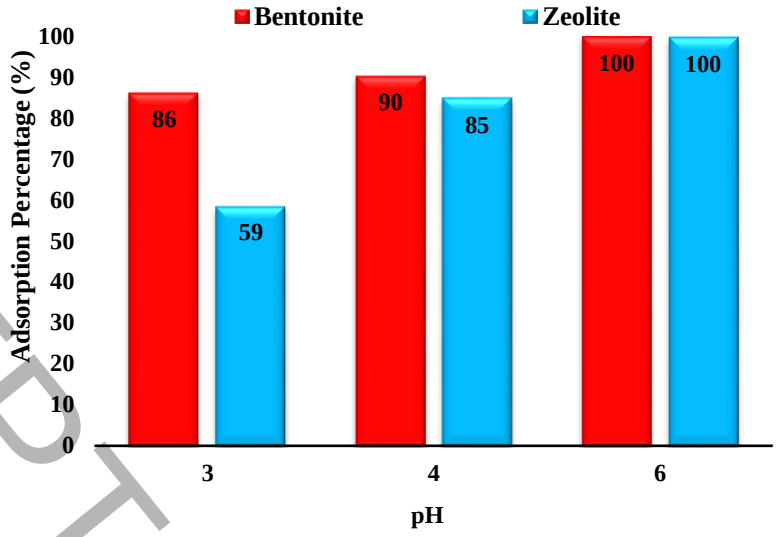


Figure 8. Adsorption percentages of the adsorbents at different pH levels of the lead nitrate contaminant.

4.4. Effect of Contamination and Contaminant pH on Unconfined Compressive Strength (UCS)

For the UCS tests, sand–adsorbent mixtures were first mixed with the contaminant solution at the optimum moisture content, dried in an oven, and then remixed with distilled water. The mixtures were subsequently compacted into cylindrical molds measuring 39 × 75 mm in seven layers at 95% of the maximum dry density. The samples were wrapped in plastic and stored for curing periods of 0, 7, 14, and 28 days. The proportion of 80% sand to 20% fine fraction was selected based on previous studies [39, 44-46].

Initially, UCS was determined for sand containing 20% bentonite, followed by tests on mixtures containing 10% bentonite and 10% zeolite. Figures 9 and 10 present the variations in unconfined compressive strength of sand with 20% adsorbent, both uncontaminated and contaminated with lead nitrate at different pH levels, over a 28-day curing period.

As shown in Figure 9, the compressive strength of bentonite-containing samples (both uncontaminated and contaminated) increases over time. A substantial portion of this increase appears to be independent of contamination and is likely attributable to the thixotropic behavior of clay soils. The UCS of the uncontaminated bentonite sample on day 28 increased by 93% relative to the uncured sample. For contaminated samples BL6, BL4, and BL3, the corresponding increases were 100%, 129%, and 246%, respectively. Furthermore, the UCS of BL6 and BL4 exceeded that of the uncontaminated sample. Comparison of contaminated and uncontaminated samples on day 28 shows an increase of 14% and 16% in UCS for BL6 and BL4, respectively, and a slight decrease of approximately 4% for BL3.

These results suggest that lead nitrate contamination enhances the compressive strength of mixtures containing 20% bentonite, while at the highest contaminant concentration (the lowest studied pH), only a minor reduction in strength is observed. A similar trend of increased UCS for sand–bentonite mixtures contaminated with lead nitrate up to 20,000 ppm (equivalent to pH ≈ 4.5) has been reported by Hassanlourad et al. (2024) [38]. Another notable observation from Figure 9 is that while the strength of the uncontaminated sample increases steadily over time, the contaminated samples exhibit a more fluctuating trend.

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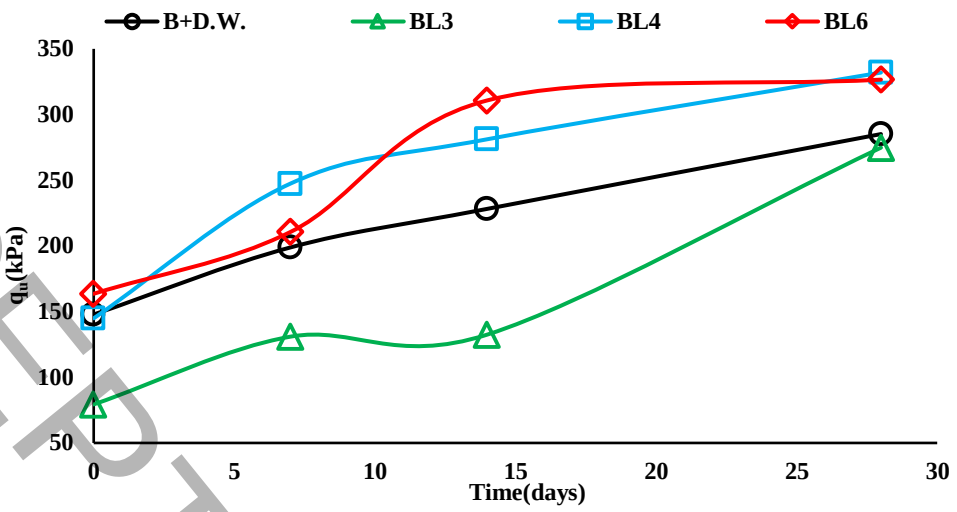


Figure 9. Variations in unconfined compressive strength of uncontaminated and lead nitrate–contaminated sand–bentonite mixtures.

According to Figure 10, in terms of UCS development over time, the higher strength of samples containing bentonite and zeolite at pH 6 and 4 is consistent with the trends observed in Figure 9. Over the 28-day curing period, samples SZB+D.W., SZB6, and SZB4 exhibited strength increases of 62%, 76%, and 128%, respectively, compared with their uncured counterparts. In contrast, the sample contaminated at pH 3 showed a slight decline in strength over time, with UCS on day 28 being 19% lower than that of the uncured sample.

Comparison of the curves in Figures 9 and 10 indicates that reducing the bentonite content in the mixture slightly decreases the overall strength gain over time. The percentage increase in UCS for sand–zeolite–bentonite mixtures is slightly lower than that of sand–bentonite mixtures, which can be partly attributed to the reduced contribution of bentonite and its thixotropic properties. The strength development of bentonite–zeolite samples over time, in addition to chemical interactions between the adsorbent and contaminant, may also be influenced by thixotropic-like behavior in zeolite. These results suggest that the inclusion of zeolite contributes to greater stability in sample strength, as evidenced by the smaller variations in UCS for mixtures containing zeolite.

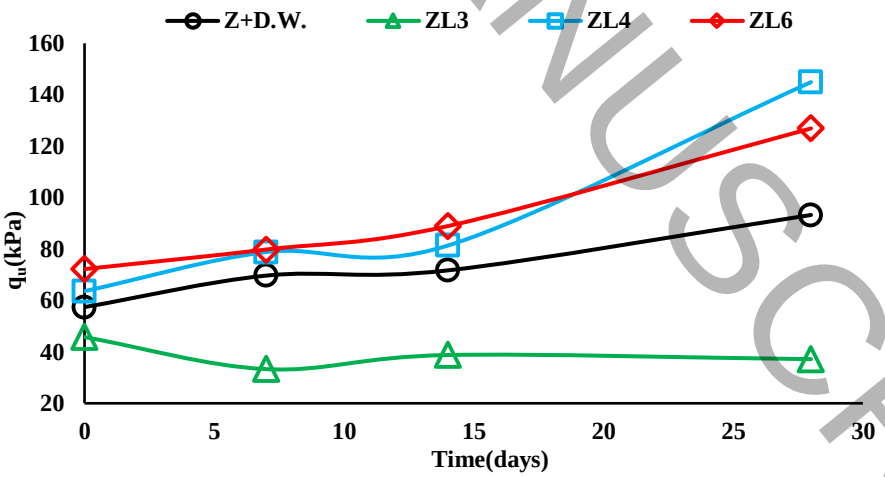


Figure 10. Variations in unconfined compressive strength of uncontaminated and lead nitrate–contaminated sand–zeolite–

.bentonite mixtures

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As shown in Figures 9 and 10, when the contaminant pH decreases to intermediate levels studied (pH = 4), an increase in UCS is observed; however, at the lowest pH, a reduction in strength occurs not only over time but throughout the entire testing period compared with other samples. Specifically, comparison of the SZBL3 results in Figure 10 with the atomic absorption spectroscopy data in Figure 8 indicates the presence of a significant amount of unabsorbed (free) heavy metal ions in zeolite-containing samples at pH 3.

The observed decrease in strength for SZBL3 can therefore be attributed to the presence of free Pb^{2+} ions in the pore fluid, which surround the more reactive fraction of the sample (fine fraction/adsorbent). At very high contaminant concentrations, the available adsorption sites in the adsorbents become saturated, leaving a portion of metal ions unattached in the pore solution. The like-charged free ions generate local electrostatic repulsion, increasing interparticle spacing, which is reflected in the increased liquid limit (Figure 6) and plasticity index (Figure 7).

The increased particle spacing and reduced interparticle attraction led to a shift from a semi-flocculated arrangement toward a more dispersed structure. Greater dispersion has two main consequences: fewer effective particle contacts and weakened stress transfer, resulting in reduced and less stable strength during curing. This behavior is clearly observed in the SZBL3 curve in Figure 10, both relative to other samples and over time.

The results highlight that while moderate lead contamination can enhance UCS, long-term accumulation of contaminants may reduce strength, and this effect should be considered in the design and performance assessment of geotechnical structures containing adsorbents.

5. Conclusion

This study investigated the effects of lead nitrate contamination at different pH levels (6, 4, and 3) on the geotechnical and adsorption behavior of bentonite and zeolite, as well as on the mechanical performance of sand mixtures containing these adsorbents. The main findings can be summarized as follows:

- ✓ Both bentonite and zeolite exhibit slightly alkaline behavior in uncontaminated conditions, with negligible pH variation over time. Lead nitrate contamination induces mild acidity, with a greater pH reduction observed at higher contaminant concentrations, particularly in zeolite.
- ✓ Lead contamination and decreasing pH reduce the liquid limit and plasticity index of bentonite, whereas zeolite shows an increase in these parameters, especially at moderate contamination levels. This highlights the different physicochemical responses of the two adsorbents to lead nitrate.
- ✓ Adsorption tests indicate that both adsorbents achieve high lead removal efficiency (>80%) at pH 6 and 4. At pH 3, bentonite maintains high adsorption efficiency, while zeolite performance decreases significantly, indicating adsorption site saturation at very high contaminant concentrations.
- ✓ Unconfined compressive strength results show that contamination at pH 6 and 4 enhances the strength of sand–bentonite and sand–bentonite–zeolite mixtures. In contrast, very high contaminant concentration (pH 3) leads to reduced strength, which is attributed to adsorption site saturation, increased free Pb^{2+} ions in pore water, and expansion of the diffuse double layer.

6. References

1. Karkush MO, Ali SD. "Effects of copper sulfate contamination on the geotechnical behavior of clayey soils." Journal of GeoEngineering 14(2019):47–52.

2. Nayak S, Sunil BM, Shrihari S. "Hydraulic and compaction characteristics of leachate-contaminated lateritic soil." Engineering Geology 94(2007).

3. Negahdar A, Shabanian MR, Nikghalbpour M. "The effect of heavy metal contaminants on the strength parameters of sandy clay." AmirKabirjournalofcivilengineering 50(2018):835–44.

4. Ouhadi VR, Amiri M, Deiranloo M. "Morphology and microstructure maintainability of heavy metal in dispersed soils."

Environmental Science and Technology 19(2016):101–13.

ACCEPTED MANUSCRIPT

5. Sunil BM, Shrihari S, Nayak S. "Shear strength characteristics and chemical characteristics of leachate-contaminated lateritic soil." Engineering Geology 106(2009):20–5.

6. Abedi Koupai J, Fatahizadeh M, Mosaddeghi MR. "Effect of pore water pH on mechanical properties of clay soil." Bulletin of Engineering Geology and the Environment 79(2020):1461–9.

7. Gori U. THE pH INFLUENCE ON THE INDEX PROPERTIES OF CLAYS INFLUENCE DU pH SUR LES PROPRII~TES DES ARGILES.

8. Huang K, Yu F, Zhou Z, Tong K, Zhang W, Dai Z, et al. Influence of pH on moisture-absorbing swelling cracks of red layer in central Sichuan and its micro-mechanism. 2022.

9. Momeni M, Bayat M, Ajalloeian R. "Laboratory investigation on the effects of pH-induced changes on geotechnical characteristics of clay soil." Geomechanics and Geoengineering 17(2022):188–96.

10. Mohapatra D, Mishra D, Chaudhury GR, Das RP. "Arsenic adsorption mechanism on clay minerals and its dependence on temperature." Korean Journal of Chemical Engineering 24(2007).

11. Potgieter JH, Potgieter-Vermaak SS, Kalibantonga PD. "Heavy metals removal from solution by palygorskite clay." Minerals Engineering 19(2006).

12. Wahba MM, Labib BF, Darwish KM, Zaghloul MA. "Application of some clay minerals to eliminate the hazards of heavy metals in contaminated soils." 15th International Conference on Environmental Science and Technology (2017).

13. Zhang D, Zhou CH, Lin CX, Tong DS, Yu WH. Synthesis of clay minerals. Applied Clay Science2010.

14. Otunola BO, Ololade OO. A review on the application of clay minerals as heavy metal adsorbents for remediation purposes. Environmental Technology and Innovation: Elsevier B.V.; 2020.

15. Green-Ruiz C. "Effect of salinity and temperature on the adsorption of Hg(II) from aqueous solutions by a Ca-montmorillonite." Environmental Technology 30(2009).

16. Hosseinzade M, Hassanlourad M, Naeini SA. "Investigating the zeolite and bentonite adsorbent effect on different parameters of soil." Proceedings of the Institution of Civil Engineers: Ground Improvement 176(2022):261–72.

17. Usman ARA, Kuzyakov Y, Stahr K. "Effect of clay minerals on extractability of heavy metals and sewage sludge mineralization in soil." Chemistry and Ecology 20(2004):123–35.

18. Zhang Z, Chen Y, Fang J, Guo F. "Study on shear behavior of kaolinite contaminated by heavy metal Cu (II)." Environmental Science and Pollution Research 26(2019):13906–13.

19. Resmi G, Thampi SG. Impact of Lead Contamination on the Engineering Properties of Clayey Soil. 2011.

20. Li Js, Xue Q, Wang P, Li Zz. "Effect of lead (II) on the mechanical behavior and microstructure development of a Chinese clay." Applied Clay Science 105-106(2015):192–9.

21. Ruhl JL, Daniel DE. "Geosynthetic Clay Liners Permeated with Chemical Solutions and Leachates." Journal of Geotechnical and Geoenvironmental Engineering 123(1997).

22. Singh S, Prasad A. "Effects of chemicals on compacted clay liner." Electronic Journal of Geotechnical Engineering 12(2007):1–15.

23. Sivapullaiah PV. "Effects of soil pollution on geotechnical behaviour of soils." Indian Geotechnical Conference 2009 (2009).

24. Hassanlourad M, Hossein Zade M, Naeini SA. "Effect of Lead Nitrate on the Behavior and Shear Strength Parameters of clayey sand." Amirkabir Journal of Civil Engineering 53(2021):575–88.

25. Sridharan A, Rao SM, Murthy NS. "Liquid Limit of Montmorillonite Soils." Geotechnical Testing Journal 9(1986).

26. Sunil BM, Nayak S, Shrihari S. "Effect of pH on the geotechnical properties of laterite." Engineering Geology 85(2006):197–203.

ACCEPTED MANUSCRIPT

27. Hassanlourad M, Khatami MH, Ahmadi MM. "Effects of sulphuric acid pollutant on the shear behaviour and strength of sandy soil and sand mixed with bentonite clay." International Journal of Geotechnical Engineering 11(2017):114–9.

28. Torabi A, Hassanlourad M. "Effect of sulfuric acid contaminant on shear strength and consolidation parameters of clay soil." Amir Kabir Journal of Civil Engineering 5(2018):1127–36.

29. Karimdad E, Bashirgonbadi M, Rahimi E. "A chemo-geotechnical approach to obtain optimal mixtures of zeolite-bentonite as heavy metal adsorbents." Bulletin of Engineering Geology and the Environment 80(2021):1193–203.

30. Soil ACD-o, Rock. Standard test method for particle-size analysis of soils: ASTM international; 2007.

31. D854-23 A. "Standard test methods for specific gravity of soil solids by the water displacement method." ASTM International, West Conshohocken, PA (2023).

32. Soil ACD-o, Rock. Standard test methods for liquid limit, plastic limit, and plasticity index of soils: ASTM international; 2010.

33. BS. "Methods of test for soils for civil engineering purposes." British Standards Institution London UK (1990).

34. Standard A. "Standard Test Method for Unconfined Compressive Strength of Cohesive Soil." (2010).

35. Soil ACD-o, Rock. Standard test methods for laboratory compaction characteristics of soil using standard effort (12 400 Ft-lbf/ft3 (600 KN-m/m3)) 1: ASTM international; 2007.

36. Bharat TV, Yadav H, Mahaur JP, Kushwaha S. "Effect of Aging Time on Consistency Limits of Bentonites." Geotechnical and Geological Engineering 38(2020).

37. Chu Y, Liu SY, Cai GJ, Bian HL, editors. A study in the micro-characteristic and electricity properties of silt clay contaminated by heavy metal zinc. 15th Asian Regional Conference on Soil Mechanics and Geotechnical Engineering, ARC 2015: New Innovations and Sustainability; 2015: Asian Regional Conference on Soil Mechanics and Geotechnical Engineering.

38. Hassanlourad M, Hosseinzade M, Karimian A, Kouhpeyma A. "Assessment of the lead and zinc contaminations on the strength and physical properties of sand mixed with kaolinite, bentonite, and zeolite fines." Bulletin of Engineering Geology and the Environment 83(2024):250.

39. Nosrati SA, Negahdar A, Negahdar H, Siavoshniaa M. "Effect of Adsorbents on Resistance Parameters of Heavy Metal-contaminated Clayey Sand Soils." International Journal of Engineering, Transactions A: Basics 35(2022):1184–91.

40. Nartowska E. "The effects of potentially toxic metals (copper and zinc) on selected physical and physico-chemical properties of bentonites." Heliyon 5(2019).

41. Ray S, Mishra AK, Kalamdhad AS. "Effect of Lead, Copper, and Zinc on Mechanical Properties of Compacted Bentonites." Journal of Hazardous, Toxic, and Radioactive Waste 26(2022).

42. Grifasi N, Ziantoni B, Fino D, Piumetti M. "Fundamental properties and sustainable applications of the natural zeolite clinoptilolite." Environmental Science and Pollution Research 32(2025):27805–40.

43. Ouhadi V, Zareie T. "The Role of Polyacrylamide Polymer in Retention of Lead Heavy Metal Contaminant." Modares Civil Engineering journal 22(2022):203–22.

44. Devapriya AS, Thyagaraj T. "Evaluation of red soil-bentonite mixtures for compacted clay liners." Journal of Rock Mechanics and Geotechnical Engineering 16(2024).

45. Gueddouda MK, Lamara M, Abou-bekr N, Taibi S. "Hydraulic behaviour of dune sand-bentonite mixtures under confining stress." Geomechanics and Engineering 2(2010).

46. Thakur Y. "Geotechnical Characteristic of Compacted Sand Bentonite Mixture." International Journal for Research in Applied Science and Engineering Technology 6(2018).

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