

Article

Application of Natural and Modified Zeolite Sediments for the Stabilization of Cadmium and Lead in Contaminated Mining Soil

Sami S. Alotaibi, Hesham M. Ibrahim *  and Abdulaziz G. Alghamdi 

Department of Soil Sciences, College of Food and Agricultural Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia; 439106000@student.ksu.edu.sa (S.S.A.); agghamdi@ksu.edu.sa (A.G.A.)

* Correspondence: habdou@ksu.edu.sa

Featured Application: The modification of natural zeolite sediments can provide a low-cost and eco-friendly adsorbent with high sorption capacity that can help to remediate mining soil and other soils contaminated with heavy metal contaminants.

Abstract: Soil contamination by many kinds of anthropogenic operations, such as industrial and mining activities, results in the accumulation of various heavy metal contaminants in the environment. Cadmium (Cd) and lead (Pb) are commonly found heavy metals in the Mahad Adahab mining area in Saudi Arabia. In this study, natural and modified zeolite sediments were fractioned by size to nano- and macrosizes and were applied to stabilize Cd and Pb from contaminated mining soil. Among the tested adsorbents, zeolite sediment in the nanosize that was modified by layered double hydroxides (LDH-N) showed the highest sorption and removal efficiency (>98%) for Cd and Pb, followed by nanosized natural zeolite (NZ-N) and HCl-modified nanosized natural zeolite sediment (HCl-N), which removed >90% Cd and Pb from contaminated soil. A pH of 7 was found to be optimal for Cd and Pb sorption, and the kinetics study revealed that first-order and pseudo-second-order kinetic models best fitted the experimental data ($R^2 = 0.94\text{--}0.98$) for Cd and Pb sorption by the tested sediments. An incubation period of 16 weeks revealed that LDH-N, HCl-N, and NZ-N reduced the ammonium acetate extractable fraction of Cd by 89.26, 83.70, and 80.54% and Pb by 86.19, 81.42, and 77.98%, respectively. Electrostatic interaction and ion exchange were found to be the principal mechanisms for Cd and Pb sorption. The findings of this study indicate that the utilization of modified zeolite sediment in the nanosize fraction (LDH-N, HCl-N, and NZ-N) could be an effective and feasible strategy in stabilizing heavy metals and mitigating their toxicity in contaminated mining soil.

Keywords: natural zeolite sediment; zeolite modification; soil contamination; soil remediation; stabilization of heavy metals; sorption



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1. Introduction

In recent decades, the large increase in anthropogenic operations, including industrial productions, mining activities, and fossil fuel extraction, has resulted in widespread environmental pollution. Such actions generate a pathway for the accumulation of many kinds of harmful substances and heavy metals into terrestrial and aquatic ecosystems, which consequently disturbs the biogeochemical balance of the ecosystem. When they are in their natural balance, such heavy metals do not present any significant contamination risk, but due to their toxic, persistent, and nondegradable nature, their continuous and excessive release into the environment results in severe environmental pollution, disrupts flora and fauna, and imperils human health [1–3]. Mining activities are linked to the discharge of many kinds of toxic heavy metals into the terrestrial and aquatic environment, causing bleak contamination of these natural resources, disturbing the landscape, and subsequently

increasing soil degradation and making the soil unsuitable for agricultural practices [4,5]. It is quite challenging to perform agricultural activities with heavy-metal-contaminated soils that are found in the vicinity of mining areas. In addition, plants grown in such contaminated sites were found to accumulate larger concentrations of hazardous heavy metals in their edible parts. Among these heavy metals, lead (Pb) ranks second after arsenic (As) in the list of hazardous heavy metals due to its potentially toxic nature and global manifestation [6]. The higher accumulation of Pb in the ecosystem severely affects the soil and water bodies, threatens plant growth and microbial activity, and poses a health risk to human beings, including abridged educational performance in children, truncated social skills, and inhibited physical activities among adults [7]. In addition to Pb, cadmium (Cd), which is usually released from mining activities and domestic wastes, is also classified as a hazardous heavy metal, which severely disturbs soil quality, interrupts plant growth, and poses serious human health risks, including kidney damage and bone fracture [8].

Restoration of such mining-contaminated soils to make them suitable for regular agricultural activities is extremely important to sustain environmental resources and to protect human health. Many kinds of physical, chemical, and biological techniques have been applied to rehabilitate such contaminated soils [9]. Metal stabilization and soil immobilization are key strategies by the application of chelating agents, solvent extraction techniques, thermally treating soil, and various soil amendments; adsorption is also a frequently practiced technique to remediate soils contaminated with heavy metals [10]. Most of these techniques are expensive, employ costly chemicals and excessive salts, and generate secondary pollution [11]. Recently, soil remediation with inorganic amendments and reactive minerals, such as carbonates, phosphate rocks, natural clay deposits, and zeolites, have gained desirable attention as a feasible and economical technique to reduce metal accumulation in soil without disturbing the soil's natural functions [12,13].

Natural zeolites, which are found globally, have a three-dimensional silicon and oxygen tetrahedron lattice crystal structure and possess a unique structural composition and mineral contents [14]. An estimated 70 different kinds of natural zeolites have been discovered, and more than 250 different zeolites have been prepared synthetically [15]. Owing to their unique characteristics, such as promising physiochemical properties, easy availability, economic feasibility, and excellent adsorptive characteristics, natural zeolites have attained ample attention as an environmentally friendly material to stabilize and remove toxic heavy metals from soil and aqueous media [16]. The structural properties and composition provide zeolites with great ion exchangeability, which subsequently results in the strong and selective adsorption of some specific metal ions. Also, the removal efficiency of zeolites depends on the physiochemical and structural properties of zeolites and the type of pollutants, such as mono- and divalent cations, mono- and divalent anions, and organic and inorganic pollutants [17]. However, due to the abundant presence of some impurities, the porous surface of natural zeolite can become clogged, which ultimately decreases its specific surface area and reduces its efficiency in removing heavy metals and other pollutants from the environment. Many kinds of techniques have been employed to improve natural zeolite performance for environmental remediation by enhancing its surface porosity and specific surface area; however, the efficiency of each technique is limited to the zeolite's structural stability [18]. The modification of natural zeolites with surfactants, metal oxides, single or combined thermal treatment, and reaction with chemicals (acid, base, and inorganic salts) are commonly practiced techniques to increase performance in environmental remediation [19]. Christidis et al. [20] found enhanced surface area and surface porosity after pretreating natural zeolites with acid and base compounds, which ultimately enhanced their performance for heavy metal stabilization.

In addition to chemical modification, physical/mechanical modification of natural zeolites to nanoparticle size exhibits great potential in immobilizing heavy metals in soil. Converting zeolite amendments to nanosize particles enhances specific surface area and improves pore size and pore volume, which ultimately results in more available active sites to stabilize and adsorb heavy metals [21,22]. Li et al. [23] reported that application

of a 5% micro-sized zeolite amendment reduced soil Cd contents by 22%, while reducing the zeolite size to nanoscale (NZ) improved its efficiency exponentially by mitigating Cd and Cu concentration in soil by 20 folds [24,25]. In another study, Nguyen and Van [26] reported amplification of surface area and higher adsorption capacity of NZ sediments by mechanically modifying their size to nanoscale. Likewise, Van et al. [27] conducted an incubation study to assess the potential impact of NZ and its derivative layered double hydroxide (LDH)-modified NZ in mitigating the availability of Cd and Pb in contaminated soil and found a 50% reduction of extractable Cd concentration from 22.17 mg kg^{-1} to 11.03 mg kg^{-1} using NZ, and from 22.17 mg kg^{-1} to 6.47 mg kg^{-1} using LDH-NZ, whereas Pb extractable concentration was dropped from 23.28 mg kg^{-1} to 14.12 mg kg^{-1} in NZ-treated soil and from 23.28 mg kg^{-1} to 9.47 mg kg^{-1} in LDH-NZ-treated soil.

To the best of our knowledge, most of the research work on zeolite application has focused on the utilization of natural zeolite sediments to remove heavy metals from terrestrial and aqueous systems. In contrast, limited research has focused on the chemical and physical modification of zeolite and their impacts on the stabilization of heavy metals from contaminated soil. Therefore, the objective of this research was to evaluate the effect of chemical modification of locally collected zeolite sediments with a combination of techniques using acid, base, and LDH compounds and the physical separation of zeolite sediments to micro- and nanoparticle sizes on the physiochemical and surface characteristics of zeolite sediments and their efficiency in the stabilization of Cd and Pb from contaminated mining soil.

2. Materials and Methods

2.1. Collection of Soil and Zeolite Sediments

Soil samples were collected from the Mahad Adahab gold mining area, located in the western north part of the Kingdom of Saudi Arabia (KSA) ($23^{\circ}29'59.88''$ N and $40^{\circ}51'56.72''$ E). The climate in the study area is mostly warm and dry, with temperatures reaching $40\text{--}45^{\circ}\text{C}$ during summer, but it is often cold during winter, with temperatures reaching as low as 7°C . Soil samples were collected in patches at 0–20 cm depth, and a composite soil sample was prepared by mixing collected soil samples. Natural zeolite deposits were collected from Harrat Shama, which is in the western part of KSA, about 120 km southeast of Jeddah city ($20^{\circ}41'1.66''$ N and $39^{\circ}41'45.15''$ E). Collected soil and sediment samples were sealed in airtight plastic bags and carefully moved to the Soil Physics Laboratory, Soil Science Department, King Saud University, Riyadh, Saudi Arabia. The soil samples were air-dried and sieved using a 2 mm sieve to remove gravel and other bigger particles.

2.2. Preparation and Modification of Zeolite Sediments

The collected sediments were washed with deionized water (DI) to remove impurities, air-dried at room temperature for 48 h, crushed, and sieved to $<0.1 \text{ mm}$ particle size. The sieved zeolite sample was saved in an airtight acrylic container and tagged as NZ. Later, the NZ sample was treated with Mg/Al layered double hydroxides (LDHs) by following the coprecipitation method proposed by Dang et al. [28]. Briefly, in a glass beaker, $0.01 \text{ M Al}(\text{NO}_3)_3$ and $0.02 \text{ M Mg}(\text{NO}_3)_2$ were mixed in 100 mL DI water, followed by the addition of NZ and LDH/NZ in a 3:7 ratio. The solution pH was adjusted to 11 using 1 M NaOH and $0.5 \text{ M Na}_2\text{CO}_3$ solutions. The solution was shifted to a hotplate and mixed thoroughly at 80°C for 4 h until a homogeneous mixture was obtained. Later, the solution was removed from the hotplate and was filtered by Whatman filter paper 42. The solid material was collected from filter paper, which was further washed three times with DI water to remove impurities. The collected solid material was oven-dried at 70°C , grounded to a fine particle size, stored in airtight acrylic containers, and tagged as LDH-Z. The NZ also was treated with HCl, NaOH, and NaCl solutions of different concentrations by following the Wen et al. [29] method to produce HCl-Z, NaOH-Z, and NaCl-Z. Briefly, in a conical flask, 5 g of NZ was mixed with 2 M HCl , NaOH, and NaCl solutions separately. The flask

was placed in a bathtub, and it was shaken for 3 h at 75 °C, followed by centrifugation at 3000 rpm for 15 min. The supernatant liquid was discarded, and solid residues of sediments were collected, washed with DI water, filtered, and oven-dried at 70 °C for 48 h. Later, oven-dried sediments were collected and stored in an airtight acrylic container with separate tags for HCl-Z, NaOH-Z, and NaCl-Z. All the collected and modified NZ sediments (HCl-Z, NaOH-Z, NaCl-Z, and LDH-Z) were further grounded to micro- and nanosize particles separately. The dried particles of NZ and modified NZ were crushed and sieved to obtain the macroparticle size of <50 µm. To obtain nanoparticle size of NZ and modified NZ, 10 g of dried NZ and modified NZ particles (<0.1 mm) were immersed in 1 L of DI water. The suspension was sonicated for 30 min (Ultrasonic sonicator Q700, Qsonica, Newtown, CT, USA) and left for gravity sedimentation for 24 h. Nanoparticles suspended in the upper 5 cm of the beaker were extracted using a siphon method. Later, more DI water was added to the suspension to make a final 1 L suspension volume, and the suspension was sonicated for 5 min. The cycle was repeated until large enough amounts of nanoparticles of NZ and modified NZ were collected. The collected nanoparticles were oven-dried at 40 °C and stored in tight containers until use. Table 1 describes a full list of the natural and modified sediments. Analytical-grade chemicals (HCl, NaOH, NaCl, Ca(OH)₂, Na₂CO₃, NaOH, K₂CrO₄, Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, NH₄OAc, and HNO₃) were purchased from local suppliers in Riyadh city and were used to modify NZ sediments and for further studies.

Table 1. The natural and modified sediments with micro- and nanoparticle sizes.

No	Sediment Name	Description
1	NZ-M	Natural zeolite with microparticle size.
2	NZ-N	Natural zeolite with nanoparticle size.
3	LDH-M	LDH-modified zeolite with microparticle size.
4	LDH-N	LDH-modified zeolite with nanoparticle size.
5	HCl-M	HCl-modified zeolite with microparticle size.
6	HCl-N	HCl-modified zeolite with nanoparticle size.
7	NaOH-M	NaOH-modified zeolite with microparticle size.
8	NaOH-N	NaOH-modified zeolite with nanoparticle size.
9	NaCl-M	NaCl-modified zeolite in the microparticle size.
10	NaCl-N	NaCl-modified zeolite in the nanoparticle size.

2.3. Characterization of Soil Samples

Air-dried and sieved soil samples were analyzed for their physiochemical and surface characteristics. Soil pH and electrical conductivity (EC) were measured using the soil paste extraction method [30]. The soil paste extract was analyzed by pH (WTW-pH 523) and an EC meter (YSI Model 35) to determine soil pH and EC value. The sparks [31] method was followed to determine cation exchange capacity (CEC), while CaCO₃ contents of soil were determined using the calcimeter method [32]. Soil texture was examined using the hydrometer method [33], while the Walkley and Black [34] method was followed to determine soil organic matter (OM) contents. To determine trace elements, soil samples were digested using the Hossner [35] method, and digested soil samples were analyzed by inductively coupled plasma-optical emission spectrometry (Perkin Elmer Optima 4300 DV ICP-OES, Shelton, CT, USA).

2.4. Characterization of Natural and Modified Zeolite Sediments

Collected and modified NZ samples were analyzed for their physiochemical and surface properties by following standard protocol. Briefly, pH and EC were measured by making a suspension in deionized water in a 1:5 *w/v* ratio [36], while CEC was measured by following the standard method of Sparks [37]. Likewise, collected and synthesized sediments were analyzed by scanning electron microscopy (SEM, EFI S50 Inspect, Eindhoven, The Netherlands) for their surface morphology, while crystallinity and mineral composition of samples were determined by an X-ray diffractometer (MAXima_X XRD-7000, Shimadzu,

Tokyo, Japan). The surface area, pore volume, and pore size of NZ and modified zeolites were measured using the Brunauer–Emmett–Teller (BET) method, using N₂ gas at 77 K (Accelerated Surface Area and Porosity, ASAP 2020, Micromeritics, Norcross, GA, USA). The thermogravimetric analysis (TGA, DTG-60H, Shimadzu, Tokyo, Japan) technique was used for the measurement of changes in the physical and chemical properties of NZ and modified zeolites with constant temperature increase. Weight loss of NZ and modified zeolites was recorded with the rise in temperature from 0 to 800 °C. Fourier transform infrared spectroscopy (Bruker Alpha-Eco ATR-FTIR, Bruker Optics, Inc., FTIR, Billerica, MA, USA) was used to identify various functional groups in NZ and modified zeolite samples.

2.5. Adsorption Experiment

To assess the efficiency of collected and modified NZ sediments for heavy metal (Pb, Cd) sorption from contaminated soil, a series of adsorption batch experiments were conducted to examine the effect of initial solution pH, adsorbent (sediments) dose, particle size, and contact time. Initially, 5 g of collected soil (contaminated mining soil) was added to polypropylene tubes; adsorbents (Table 1) were added at 0.5, 1, 2, 4, and 8.0% (*w/w*). Twenty-five mL of DI water (1:5 *w/v*) was added, and the tubes were placed in a reciprocal shaker for 24 h at 140 rpm. Solution pH was adjusted to 7 using 0.1 M solutions of HCl and NaOH. The pH of the suspension was also measured before and after shaking to examine variation in pH values. The pH measurements showed no significant variations in the adjusted pH values throughout the adsorption experiment. Tubes were removed from the shaker and centrifuged for 15 min at 3000 rpm. Afterwards, supernatant liquid was collected and analyzed by ICP-OES for Pb and Cd concentrations. All treatments were performed in triplicate, and a control treatment was added with soil only and no added adsorbent.

To observe the effect of pH on adsorbent efficiency for Pb and Cd adsorption, a separate adsorption experiment was conducted. Briefly, out of total adsorbents (10) employed in the previous adsorption batch experiment, three best-performing adsorbents were selected. Similar to previous adsorption trials, 5 g of contaminated soil was taken in polypropylene tubes, adsorbents were added at 2% (*w/w*), and pH was adjusted at 5, 6, 7, 8, and 9 using 0.1 M solutions of HCl and NaOH. Again, the pH of the suspension was measured before shaking and after the completion of the shaking time to examine any variation in pH values. The pH measurements showed no significant variations in the adjusted pH values throughout the experimental time. All treatments were performed in triplicate, and a control treatment was added with soil only and no added adsorbent.

The removal efficiency of adsorbent for heavy metals (Pb, Cd) was calculated using the following equation:

$$\text{Removal efficiency (\%)} = \left(1 - \frac{C_e}{C_i}\right) \times 100 \quad (1)$$

where C_i and C_e are the initial and supernatant concentrations of Cd and Pb, respectively. Adsorption of Pb and Cd per unit volume of adsorbent was investigated using the following equation [38]:

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (2)$$

where C_o is the initial concentration of Pb and Cd (mg L^{−1}), C_e is the equilibrium concentration of Pb and Cd (mg L^{−1}), V is the volume of the DI water (L), m is the mass of the adsorbent (g), and q_e is the adsorbed Pb and Cd concentration (mg g^{−1}) at equilibrium.

2.6. Kinetics Study

A kinetic experiment was conducted to check the impact of contact time on the adsorption of the tested heavy metals by the employed adsorbents. A similar protocol was followed as in the adsorption experiment, except for using variable contact time. The best-

performing three adsorbents were added to 5 g of contaminated soil at a 2% *w/w* application rate in a polypropylene tube with 25 mL DI water. The pH was adjusted at 7 using 0.1 M solutions of HCl and NaOH. The tubes were placed in a reciprocal shaker, and samples were taken at regular time intervals of 0.5, 1, 4, 8, 16, and 24 h. Collected samples were analyzed by ICP-OES to observe Pb and Cd concentrations in solution. All treatments were performed in triplicate, and a control treatment was added with soil only and no added adsorbent. Additionally, the experimental data were further analyzed by employing first-order and pseudo-second-order kinetic models, as described in Equations (3) and (4) [37].

$$\text{First-order model : } \ln q_t = \ln q_o - k_1 t \quad (3)$$

$$\text{Pseudo-second-order model : } \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q} t \quad (4)$$

where q_t is the adsorbed quantity of Pb and Cd (mg kg^{-1}) by the sorbents at time t (min), and q_o is the adsorbed quantity of Pb and Cd at $t = 0$. k_1 and k_2 represent rate constants of the first order and second order ($\text{mg kg}^{-1} \text{min}^{-1}$), respectively.

2.7. Effect of Incubation Period on Metal Stabilization

A separate experimental study was conducted to assess the effect of the incubation period on the stabilization of metals by tested adsorbents in the contaminated mining soil. Briefly, 50 g of the contaminated soil was placed in an airtight plastic container (5 cm ID and 10 cm height). The contaminated soil was thoroughly mixed with the best three selected adsorbent materials at an application rate of 2% (*w/w*). The soil moisture inside the plastic containers was kept at 60% of field capacity (FC). Water loss was compensated every 2 days to maintain moisture content at the designated level. The plastic containers were incubated at 23 ± 2 °C in the laboratory for a period of 1, 2, 4, 8, and 16 weeks. At the end of each incubation period, soil samples were collected from the plastic containers and were extracted with 1 M ammonium acetate (NH_4OAc) to determine extractable Cd and Pb contents in soil. Each treatment was analyzed in triplicate to minimize potential analytical errors.

2.8. Statistical Analysis

Statistical analysis of the experimental data was carried out using the software SPSS for Windows (version 18, SPSS Inc., Chicago, IL, USA). All experiments were conducted in three replicates. Data are presented as averages followed by their standard deviation (± 1 SD). To assess the differences among the means of the three replicates, the least significant difference (LSD at $p < 0.01$) test was applied.

3. Results and Discussion

3.1. Characterization of the Collected Soil

The soil was found to be slightly alkaline ($\text{pH} = 7.8$), with a low EC value (0.38 dSm^{-1}), which indicates that the soil has a low concentration of soluble salts (Table 2). Similarly, CaCO_3 (2.38%) and OM (0.84%) contents of the soil were found consistently in the lower range, which indicates that the soil is not calcareous and has low OM content. Soil texture was classified as sandy loam with a higher percentage of sand particles (73.52%). Contrarily, the total contents of trace elements were found in higher concentrations in the soil sample; especially, Cd, Pb, Zn, and Cu were found to be above the standard limits of the World Health Organization (WHO), which recommend concentrations of heavy metals to be less than 3 mg kg^{-1} for Cd, 100 mg kg^{-1} for Pb, 100 mg kg^{-1} for Cu, and 300 mg kg^{-1} for Zn [39]. These results indicate that the soil around the Mahad Adahab gold mining area is contaminated with multiple heavy metals. Contamination of the soil around mining areas is quite anticipated due to mining activities [40].

Table 2. Physiochemical characteristics and total contents of trace elements in the collected soil.

EC (dSm ^{−1})	pH (1:2.5)	CEC (cmol kg ^{−1})	OM (%)	CaCO ₃ (%)	Texture
0.4 ± 0.1	7.8 ± 0.2	9.3 ± 1.2	0.8 ± 0.1	2.4 ± 0.4	Sandy loam
Total Metal Concentration (mg/kg)					
Cd	Cu	Ni	Pb	Zn	As
13.0 ± 1.6	458.1 ± 8.6	116.7 ± 0.4	193.5 ± 0.3	1864.1 ± 0.9	16.2 ± 0.8

EC, electrical conductivity; CEC, cation exchange capacity; OM, organic matter; CaCO₃, calcium carbonate. Values are presented as averages followed by ±1 SD.

3.2. Characterization of the Zeolite Sediments

Chemical analysis of NZ and its modified variants showed distinctive variations among chemical properties (Table 3). NaOH-modified NZ showed the highest pH (9.76–11.23), which was quite anticipated due to the alkali treatment of NZ. On average, pH values were increased by 3.10 and 2.11 units, respectively, for micro and nano variants of NaOH-treated sediments. pH was decreased by 3.01 and 3.62 units in HCl-M and HCl-N sediments against NZ sediments, suggesting a possible impact of acidic treatment of NZ, whereas minor variations were found among pH of NZ (NZ-M, NZ-N), LDH (LDH-M), and NaCl (NaCl-M, NaCl-N) sediments, and pH was increased by the following trend: NaCl > LDH > NZ. In general, a decline in pH value was noted by converting sediments from microparticle size to nanoparticle size, suggesting protonation of surface functional groups by pretreatment of NZ sediments [22]. The EC of all examined sediments was found to be consistently low, and the highest EC was found in NaOH-M (2.30 dS m^{−1}), followed by NaCl-M (1.99 dS m^{−1}) and NZ-M (1.89 dS m^{−1}). Similar to pH, a decline in EC value was recorded by converting sediment particle size from micro- to nanoparticles.

Table 3. Chemical characteristics of collected and modified NZ sediments.

No	Sediments	pH (1:5 w/v)	EC (dSm ^{−1})	CEC (cmol kg ^{−1})
1	NZ-M	8.1 ± 0.1	1.9 ± 0.1	17.1 ± 1.1
2	NZ-N	7.6 ± 0.1	0.3 ± 0.1	62.4 ± 1.4
3	LDH-M	8.3 ± 0.1	0.7 ± 0.1	72.2 ± 1.5
4	LDH-N	7.9 ± 0.1	0.6 ± 0.1	81.7 ± 1.9
5	HCl-M	6.1 ± 0.1	0.3 ± 0.1	35.2 ± 1.0
6	HCl-N	6.0 ± 0.1	0.2 ± 0.1	60.3 ± 1.4
7	NaOH-M	11.2 ± 0.2	2.3 ± 0.1	36.1 ± 1.1
8	NaOH-N	9.7 ± 0.2	1.3 ± 0.1	68.8 ± 1.8
9	NaCl-M	8.9 ± 0.1	1.9 ± 0.1	24.8 ± 1.1
10	NaCl-N	8.0 ± 0.1	0.8 ± 0.1	49.7 ± 1.3

NZ-M = natural zeolite with microparticle size, NZ-N = natural zeolite with nanoparticle size, LDH-M = LDH-zeolite with microparticle size, LDH-N = LDH-zeolite with nanoparticle size, HCl-M = HCl-zeolite with microparticle size, HCl-N = HCl-zeolite with nanoparticle size, NaOH-M = NaOH-zeolite with microparticle size, NaOH-N = NaOH-zeolite with nanoparticle size, NaCl-M = NaCl-zeolite in the microparticle size, NaCl-N = NaCl-zeolite in the nanoparticle size. Values are presented as averages followed by ±1 SD.

All sediments showed a high CEC value, indicating the presence of exchangeable cations and oxygenated surface functional groups. Again, nanoparticle size variants of sediments showed plausible increases in CEC, and the highest CEC was found in LDH-N (81.74 cmol kg^{−1}), followed by LDH-M (72.22 cmol kg^{−1}), NaOH-N (68.87 cmol kg^{−1}), and NZ-N (62.43 cmol kg^{−1}). Similar results were reported by Bezerra et al. [41] and Ates and Akgül [42], who found an increment in CEC of LDH and NaOH-treated NZ sediments. Also, the occurrence of oxygenated surface functional groups in LDH and NaOH-treated NZ was confirmed by FTIR, which could be a possible reason for the high CEC value of these sediments.

The XRD analysis of raw and modified zeolite sediments indicated the presence of the mineral clinoptilolite (CP) (Figure 1). Characteristic peaks of clinoptilolite (CP) were found at 10.06 Å, 9.01 Å, 4.78 Å, 4.02 Å, 3.94 Å, 3.41 Å, 3.03 Å, and 2.88 Å in all sediments [43]. In the microparticle size of NZ (NZ-M), small to medium peaks of CP were found, which became sharp and slightly shifted to the right side in the nanoparticle size of NZ (NZ-N), which indicated a possible impact of the pretreatment on the modification of the particle size of NZ. Similar to NZ-N, sharp peaks of CP were found in LDH-N, HCl-N, NaOH-N, and NaCl-N against their microparticle size variants, which, again, showed the possible impact of the pretreatment process of extracting the nanosized particles of the NZ sediments. Especially in NaCl-N, sharp vibrations of CP minerals were found along with broad peaks, which were also observed slightly in its microparticle size variant. In addition to CP, calcite (1.60 Å, 1.54 Å), quartz (2.18 Å, 2.59 Å), and feldspar (3.94 Å, 2.88 Å) minerals were also found in the crystalline composition of natural and modified zeolites [44]. Multiple characteristic peaks in LDH-N indicated effective growth of LDH crystals on NZ particles, and peak intensity showed a higher degree of crystallinity in LDH-NZ composites [22,45]. Likewise, an additional peak of hydroxysodalite was found at 2.31 Å in the NaOH-treated NZ sample [42].

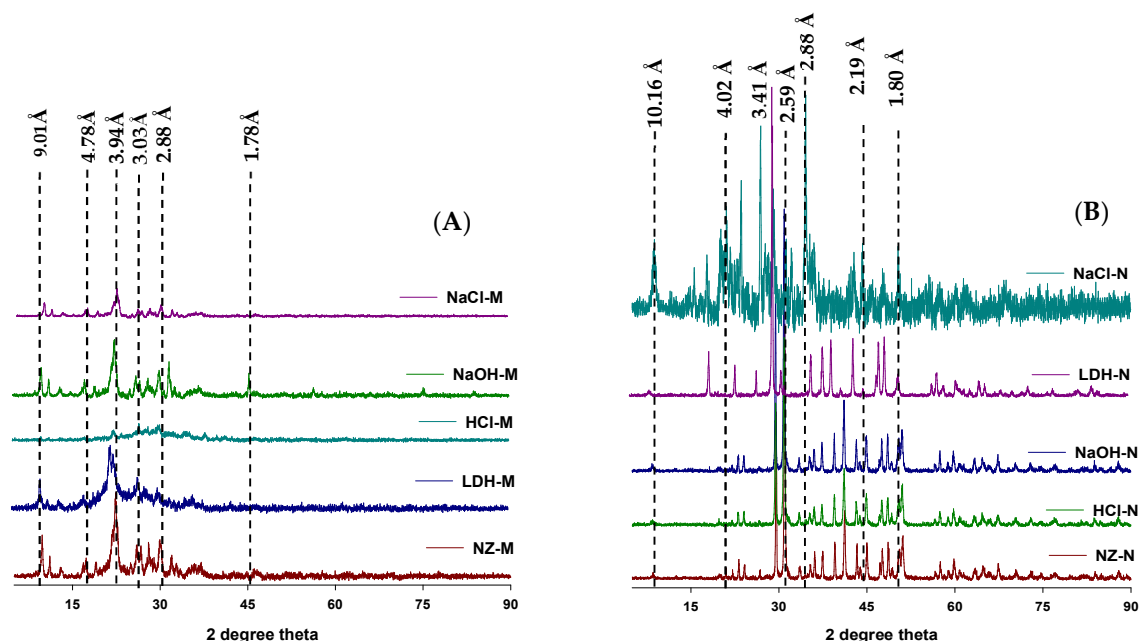


Figure 1. XRD analysis of natural and modified zeolite sediments. (A) NZ-M, natural zeolite with microparticle size; LDH-M, LDH-zeolite with microparticle size; HCl-M, HCl-zeolite with microparticle size; NaOH-M, NaOH-zeolite with microparticle size; NaCl-M, NaCl-zeolite in the microparticle size. (B) NZ-N, natural zeolite with nanoparticle size; HCl-N, HCl-zeolite with nanoparticle size; NaOH-N, NaOH-zeolite with nanoparticle size; LDH-N, LDH-zeolite with nanoparticle size; NaCl-N, NaCl-zeolite in the nanoparticle size.

The morphological structures of natural and modified NZ sediments were analyzed by SEM analysis (Figure 2). The SEM analysis indicated that by converting microparticle size into nanoparticle size, all sediments showed smoother surfaces and developed surface porosity, which was quite anticipated. It enhanced specific surface area, which was also confirmed by BET analysis of sediments (Table 3). While treating NZ sediments with alkali, acid and LDH made the NZ surface rough, indicating accumulation of Al and Si clusters, which was also found by FTIR analysis of NZ and its modified variants [46]. HCl and NaOH-treated NZ showed higher surface porosity with channeled and tubular structures, while LDH-treated NZ surface became amorphous due to the accumulation of Al-O and Si-O clusters during pretreatment.

The FTIR spectra of collected and modified NZ sediments indicated the presence of diverse surface functional groups (Figure 3). Bands at $3500\text{--}3700\text{ cm}^{-1}$ indicated the bending mode of OH, indicating water molecules in all natural and modified zeolite sediments, which were steeper and sharper in NZ-N and NaCl-N [42]. These bands and small peaks presenting water molecules appeared again at the $1600\text{--}1650\text{ cm}^{-1}$ wavelength range. The intensities of OH were slightly affected by acidity (HCl), alkalinity (NaOH), and LDH treatment of NZ. Also, small vibrations of NO_3^- groups were found in LDH-treated NZ, which indicated successful incorporation between LDH and NZ particles [41]. The bands at the $500\text{--}700\text{ cm}^{-1}$ range were assigned to Si-O groups, while Al-O peaks were located in the 1000 cm^{-1} and 1500 cm^{-1} wavelength ranges [47]. The strong peaks at 800 cm^{-1} were assigned to Al-O and Si-O groups, which were located again at 2500 cm^{-1} . Water molecules were found combined with Al-O and Si-O, indicating the occurrence of hydroxides of Al and Si [18]. Overall, most of the peaks and bands were found at strong intensity, which was ascribed to the strong absorbance of NZ and its modified variants.

Thermal stability of NZ and its fabricated zeolite sediments was studied as a function of weight loss against increasing temperature (Figure 4). Various decomposition stages of zeolite samples were observed. The first degradation stage was found at $100\text{--}130\text{ }^\circ\text{C}$, which described the removal of water molecules by thermal treatment of zeolite sediments [48]. All tested sediments showed initial thermal degradation except for NZ-N, NaCl-M, HCl-N, and NaOH-M. The initial weight loss (first stage) described the dehydration of loosely bonded and physisorbed water, while the later stage (second stage) of weight loss as a function of dehydration of zeolite samples was attributed to the desorption of strongly bonded water molecules with extra framework and ionic attachment [49]. Minimum weight loss ($<10\%$) was found in these sediments (NZ-N, NaCl-N, HCl-N, and NaOH-N) up to a $400\text{ }^\circ\text{C}$ increase in temperature, which showed strong bonding and adhesion of water molecules with zeolite particles and ample abundance of hydroxyl species. Also, these zeolite sediments (NZ-N, NaCl-N, HCl-N, and NaOH-N) showed strong stability up to $700\text{ }^\circ\text{C}$ and witnessed minimum weight loss. The higher thermal stability indicated that the tested NZ and its derived sediments had strongly adsorbed water molecules on the CP mineral, which has strong structural stability and thermal resistance [50]. The presence of water molecules and CP mineral contents were also confirmed by the results of the XRD and FTIR analysis. An abrupt and quick degradation of sediments was observed at $800\text{--}900\text{ }^\circ\text{C}$, indicating a higher dehydration rate, affected by temperature increase.

Surface area analysis of natural and modified zeolite sediments showed a significant impact of the difference in particle size (Table 4). All sediments with nanosize particles have significantly higher surface area against their microsize variants, and more than a 50% enhancement in surface area of nanosize sediments was noted against microsize particle sediments. The maximum increment in surface area was found in LDH-N ($37.195\text{ m}^2\text{ g}^{-1}$), followed by HCl-N ($36.145\text{ m}^2\text{ g}^{-1}$) and NaOH-N ($35.146\text{ m}^2\text{ g}^{-1}$). The surface area of micro- and nanosize particles of modified sediments was found to be almost double that of the unmodified NZ sediments, which also confirms the successful modification of the employed sediments. Contrarily, the pore volume was reduced in nanosize sediments except for NaOH-N ($0.112\text{ cm}^3\text{ g}^{-1}$), whose microsize variants have a smaller pore volume ($0.067\text{ cm}^3\text{ g}^{-1}$). Likewise, pore size was also decreased in nanosize sediments, and LDH-N pronounced a maximum decrease in pore size of 50.36%, followed by a decrease of 48.73% in NZ-N and 45.80% in NaCl-N. Smaller pore volume and smaller pore size are obvious in materials with a higher surface area. Higher surface area and smaller pore size in LDH-N sediments indicated excellent surface porosity, which could be due to deeper incorporation of LDH particles with NZ particles during pretreatment [41]. It is expected that as the particle size of the zeolite sediment becomes smaller, more surface becomes exposed and, hence, the specific surface area increases. In addition, at a smaller particle size fraction, microporosity could increase, leading to the formation of additional internal surfaces that contribute to the increase in the total surface area of the zeolite sediment in the nanosized

fraction. A similar trend of increasing zeolite sediment surface area with smaller particle size was reported by Wahono et al. [21] and Elkartehi et al. [22].

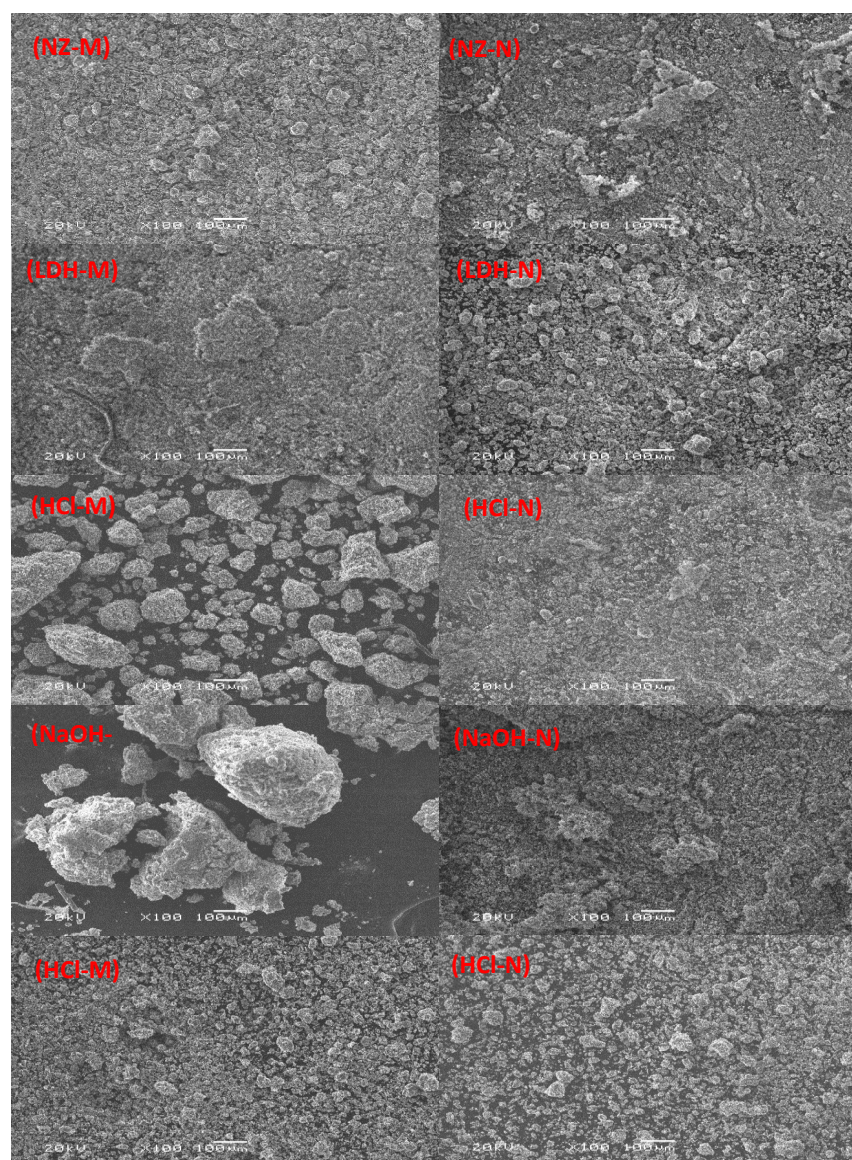


Figure 2. SEM analysis of natural and modified zeolite sediments. NZ-M, natural zeolite with microparticle size; NZ-N, natural zeolite with nanoparticle size; LDH-M, LDH-zeolite with microparticle size; LDH-N, LDH-zeolite with nanoparticle size; HCl-M, HCl-zeolite with microparticle size; HCl-N, HCl-zeolite with nanoparticle size; NaOH-M, NaOH-zeolite with microparticle size; NaOH-N, NaOH-zeolite with nanoparticle size; NaCl-M, NaCl-zeolite in the microparticle size; NaCl-N, NaCl-zeolite in the nanoparticle size.

Table 4. Surface area and microporosity analysis of natural and modified zeolite sediments.

Sample	BET Surface Area	Pore Volume	Pore Size
	($\text{m}^2 \text{g}^{-1}$)	($\text{cm}^3 \text{g}^{-1}$)	($\text{\AA}$)
NZ-M	9.1 ± 0.1	0.023	101.328
NZ-N	20.8 ± 0.2	0.027	51.947

Table 4. Cont.

Sample	BET Surface Area (m ² g ^{−1})	Pore Volume (cm ³ g ^{−1})	Pore Size (Å)
LDH-M	19.7 ± 0.1	0.051	103.852
LDH-N	37.2 ± 0.3	0.046	51.551
HCl-M	14.8 ± 0.1	0.028	76.746
HCl-N	36.1 ± 1.3	0.115	124.087
NaOH-M	15.4 ± 0.2	0.067	175.916
NaOH-N	35.1 ± 0.7	0.112	128.437
NaCl-M	11.3 ± 0.1	0.027	96.939
NaCl-N	23.4 ± 0.3	0.025	49.919

NZ-M, natural zeolite with microparticle size; NZ-N, natural zeolite with nanoparticle size; LDH-M, LDH-zeolite with microparticle size; LDH-N, LDH-zeolite with nanoparticle size; HCl-M, HCl-zeolite with microparticle size; HCl-N, HCl-zeolite with nanoparticle size; NaOH-M, NaOH-zeolite with microparticle size; NaOH-N, NaOH-zeolite with nanoparticle size; NaCl-M, NaCl-zeolite in the microparticle size; NaCl-N, NaCl-zeolite in the nanoparticle size.

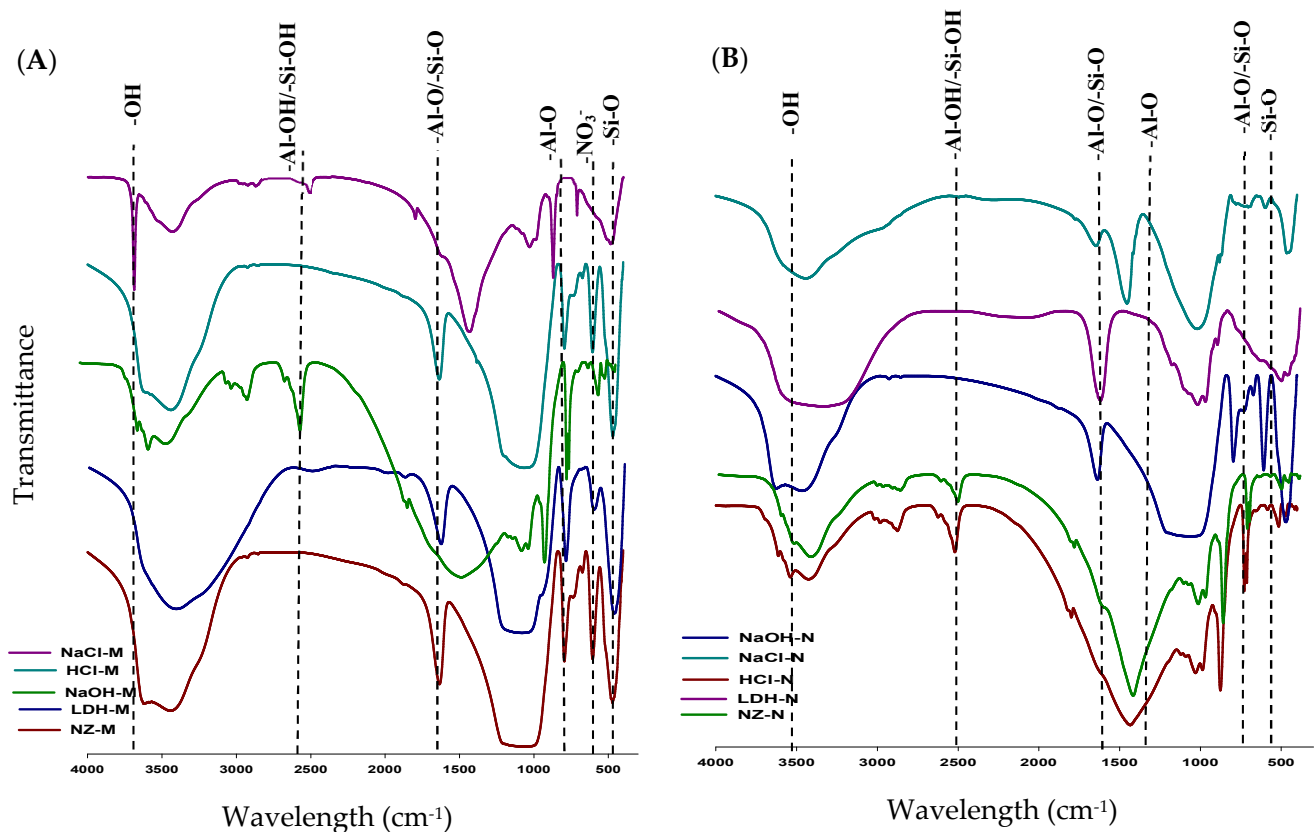


Figure 3. FTIR spectra of natural and modified zeolite sediments. (A) NZ-M, natural zeolite with microparticle size; LDH-M, LDH-zeolite with microparticle size; NaOH-M, NaOH-zeolite with microparticle size; HCl-M, HCl-zeolite with microparticle size; NaCl-M, NaCl-zeolite in the microparticle size. (B) NZ-N, natural zeolite with nanoparticle size; LDH-N, LDH-zeolite with nanoparticle size; HCl-N, HCl-zeolite with nanoparticle size; NaCl-N, NaCl-zeolite in the nanoparticle size; NaOH-N, NaOH-zeolite with nanoparticle size.

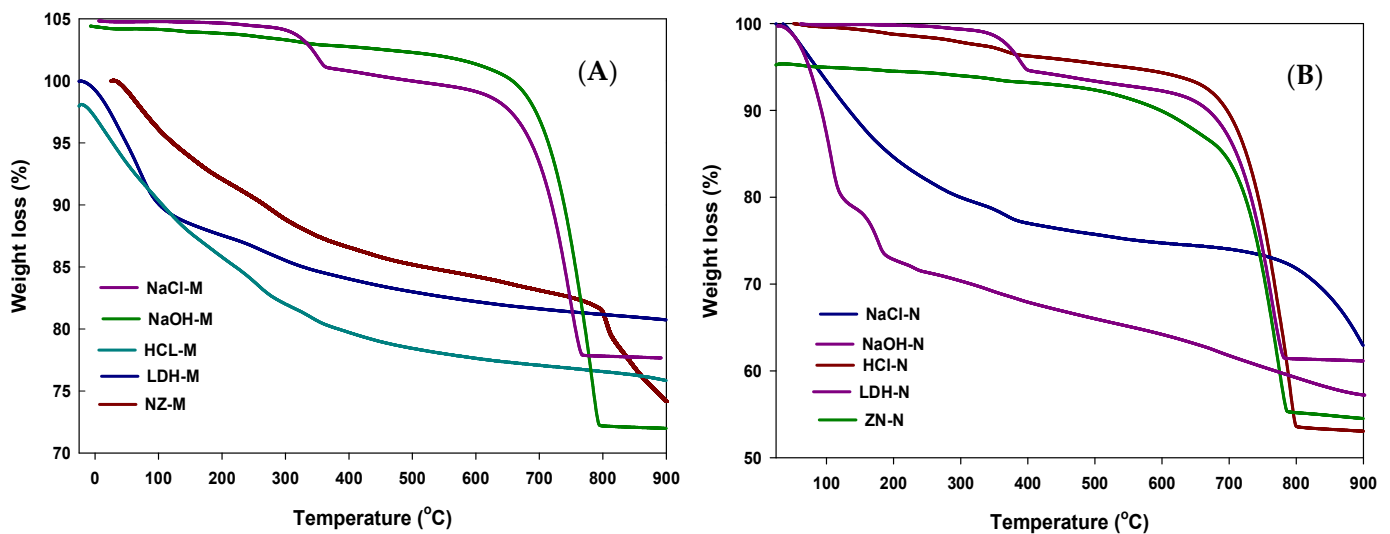


Figure 4. TGA analysis of natural and modified zeolite sediments. **(A)** NZ-M, natural zeolite with microparticle size; LDH-M, LDH-zeolite with microparticle size; HCL-M, HCL-zeolite with microparticle size; NaOH-M, NaOH-zeolite with microparticle size; NaCl-M, NaCl-zeolite in the microparticle size. **(B)** NZ-N, natural zeolite with nanoparticle size; LDH-N, LDH-zeolite with nanoparticle size; HCL-N, HCL-zeolite with nanoparticle size; NaOH-N, NaOH-zeolite with nanoparticle size; NaCl-N, NaCl-zeolite in the nanoparticle size.

3.3. Adsorption Batch Experiments

3.3.1. Effect of Adsorbent Dose and Particle Size

An adsorption batch experiment was conducted to investigate the adsorption and stabilization efficiency of employed adsorbents for Cd and Pb as affected by adsorbent dose and adsorbent particle size. As previously described in the Material and Methods section, all adsorbent materials were converted to micro- and nanoparticle sizes and were applied at 0.5, 1, 2, 4, and 8.0% (*w/w*) application rates. Adsorbents with nanosize particles showed higher sorption efficiency for Cd and Pb (Figure 5A,D) against microparticle-sized adsorbents. Higher removal efficiency from nanosized adsorbents could be due to enhanced net external surface area (Table 4), which generated more surface porosity and ultimately induced more active sites available to fix heavy metals (Cd, Pb) on them [51]. Furthermore, higher surface area and more available active sites shortened the diffusion path of metals, which consequently increased the removal efficiency of nanosized adsorbents [52]. An increase in removal percentage was noted by increasing adsorbent application rates. An anticipated increase in removal efficiency of Cd and Pb by increasing adsorbent dose was mainly due to the abundance of more available active sites by increasing adsorbent application rate. Also, higher specific surface areas, which enhanced surface porosity and abundance of attached surface functional groups, could be responsible for higher removal of tested heavy metals [53]. Among all tested adsorbents, LDH-N, NZ-N, and HCL-N performed excellently and showed the highest removal efficiency and adsorption rate for Cd and Pb. The removal efficiency and adsorption rate were found in the following order: LDH-N > NZ-N > HCL-N. Comparatively more removal and adsorption of heavy metals by LDH-modified zeolite adsorbent could be due to the abundance of diverse surface functional groups, especially the addition of NO_3^- , which ultimately generated more electrostatic interaction between cationic heavy metal ions and the zeolite adsorbent surface [41]. Additionally, the highest surface area among all tested adsorbents also favored more removal and adsorption of heavy metals by the LDH-modified nanozeolite adsorbent. The best-performing adsorbents (LDH-N, NZ-N, and HCL-N) were selected and tested for Cd and Pb removal and adsorption at variable initial pH.

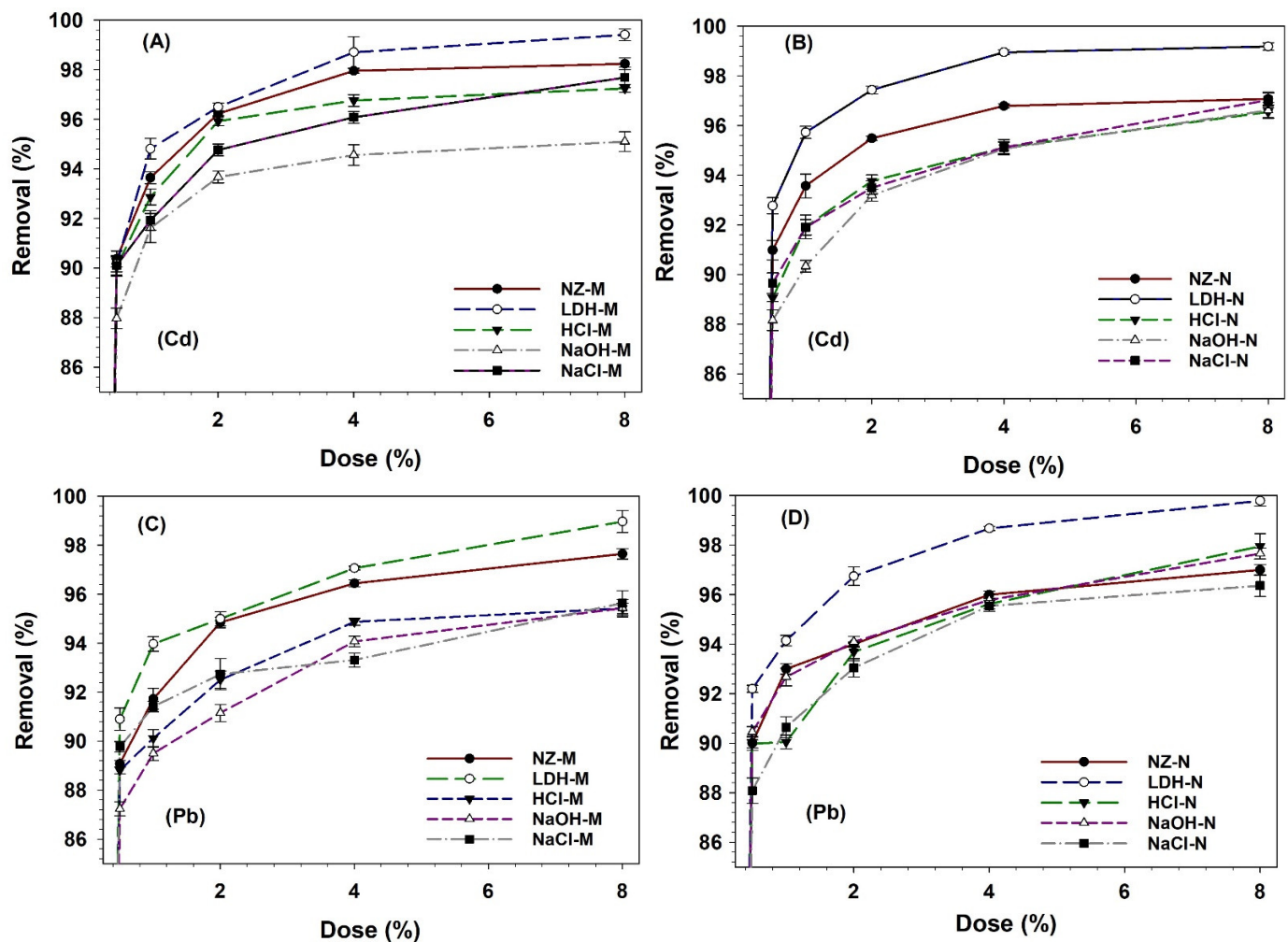


Figure 5. Effect of adsorbent dose and particle size on removal efficiency of adsorbents for Cd (A,B) and Pb (C,D) removal from contaminated soil. NZ-M, natural zeolite with microparticle size; NZ-N, natural zeolite with nanoparticle size; LDH-M, LDH-zeolite with microparticle size; LDH-N, LDH-zeolite with nanoparticle size; HCl-M, HCl-zeolite with microparticle size; HCl-N, HCl-zeolite with nanoparticle size; NaOH-M, NaOH-zeolite with microparticle size; NaOH-N, NaOH-zeolite with nanoparticle size; NaCl-M, NaCl-zeolite in the microparticle size; NaCl-N, NaCl-zeolite in the nanoparticle size.

3.3.2. Effect of Initial pH

The efficiency of heavy metal removal and adsorption processes is strongly influenced by the pH of the solution, which ultimately affects the ionization process and ionic strength of the adsorbate and adsorbent surface charge [54]. A diverse change in adsorption was noted under the influence of variable pH values (5, 6, 7, 8, and 9). A pH value of 7 was found to be the optimum pH for the adsorption of both Cd and Pb, and the highest adsorption was noted at this pH range (Figure 6A,B). Consistently lower adsorption of Cd and Pb was found in the acidic pH range, which could be due to fixation or complexation of metal ions. Similarly, a sharp decrease in adsorption of both heavy metals was noted in the alkaline pH range, which indicated precipitation of metal ions [55]. A similar trend of heavy metal removal was observed, and maximum removal efficiency of employed adsorbents was found at a pH of 7, which again endorsed the strong influence of pH on the stabilization of Cd and Pb in the contaminated soil (Figure 6C,D). At a pH value of 5, the removal efficiency of Cd ranged between 36 and 50% for all adsorbents, which was significantly increased to 85–90% at pH 7. A gradual decrease in the removal efficiency of Cd and Pb was observed by increasing the pH from 7 to 9. Similarly, for Pb, the highest removal

(>88%) was found at pH 7, while at acidic pH, removal efficiency was recorded in the 35–39% range. Generally, at lower pH values, the zeolite surface is positively charged due to protonation of surface functional groups, which subsequently repel cationic Cd^{+2} and Pb^{+2} ions and hinder adsorption and removal of heavy metals [56]. Increasing pH resulted in the deprotonation of surface functional groups, which caused zeolite surfaces to become more electrostatically charged and enhanced adsorption of Cd and Pb with higher removal efficiency [57]. Also, the higher removal efficiency of adsorbent at increasing pH value could be due to the presence of fewer H^+ ions, which compete with Cd^{+2} and Pb^{+2} ions for sorption at surface active sites of zeolites [58]. The reduction in adsorption and lower removal efficiency of adsorbents for Cd could also be attributed to the formation of $\text{Cd}(\text{OH})_2$ crystalline ionic compounds, which precipitate at higher pH [59]. Our findings are consistent with Zou et al. [60], who found higher adsorption of Pb at a pH value of 6.5–7 using raw natural zeolites as an adsorbent. At high pH values, the formation of complex hydrated ions of Pb ($\text{Pb}(\text{OH})_2$) along with precipitation reactions caused a decline in Pb adsorption and removal efficiency [61]. Among all tested adsorbents, LDH-modified NZ showed maximum adsorption and removal efficiency.

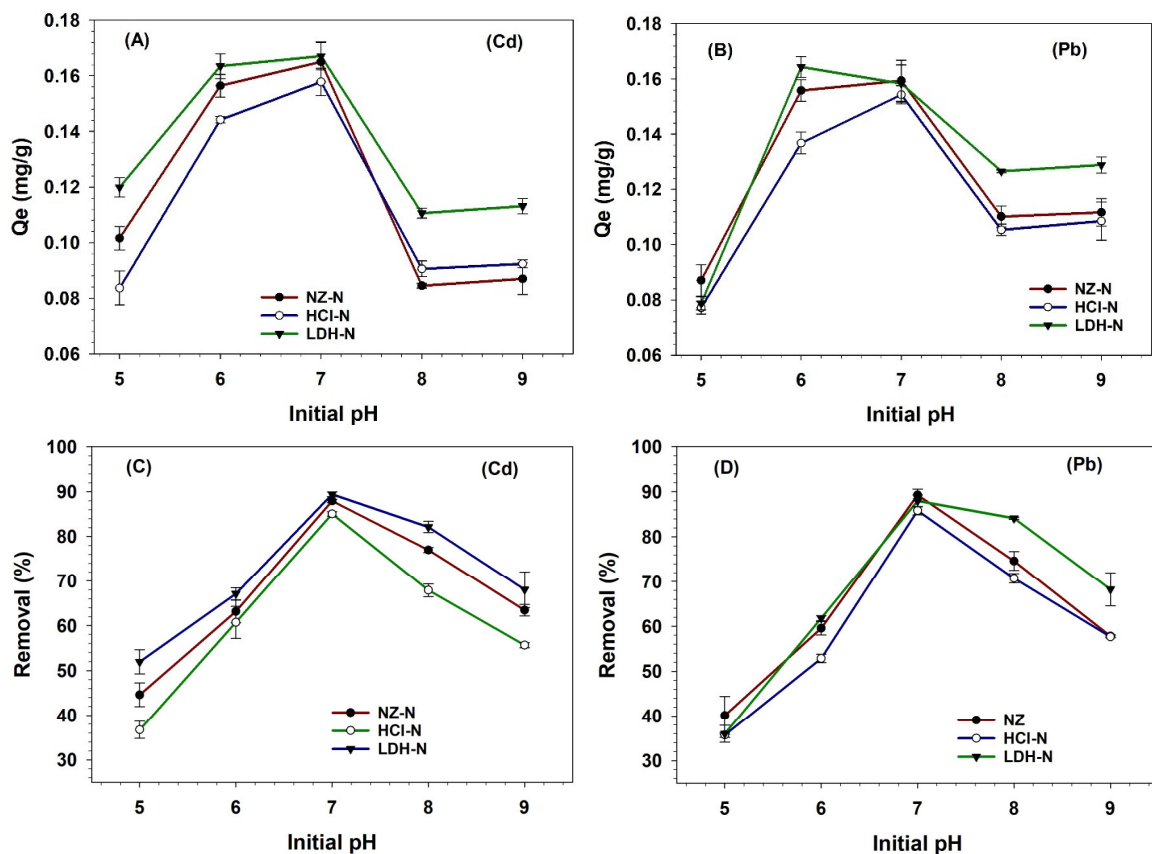


Figure 6. Effect of pH on adsorption and removal efficiency of adsorbents for Cd (A,C) and Pb (B,D) removal from contaminated soil. NZ-N, natural zeolite with nanoparticle size; LDH-N, LDH-zeolite with nanoparticle size; HCl-N, HCl-zeolite with nanoparticle size.

The presence of the Si-O functional group on the surfaces of the natural and modified zeolite surfaces was confirmed by the FTIR analysis (Figure 3). In this regard, previous research has indicated that the formation of silica (Si-O) results in an increase in the density of hydroxyl (-OH), hence increasing the negative charges on the surfaces of the adsorbent, as evidenced by the larger zeta potential, which enhances hydration lubrication and increases the sorption of hydrated cations on negatively charged surfaces [62]. In addition, surface modification of natural zeolite with chemical solutions (e.g., acids) might have contributed to enhancing superlubricity by reducing friction and enhancing the

hydrodynamic lubrication effect, which improves surface negative charges and increases the sorption of cationic ions [63].

3.4. Kinetics Experiment

The kinetics study of Cd and Pb adsorption revealed an initial quick adsorption, which then moved toward gradual equilibrium with specific contact time. The kinetics study was conducted at time intervals of 0.5, 1, 4, 8, 16, and 24 h. A quick adsorption in the beginning attained equilibrium at 8 h, and after that, a steady increase in adsorption was observed (Figure 7). Among all examined adsorbents, LDH-N displayed the highest adsorption capacity for Cd and Pb, followed by NZ-N and HCl-N. Initially, quick adsorption illustrated more available active sites, which were filled gradually to attain steady equilibrium sorption. Similarly, higher removal of Cd and Pb was found, which moved toward steady equilibrium with time. The experimental data were further interpreted with first-order and pseudo-second-order kinetic models to further explore metal adsorption mechanisms. Both applied kinetics models fitted well to experimental data ($R^2 = 0.94\text{--}0.99$) and described that the adsorption was both surface and chemisorption (Table 5). The suitability of the pseudo-second-order kinetics model indicates chemisorption among adsorbent and adsorbate. In our study, we found ion exchange and metal complexation mechanisms for Cd and Pb adsorption, which could be due to chemical interaction between metal ions and surface functional groups. During the ion exchange mechanism, metal ions (Cd and Pb) move through the porous surface of zeolite and are exchanged with an abundance of cations, e.g., Ca and Mg, while in surface complexation, metal ions make complex ions with reactive ions of surface functional groups such as metal oxides. The applied kinetics models explained that surface electrostatic interaction between metal ions and adsorbent surfaces was not the only mechanism behind adsorption, and chemical interactions between metal ions and surface functional groups present on adsorbent surfaces showed that adsorption was also governed chemically [64]. A higher constant rate for Cd and Pb was found with LDH-N in applied first-order (0.07 and 0.08) and pseudo-second-order (0.172 and 0.874) models, respectively. In addition, higher obtained sorption capacity (1.599 and 0.382 mg g^{−1}) indicated better performance and higher affinity of LDH-N for Cd and Pb, respectively. Fu et al. [65] found similar sorption and removal efficiency of zeolite composite for Pb, which confirmed chemisorption by the best fitness of the pseudo-second-order kinetics model.

Table 5. Derived parameters of the kinetics of Cd and Pb adsorption and removal by natural and modified zeolite adsorbents.

Cd								
Adsorbents	First Order			Pseudo-Second Order				
	r^2	k1	SEE	r^2	SEE	k2'	qe (mg g ^{−1})	h
NZ-N	0.95	0.06	0.0003	0.97	0.0007	0.171	1.529	0.438
LDH-N	0.96	0.07	0.0003	0.99	0.0009	0.172	1.599	0.399
HCl-N	0.93	0.06	0.0002	0.99	0.0007	0.170	1.556	0.411
Pb								
Adsorbents	r^2	k1	SEE	r^2	SEE	k2'	qe (mg g ^{−1})	h
	r^2	k1	SEE	r^2	SEE	k2'	qe (mg g ^{−1})	h
NZ-N	0.95	0.04	0.0003	0.99	0.0002	0.634	0.374	0.104
LDH-N	0.96	0.08	0.0009	0.99	0.0014	0.874	0.382	0.089
HCl-N	0.94	0.06	0.0004	0.98	0.0006	0.713	0.334	0.097

NZ-N, natural zeolite with nanoparticle size; LDH-N, LDH-zeolite with nanoparticle size; HCl-N, HCl-zeolite with nanoparticle size.

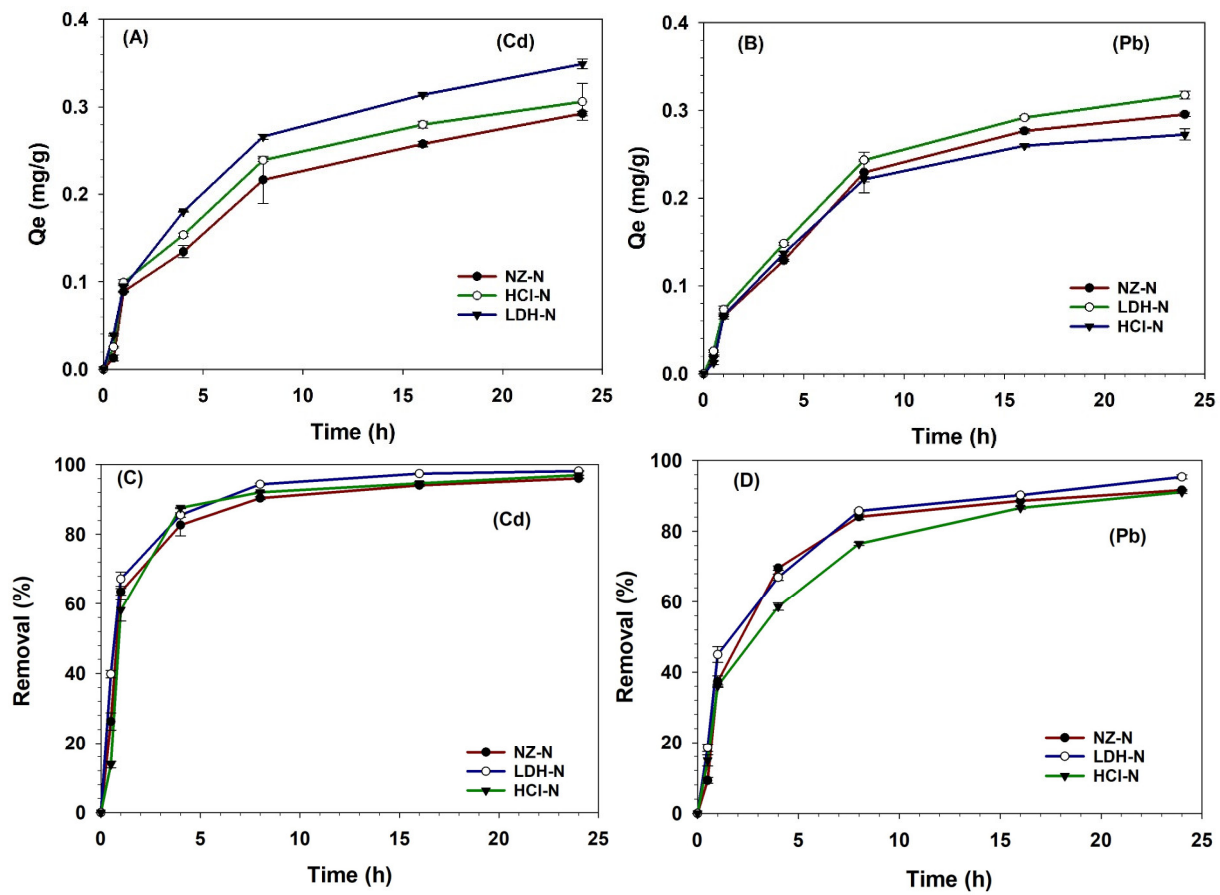


Figure 7. Kinetics of Cd (A,C) and Pb (B,D) adsorption and removal by natural and modified zeolite adsorbents. NZ-N, natural zeolite with nanoparticle size; LDH-N, LDH-zeolite with nanoparticle size; HCl-N, HCl-zeolite with nanoparticle size.

3.5. Incubation Study

The findings of the incubation study revealed a similar trend of removal of Cd and Pb by tested zeolite sediments. The highest removal efficiency of Cd was found in the LDH-N sediment, suggesting complete removal (~100%) after an 8-week incubation period, whereas for the NZ-N and HCl-N sediments, the removal efficiency of Cd after 8 weeks was 91.80% and 94.26%, respectively, and it reached 100% removal after the 16-week incubation period (Figure 8A). Similarly, LDH-N recorded the highest removal efficiency for Pb, suggesting 92.26% removal after 8 weeks of incubation and 100% removal after the 16-week incubation period, whereas HCl-N and NZ-N removed 89.56% and 87.20% Pb, respectively, after the 8-week incubation period and showed a 100% removal after the completion of the 16-week incubation period (Figure 8B). Additionally, during the incubation period, soil samples were taken at regular incubation times and were extracted with ammonium acetate (AA) extractant to assess the ability of sediments to hold and fix heavy metals in soil. Our findings indicate that all utilized sediments demonstrated credible potential in fixing and stabilizing heavy metals, and very low contents of heavy metals were extracted in the AA solution, while control soil treatment with no added sediments showed higher extracted concentrations of heavy metals than soil with added sediments (Figure 9A,B). It was found that extracted Cd contents were 88.4% higher in the control soil (CK) compared to its concentration in the best-performing NZ sediment (LDH-N), which recorded only 0.029 mg kg⁻¹ of Cd extracted after the first week of incubation. A trend of gradual decrease in the extracted quantity of Cd was noted, indicating the exhaustion of Cd contents in CK soil and the excellent ability of sediments to hold and fix Cd contents in active sites. At the end of the incubation period, CK soil still showed

0.044 mg kg⁻¹ extractable Cd contents, while LDH-N sediment-treated soil showed zero extractable Cd contents after 8 weeks of incubation (Figure 9A). For the HCl-N and NZ-N treated soil samples, no AA extractable Cd contents were found in the soil after the 16th week of incubation. In the same manner, the extraction of Pb with AA indicated the highest Pb quantity in CK soil samples and recorded 3.63 mg kg⁻¹ of AA extractable Pb contents at the first week of incubation. By the end of the 16th week of incubation, the concentration of AA extractable Pb in the CK soil was decreased to 1.31 mg kg⁻¹. In contrast, the soil treated with LDH-N indicated a maximum decrease in Pb extractable contents (0.77 mg kg⁻¹) after the first week of incubation. AA extractable Pb contents for soils treated with NZ-N (1.1 mg kg⁻¹) and HCL-N (1.01 mg kg⁻¹) were also found to be lower than that in the CK soil after the first week of incubation (Figure 9B). A similar trend of reduction in Pb extraction with AA was observed with time, with all tested sediments recording zero extractable Pb contents at the 16th week of incubation. Overall, all tested sediments recorded excellent removal and metal stabilizing ability against CK soil, while among employed sediments, LDH-N showed significantly better performance in removing and fixing heavy metals in soil.

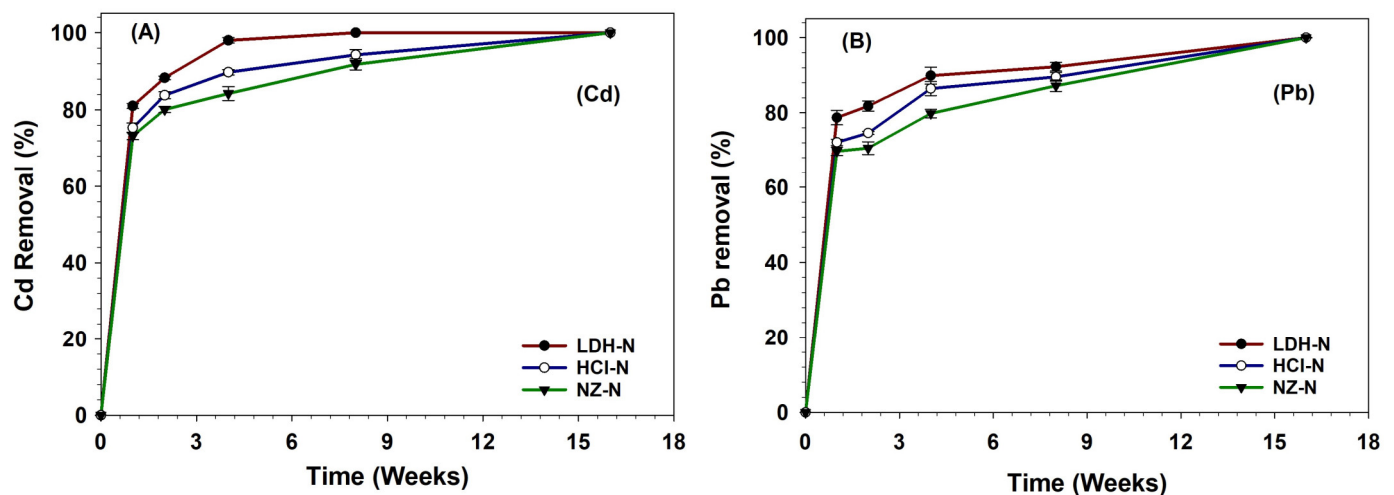


Figure 8. Efficiency of natural and modified zeolite adsorbents in removing Cd (A) and Pb (B) from incubated mining contaminated soil. NZ-N, natural zeolite with nanoparticle size; LDH-N, LDH-zeolite with nanoparticle size; HCl-N, HCl-zeolite with nanoparticle size.

The higher removal efficiency of LDH-N sediments clearly indicated its excellent ability to stabilize heavy metals, fixing heavy metals on its surface and making complexation with surface functional groups. The higher efficiency of LDH-N sediment for removal of heavy metals over other tested sediments could be due to the higher surface area (Table 4) and presence of additional surface functional groups [26]. In this regard, Dang et al. [28] reported an excellent efficiency of LDH-modified natural zeolite in removing Cd and Pb from artificially contaminated soil. They reported more than 70% removal of Cd and Pb at pH 7 in adsorption and incubation studies. In comparison with pristine zeolite samples, they reported a 1.5–1.6 times higher removal efficiency of LDH-modified zeolites. Electrostatic interaction, coprecipitation, and metal complexation with LDH surface functional groups were reported as the main mechanisms in the stabilization of Cd and Pb. Table 6 provides a comparison between the removal efficiency of Cd and Pb contaminants by different adsorbents of natural and modified zeolite based on the findings of this study and previous research in the literature.

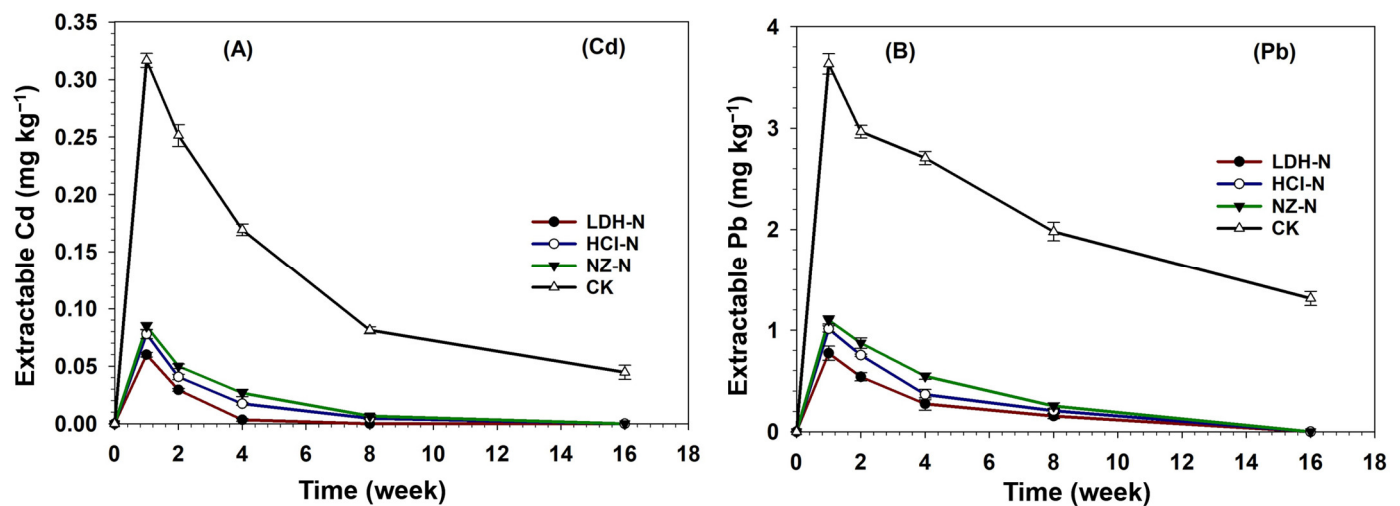


Figure 9. Efficiency of natural and modified zeolite adsorbents in stabilizing extractable Cd (A) and Pb (B) from incubated mining contaminated soil. NZ-N, natural zeolite with nanoparticle size; LDH-N, LDH-zeolite with nanoparticle size; HCl-N, HCl-zeolite with nanoparticle size; CK, control soil.

Table 6. Comparison of removal efficiency of heavy metal contaminants by different adsorbents.

Adsorbent	Metal	Removal Efficiency (%)	Reference
NZ	Cd, Pb	85, 34%	[59]
NZ	Cd, Pb	>99%	[55]
NZ	Cd, Pb	91, 80%	[64]
LDH-MZ	Cd, Pb	>70%	[28]
NaCl-Z	Cd, Pb	73, 56%	[59]
LDH-N	Cd, Pb	>98%	This study
NZ-N	Cd, Pb	97, 96%	This study
HCl-N	Cd, Pb	96, 97%	This study

NZ-N, natural zeolite with nanoparticle size; LDH-MZ, LDH modified zeolite; LDH-N, LDH-zeolite with nanoparticle size; HCl-N, HCl-zeolite with nanoparticle size.

Our results indicate that similar mechanisms could be responsible for the strong sorption of Cd and Pb, as evident by our findings of concentration of the AA extraction in the incubation study. Moreover, HCl-N and ZN-N also showed credible ability in removing heavy metals, which could be due to the three-dimensional framework of alumina and silicate tetrahedral units in zeolite composition, containing interconnected channels and pores, which helps zeolite to hold and adsorb heavy metal contaminants [51]. In research work on contaminated soil, Zheng et al. [66] reported that NZ reduced the extractable concentration of Cd and Pb in soil and removed 90.7 and 80.4% of Cd and Pb, respectively. Shi et al. [67] reported a significant drop in the exchangeable fraction of Pb in contaminated soil treated with NZ. Also, porous aluminosilicate structure and net negative surface charge on NZs indicated more affinity of NZ for cationic pollutants [27]. Overall, the incubation experiment revealed a trend of removing heavy metals similar to results obtained from the kinetics experiment, indicating quick and rapid removal initially, which later moved toward equilibrium. Similarly, AA extraction revealed that with increasing incubation period, the adsorption capacity of tested sediments for Pb and Cd enhanced, and little to no quantity of Pb and Cd extractable fraction was found in the later stages of incubation.

In addition, the natural zeolite and modified zeolites as prepared in this study were very stable during the incubation experiment, and the positive characteristics of the modified zeolites (e.g., high surface area and increased surface functional groups) were not affected by the incorporation with the soil. This implies that modified zeolites will remain highly effective in the sorption of heavy metals even after the incorporation with the soil in the field for a long time.

Zeolite sediments used in this study are natural deposits, and based on the performed chemical analysis, their characteristics (e.g., EC, pH, and CEC) are within acceptable limits for healthy soil (Table 3). The only exception was the NaOH-M, which showed a high pH value of 11. Therefore, it is anticipated that the application of zeolite sediment in actual soil remediation in the field will not have any adverse effects on the chemical soil properties. As for the impact of the zeolite sediment on the physical soil properties, previous research has indicated that the application of NZ in the nanosized fraction decreased infiltration rate and hydraulic conductivity and increased water retention and availability in light-textured soils [68].

3.6. Mechanism of Adsorption

The adsorption mechanism of Cd and Pb by the different NZ tested adsorbents followed surface sorption initially. In general, electrostatic interaction, ion exchange, and surface complexation are dominant mechanisms responsible for cationic metal adsorption on zeolite adsorbents [69,70]. Usually, these mechanisms act together, leading to enhanced sorption of cationic metal contaminants on negatively charged adsorbents. However, under our experimental conditions, the better crystallinity and abundance of additional surface functional groups, including NO_3^- and metal oxides and hydroxides (Si-O, Al-O, Si-OH, and Al-OH), particularly with the LDH-N, enhanced the overall surface negativity and induced electrostatic interactions between cationic metal ions and adsorbents, suggesting that electrostatic interactions were the main mechanism for the sorption of Cd and Pb on the surfaces of the different adsorbents. The higher affinity and sorption of Cd and Pb by the LDH-N adsorbent could be due to the higher surface area, which provides more active surface sites to fix more quantity. Additionally, ion exchange and surface complexation played an important role in increasing the sorption efficiency due to the presence of metal oxides and hydroxides, which facilitates the formation of surface complexation with Cd and Pb ($\text{Cd}(\text{OH})_2$, $\text{Pb}(\text{OH})_2$), leading to higher sorption affinity.

Our findings showed that tested heavy metal sorption was influenced by initial pH, and increasing pH to a neutral pH value of 7 enhanced metal sorption, which was then decreased with further pH increase. Increasing pH resulted in deprotonation of surface functional groups of zeolite adsorbents, which generated net negative surface charge. Cationic metal ions (e.g., Cd^{+2} , Pb^{+2}) are attached to negatively charged adsorbent surfaces by developing electrostatic interactions between cationic metal ions and negatively charged adsorbent surfaces. This was also confirmed by the first-order kinetics model, which described the physical adsorption of metal ions [71], and by the abundance surface functional groups present on the adsorbent's surface. Owing to the chemical nature of zeolites, these surface-adsorbed heavy metals induced chemical interactions by ion exchange mechanism with exchangeable cations on the zeolite's surface [72]. In pH-mediated reactions, the predominant mechanism for cationic metals (Cd^{+2} , Pb^{+2}) adsorption on natural zeolites is ion exchange, which is generally facilitated at pH values above 5 and below 8 [73]. Kragović et al. [74] and Shirzadi and Nezamzadeh-Ejhi [75] reported ion exchange with exchangeable cations on natural zeolites and surface complexation with surface functional groups as principal mechanisms for Pb, Cd, and mercury (Hg) adsorption on zeolites. Also, the chemical interaction involved in Cd^{+2} and Pb^{+2} adsorption on natural and modified zeolite adsorbents was confirmed by the pseudo-second-order kinetics model.

4. Conclusions

The goal of the present study was to assess the efficiency of natural and modified zeolite sediments to stabilize heavy metals from contaminated mining soil. Collected soil samples were found to be contaminated with Cd and Pb, and characteristic variations were found among the collected and modified zeolite sediments. Generally, sediments with nanoparticle size showed a higher CEC value, while a gradual decline was noted in the pH of nanosized sediments. Sediments with nanoparticle size recorded higher potential

in stabilizing heavy metals against microparticle-sized sediments. Among all sediments, LDH-N, NZ-N, and HCL-N showed better performance in stabilizing Cd and Pb from contaminated mining soil. LDH-N possessed additional NO_3^- surface functional groups, a crystalline composition of feldspar, and the highest surface area ($37.195 \text{ m}^2 \text{ g}^{-1}$). Therefore, LDH-N showed higher removal efficiency for Cd ($>98\%$) and Pb ($>95\%$), followed by NZ-N and HCL-N. A pH of 7 was found to be the optimum pH for Cd and Pb removal and sorption. Kinetics models revealed that both the first-order and the pseudo-second-order models fitted well to the experimental data. Electrostatic interaction, ion exchange, and surface complexation were found to be the principal mechanisms for heavy metal sorption. The incubation study revealed an excellent efficiency of the tested sediments in removing Cd and Pb, with LDH removing 100% Cd even after 8 weeks of incubation, while 100% Pb was removed at the 16th week of incubation. HCL-N and NZ-N reduced extractable Cd by 83.70% and 80.54% and extractable Pb fraction by 81.42% and 77.98%, respectively, whereas LDH-N showed superior performance in reducing extractable fraction of Cd and Pb by 89.26% and 86.19%, respectively. The outcomes of this research indicate that the physical and chemical modifications of NZ could be an efficient methodology to synthesize natural zeolites in the nanoparticle size with enhanced performance in mitigating heavy metal toxicity. In particular, the modified LDH-N, NZ-N, and HCL-N zeolite sediments could be used to fix heavy metal contaminants from mining and other contaminated soils.

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References

1. Alhawas, M.S.; Rafique, M.I.; Ahmad, M.; Al-Wabel, M.I.; Usman, A.R.A.; Al-Swadi, H.A.; Al-Farraj, A.S. Ball mill, humic acid, and rock phosphate-modified conocarpus biochar for efficient removal of heavy metals from contaminated water. *Sustainability* **2023**, *15*, 11474. [\[CrossRef\]](#)
2. Rafique, M.I.; Usman, A.R.; Ahmad, M.; Sallam, A.; Al-Wabel, M.I. In situ immobilization of Cr and its availability to maize plants in tannery waste-contaminated soil: Effects of biochar feedstock and pyrolysis temperature. *J. Soils Sediments* **2020**, *20*, 330–339. [\[CrossRef\]](#)
3. Rafique, M.I.; Usman, A.R.; Ahmad, M.; Al-Wabel, M.I. Immobilization and mitigation of chromium toxicity in aqueous solutions and tannery waste-contaminated soil using biochar and polymer-modified biochar. *Chemosphere* **2021**, *266*, 129198. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Alazzaz, A.; Rafique, M.I.; Al-Swadi, H.; Ahmad, M.; Alsewaileh, A.S.; Usman, A.R.; Al-Wabel, M.I.; Al-Farraj, A.S. Date palm-magnetized biochar for in-situ stabilization of toxic metals in mining-polluted soil: Evaluation using single-step extraction methods and phytoavailability. *Int. J. Phytorem.* **2023**, *25*, 1687–1698. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Rodriguez-Franco, C.; Page-Dumroese, D.S. Woody biochar potential for abandoned mine land restoration in the US: A review. *Biochar* **2021**, *3*, 7–22. [\[CrossRef\]](#)
6. Agency for Toxic Substances and Disease Registry of the U.S. Department of Health and Human Services (ATSDR). *Toxicological Profile for Thallium*; under Contract No. 205-88-0608; Prepared by Clement International Corp., ATSDR: Atlanta, GA, USA, 2003.

7. Dong, C.; Taylor, M.P.; Kristensen, L.J.; Zahran, S. Environmental contamination in an Australian mining community and potential influences on early childhood health and behavioural outcomes. *Environ. Pollut.* **2015**, *207*, 345–356. [\[CrossRef\]](#)
8. Park, J.H.; Choppala, G.; Lee, S.J.; Bolan, N.; Chung, J.W.; Edraki, M. Comparative sorption of Pb and Cd by biochars and its implication for metal immobilization in soils. *Water Air Soil. Pollut.* **2013**, *224*, 1711. [\[CrossRef\]](#)
9. Usman, A.R.; Abduljabbar, A.; Vithanage, M.; Ok, Y.S.; Ahmad, M.; Ahmad, M.; Elfaki, J.; Sallam, S.A.; Al-Wabel, M.I. Biochar production from date palm waste: Charring temperature induced changes in composition and surface chemistry. *J. Anal. Appl. Pyrolysis* **2015**, *115*, 392–400. [\[CrossRef\]](#)
10. Makusa, G.P. *Soil Stabilization Methods and Materials*; Lulea University of Technology: Luleå, Sweden, 2012.
11. Jiang, Q.; He, Y.; Wu, Y.; Dian, B.; Zhang, J.; Li, T.; Jiang, M. Solidification/stabilization of soil heavy metals by alkaline industrial wastes: A critical review. *Environ. Pollut.* **2022**, *312*, 120094. [\[CrossRef\]](#)
12. Belviso, C. Zeolite for potential toxic metal uptake from contaminated soil: A brief review. *Processes* **2020**, *8*, 820. [\[CrossRef\]](#)
13. Rafique, M.I.; Ahmad, M.; Al-Wabel, M.I.; Ahmad, J.; Al-Farraj, A.S. Mitigating the toxic effects of chromium on wheat (*Triticum aestivum* L.) seed germination and seedling growth by using biochar and polymer-modified biochar in contaminated soil. *Sustainability* **2022**, *14*, 16093. [\[CrossRef\]](#)
14. Breck, D.W. Recent advances in zeolite science. In *Molecular Sieve Zeolites-I*; Flanigen, E., Sand, L., Eds.; ACS Publications: Washington, DC, USA, 1974; Volume 101, pp. 1–19.
15. Velarde, L.; Nabavi, M.S.; Escalera, E.; Antti, M.L.; Akhtar, F. Adsorption of heavy metals on natural zeolites: A review. *Chemosphere* **2023**, *328*, 138508. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Senila, M.; Cadar, O. Modification of natural zeolites and their applications for heavy metal removal from polluted environments: Challenges, recent advances, and perspectives. *Heliyon* **2024**, *10*, e25303. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Arunkumar, D.; Krishnani, K.K.; Kumar, N.; Sarkar, B.; Upadhyay, A.K.; Sawant, P.B.; Chadha, N.K.; Abisha, R. Mitigating abiotic stresses using natural and modified stilbites synergizing with changes in oxidative stress markers in aquaculture. *Environ. Geochem. Health* **2023**, *45*, 4565–4581. [\[CrossRef\]](#)
18. Ates, A.; Hardacre, C. The effect of various treatment conditions on natural zeolites: Ion exchange, acidic, thermal and steam treatments. *J. Colloid Interface Sci.* **2012**, *372*, 130–140. [\[CrossRef\]](#)
19. Krstić, V. Chapter 14 - Role of Zeolite Adsorbent in Water Treatment. In *Micro and Nano Technologies, Handbook of Nanomaterials for Wastewater Treatment*; Bhavase, B., Sonawane, S., Pawade, V., Pandit, A., Eds.; Elsevier: Amsterdam, The Netherlands, 2021; pp. 417–481. [\[CrossRef\]](#)
20. Christidis, G.E.; Moraetis, D.; Keheyian, E.; Akhalbedashvili, L.; Kekelidze, N.; Gevorkya, R.; Yeritsyan, H.; Sargsyan, H. Chemical and thermal modification of natural HEU-type zeolitic materials from Armenia, Georgia and Greece. *Appl. Clay Sci.* **2003**, *24*, 79–91. [\[CrossRef\]](#)
21. Wahono, S.; Prasetyo, D.J.; Jatmiko, T.H.; Suwanto, A.; Pratiwi, D.; Vasilev, K. Transformation of mordenite-clinoptilolite natural zeolite at different calcination temperatures. *IOP Conf. Series: Earth Environ. Sci.* **2019**, *251*, 012009. [\[CrossRef\]](#)
22. Elkartehi, M.E.; Mahmoud, R.; Shehata, N.; Farghali, A.; Gamil, S.; Zaher, A. LDH nanocubes synthesized with zeolite templates and their high performance as adsorbents. *Nanomaterials* **2021**, *11*, 3315. [\[CrossRef\]](#)
23. Li, J.; Zhan, Y.; Lin, J.; Jiang, A.; Xi, W. Removal of bisphenol A from aqueous solution using cetylpyridinium bromide (CPB)-modified natural zeolites as adsorbents. *Environ. Earth Sci.* **2014**, *72*, 3969–3980. [\[CrossRef\]](#)
24. Luo, H.; Law, W.W.; Wu, Y.; Zhu, W.; Yang, E.H. Hydrothermal synthesis of needle-like nanocrystalline zeolites from metakaolin and their applications for efficient removal of organic pollutants and heavy metals. *Microporous Mesoporous Mater* **2018**, *272*, 8–15. [\[CrossRef\]](#)
25. Lahori, A.H.; Zhanyu, G.; Zhang, Z.; Ronghua, L.; Mahar, A.; Awasthi, M.K.; Feng, S.; Sial, T.A.; Kumbhar, F.; Ping, W.; et al. Use of biochar as an amendment for remediation of heavy metal-contaminated soils: Prospects and challenges. *Pedosphere* **2017**, *27*, 991–1014. [\[CrossRef\]](#)
26. Nguyen, T.B.H.; Van, H.T. Application of modified zeolite in the remediation of heavy metal in contaminated soil: A short review. *Technol. Agron.* **2024**, *4*, e002. [\[CrossRef\]](#)
27. Dang, V.M.; Van, H.T.; Vinh, N.D.; Duong, T.M.H.; Nguyen, T.B.H.; Nguyen, T.T.; Tran, T.N.H.; Hoang, T.K.; Tran, T.P.; Nguyen, L.H.; et al. Enhancement of exchangeable Cd and Pb immobilization in contaminated soil using Mg/Al LDH-zeolite as an effective adsorbent. *RSC Adv.* **2021**, *11*, 17007–17019. [\[CrossRef\]](#)
28. Dang, H.H.; Nguyen, D.T.C.; Nguyen, T.T.; Nguyen, T.T.T.; Vo, D.V.N.; Nguyen, T.D.; Lee, T.; Tran, T.V. Zeolitic-imidazolate framework-derived N-self-doped porous carbons with ultrahigh theoretical adsorption capacities for tetracycline and ciprofloxacin. *J. Environ. Chem. Eng.* **2021**, *9*, 104938. [\[CrossRef\]](#)
29. Wen, J.; Yi, Y.; Zeng, G. Effects of modified zeolite on the removal and stabilization of heavy metals in contaminated lake sediment using BCR sequential extraction. *J. Environ. Manag.* **2016**, *178*, 63–69. [\[CrossRef\]](#)
30. Rhoades, J.D. Salinity: Electrical conductivity and total dissolved solids. *Methods Soil Anal. Part 3 Chem. Methods* **1996**, *5*, 417–435.
31. Sparks, D.L. *Methods of Soil Analysis*; Soil Society of American: Madison, WI, USA, 1996.
32. Loeppert, R.H.; Suarez, D.L. Carbonate and gypsum. *Methods Soil Anal. Part 3 Chem. Methods* **1996**, *5*, 437–474.
33. Gee, G.W.; Bauder, J.W. Particle-size analysis. *Methods Soil Anal. Part 1* **1994**, *1*, 377–382.
34. Walkley, A.; Black, I.A. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.* **1934**, *37*, 29–37. [\[CrossRef\]](#)

35. Hossner, L.R. Dissolution for total elemental analysis. In *Methods of Soil Analysis: Part 3e Chemical Methods*; Sparks, D., Bigham, J.M., Eds.; SSSA and ASA: Madison, WI, USA, 1996; Volume 38, pp. 2221–2295.
36. Richards, L.A. *Diagnosis and Improvement of Saline and Alkali Soils*; US Department of Agriculture: Washington, DC, USA, 1954; Volume 78, p. 154. [\[CrossRef\]](#)
37. Sparks, D.L. Kinetics of soil chemical phenomena: Future directions. *Future Prospect. Soil Chem.* **1998**, *55*, 81–101.
38. Foo, K.Y.; Hameed, B.H. Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* **2010**, *156*, 2–10. [\[CrossRef\]](#)
39. WHO/FAO. *Codex Alimentarius Commission. Food Additives and Contaminants. Joint FAO; WHO Food Standard Programme*; Geneva, Switzerland, 2001. Available online: <https://www.who.int/groups/joint-fao-who-expert-committee-on-food-additives-jecfa/about> (accessed on 1 November 2024).
40. Al-Swadi, H.A.; Usman, A.R.; Al-Farraj, A.S.; Al-Wabel, M.I.; Ahmad, M.; Al-Faraj, A. Sources, toxicity potential, and human health risk assessment of heavy metals-laden soil and dust of urban and suburban areas as affected by industrial and mining activities. *Sci. Rep.* **2022**, *12*, 8972. [\[CrossRef\]](#) [\[PubMed\]](#)
41. Bezerra, B.G.; Bieseki, L.; Mello, M.I.D.; Silva, D.R.D.; Rodella, C.B.; Pergher, S. Memory effect on a LDH/zeolite a composite: An XRD in situ study. *Materials* **2021**, *14*, 2102. [\[CrossRef\]](#)
42. Ates, A.; Akgül, G. Modification of natural zeolite with NaOH for removal of manganese in drinking water. *Powder Technol.* **2016**, *287*, 285–291. [\[CrossRef\]](#)
43. Rahmani, F.; Haghighi, M.; Amini, M. The beneficial utilization of natural zeolite in preparation of Cr/clinoptilolite nanocatalyst used in CO₂-oxidative dehydrogenation of ethane to ethylene. *J. Ind. Eng. Chem.* **2015**, *31*, 142–155. [\[CrossRef\]](#)
44. Khoshbin, R.; Haghighi, M. Direct conversion of syngas to dimethyl ether as a green fuel over CuO-ZnO-Al₂O₃/HZSM-5 nanocatalyst: Effect of aging time on physicochemical and catalytic properties. *J. Renew. Sustain. Energy* **2015**, *7*, 023127. [\[CrossRef\]](#)
45. Saleh, R.; Zaki, A.H.; El-Ela, F.I.A.; Farghali, A.A.; Taha, M.; Mahmoud, R. Consecutive removal of heavy metals and dyes by a fascinating method using titanate nanotubes. *J. Environ. Chem. Eng.* **2021**, *9*, 104726. [\[CrossRef\]](#)
46. Alshameri, A.; He, H.; Dawood, A.S.; Zhu, J. Simultaneous removal of NH₄⁺ and PO₄³⁻ from simulated reclaimed waters by modified natural zeolite. Preparation, characterization and thermodynamics. *Environ. Prot. Eng.* **2017**, *43*, 73–92. [\[CrossRef\]](#)
47. Gao, Y.; Ru, Y.; Zhou, L.; Wang, X.; Wang, J. Preparation and characterization of chitosan-zeolite molecular sieve composite for ammonia and nitrate removal. *Adv. Compos. Lett.* **2018**, *27*, 096369351802700502. [\[CrossRef\]](#)
48. Gebretsadik, T.T.; Gebremedhin, T.K. Structural studies of natural zeolites and optimizations for water hardness softening media. *J. Met. Mater. Miner.* **2020**, *30*. [\[CrossRef\]](#)
49. Kandilli, C.; Acikbas, Y.; Uzel, M. Investigation of thermophysical properties of natural zeolite plates enhanced with graphite powder for thermal management of PV thermal systems. *J. Clean. Prod.* **2021**, *318*, 128558. [\[CrossRef\]](#)
50. Aloulou, H.; Bouhamed, H.; Ghorbel, A.; Amar, R.B.; Khemakhem, S. Elaboration and characterization of ceramic microfiltration membranes from natural zeolite: Application to the treatment of cuttlefish effluents. *Desalination Water Treat.* **2017**, *95*, 9–17. [\[CrossRef\]](#)
51. Senila, M.; Neag, E.; Cadar, O.; Kovacs, E.D.; Aschilean, I.; Kovacs, M.H. Simultaneous removal of heavy metals (Cu, Cd, Cr, Ni, Zn and Pb) from aqueous solutions using thermally treated Romanian zeolitic volcanic tuff. *Molecules* **2022**, *27*, 3938. [\[CrossRef\]](#) [\[PubMed\]](#)
52. Pernyeszi, T.; Farkas, R.; Kovács, J. Methylene blue adsorption study on microcline particles in the function of particle size range and temperature. *Minerals* **2019**, *9*, 555. [\[CrossRef\]](#)
53. Kumar, P.S.; Korving, L.; van Loosdrecht, M.C.; Witkamp, G.J. Adsorption as a technology to achieve ultra-low concentrations of phosphate: Research gaps and economic analysis. *Water Res. X* **2019**, *4*, 100029. [\[CrossRef\]](#)
54. Zhang, T.; Wang, W.; Zhao, Y.; Bai, H.; Wen, T.; Kang, S.; Song, G.; Song, S.; Komarneni, S. Removal of heavy metals and dyes by clay-based adsorbents: From natural clays to 1D and 2D nano-composites. *Chem. Eng. J.* **2021**, *420*, 127574. [\[CrossRef\]](#)
55. Kumara, G.M.P.; Kawamoto, K. Use of natural zeolite and its mixtures to refine high-concentrated heavy metal-contaminated wastewater: An investigation of simultaneous removal of Cd (II) and Pb (II) by batch adsorption method. *Water Air Soil Pollut.* **2021**, *232*, 1–17. [\[CrossRef\]](#)
56. Alqadami, A.A.; Wabaidur, S.M.; Jeon, B.H.; Khan, M.A. Co-hydrothermal valorization of food waste: Process optimization, characterization, and water decolorization application. *Biomass-Convert. Biorefinery* **2023**, *14*, 15757–15768. [\[CrossRef\]](#)
57. Khan, M.A.; Wabaidur, S.M.; Siddiqui, M.R.; Alqadami, A.A.; Khan, A.H. Silico-manganese fumes waste encapsulated cryogenic alginate beads for aqueous environment de-colorization. *J. Clean. Prod.* **2020**, *244*, 118867. [\[CrossRef\]](#)
58. Khan, Z.H.; Gao, M.; Qiu, W.; Islam, M.S.; Song, Z. Mechanisms for cadmium adsorption by magnetic biochar composites in an aqueous solution. *Chemosphere* **2020**, *246*, 125701. [\[CrossRef\]](#)
59. Velarde, L.; Nikjoo, D.; Escalera, E.; Akhtar, F. Bolivian natural zeolite as a low-cost adsorbent for the adsorption of cadmium: Isotherms and kinetics. *Heliyon* **2024**, *10*, e24006. [\[CrossRef\]](#) [\[PubMed\]](#)
60. Zou, W.; Han, R.; Chen, Z.; Jinghua, Z.; Shi, J. Kinetic study of adsorption of Cu (II) and Pb (II) from aqueous solutions using manganese oxide coated zeolite in batch mode. *Colloids Surf. A Physicochem. Eng. Asp.* **2006**, *279*, 238–246. [\[CrossRef\]](#)
61. Buasri, A.; Chaiyut, N.; Phattarasirichot, K.; Yongbut, P.; Nammueng, L. Use of natural clinoptilolite for the removal of lead (II) from wastewater in batch experiment. *Chiang Mai J. Sci.* **2008**, *35*, 447–456.

62. Han, T.; Zhang, S.; Zhang, C. Unlocking the secrets behind liquid superlubricity: A state-of-the-art review on phenomena and mechanisms. *Friction* **2022**, *10*, 1137–1165. [\[CrossRef\]](#)
63. Xiao, C.; Li, J.J.; Chen, L.; Zhang, C.H.; Zhou, N.N.; Qing, T.; Qian, L.M.; Zhang, J.Y.; Luo, J.B. Water-based superlubricity in vacuum. *Friction* **2019**, *7*, 192–198. [\[CrossRef\]](#)
64. Jin, X.; Li, H.; Zhu, X.; Li, N.; Owens, G.; Chen, Z. Enhanced removal of oxytetracycline from wastewater using bimetallic Fe/Ni nanoparticles combined with ZIF-8 nanocomposites. *J. Environ. Manag.* **2022**, *318*, 115526. [\[CrossRef\]](#)
65. Fu, Q.; Zhou, S.; Wu, P.; Hu, J.; Lou, J.; Du, B.; Mo, C.; Yan, W.; Luo, J. Regenerable zeolitic imidazolate frameworks@agarose (ZIF-8@AG) composite for highly efficient adsorption of Pb(II) from water. *J. Solid State Chem.* **2022**, *307*, 122823. [\[CrossRef\]](#)
66. Zheng, R.; Feng, X.; Zou, W.; Wang, R.; Yang, D.; Wei, W.; Li, S.; Chen, H. Converting loess into zeolite for heavy metal polluted soil remediation based on “soil for soil-remediation” strategy. *J. Hazard. Mater.* **2021**, *412*, 125199. [\[CrossRef\]](#)
67. Shi, W.Y.; Li, H.; Du, S.; Wang, K.B.; Shao, H.B. Immobilization of lead by application of zeolite: Leaching column and rhizobox incubation studies. *Appl. Clay Sci.* **2013**, *85*, 103–108. [\[CrossRef\]](#)
68. Ibrahim, H.M.; Alghamdi, A.G. Effect of the Particle Size of Clinoptilolite Zeolite on Water Content and Soil Water Storage in a Loamy Sand Soil. *Water* **2021**, *13*, 607. [\[CrossRef\]](#)
69. Anari-Anaraki, M.; Nezamzadeh-Ejhieh, A. Modification of an Iranian clinoptilolite nano-particles by hexadecyltrimethyl ammonium cationic surfactant and dithizone for removal of Pb(II) from aqueous solution. *J. Colloid Interface Sci.* **2015**, *440*, 272–281. [\[CrossRef\]](#) [\[PubMed\]](#)
70. Ren, H.; Jiang, J.; Wu, D.; Gao, Z.; Sun, Y.; Luo, C. Selective adsorption of Pb(II) and Cr(VI) by surfactant-modified and unmodified natural zeolites: A comparative study on kinetics, equilibrium, and mechanism. *Water Air Soil Pollut.* **2016**, *227*, 1–11. [\[CrossRef\]](#)
71. Aloui, L.; Mezghich, S.; Mansour, L.; Hraiech, S.; Ayari, F. Swift Removal of the Heavy Metals Cadmium and Lead from an Aqueous Solution by a CAN-Zeolite Synthesized from Natural Clay. *ChemEngineering* **2023**, *7*, 113. [\[CrossRef\]](#)
72. Jimenez-Reyes, M.; Almazán-Sánchez, P.T.; Solache-Ríos, M. Radioactive waste treatments by using zeolites. A short review. *J. Environ. Radioact.* **2021**, *233*, 106610. [\[CrossRef\]](#)
73. Al-Haj-Ali, A.; Al-Hunaidi, T. Breakthrough curves and column design parameters for sorption of lead ions by natural zeolite. *Environ. Technol.* **2010**, *25*, 1009–1019. [\[CrossRef\]](#)
74. Kragović, M.; Daković, A.; Marković, M.; Krstić, J.; Gatta, G.D.; Rotiroti, N. Characterization of lead sorption by the natural and Fe(III)-modified zeolite. *Appl. Surf. Sci.* **2013**, *283*, 764–774. [\[CrossRef\]](#)
75. Shirzadi, H.; Nezamzadeh-Ejhieh, A. An efficient modified zeolite for simultaneous removal of Pb(II) and Hg(II) from aqueous solution. *J. Mol. Liq.* **2017**, *230*, 221–229. [\[CrossRef\]](#)

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