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ASSESSING THE INFLUENCE OF NATURAL ZEOLITE ON TOXIC HEAVY METALS IMMOBILIZATION AND THEIR TRANSFER INTO *ZEA MAYS* L.

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ABSTRACT. This research presents the efficiency of surfactant-modified (SMNZ) and unmodified natural-zeolite (UNZ) in the immobilization of Cr^{3+}, Pb^{2+}, and Cd^{2+} in the soil system. Phillipsite is identified as a major component of the host zeolite. Soil mixed with 20% UNZ retained the highest amount of all metals on the top layer of the soil-zeolite column. The lowest transfer of metals into the maize crop was observed at 30 mg of UNZ/kg soil. The experimental conditions such as pH, dose, stirring speed, contact time, and initial metal ions concentration showed significant effect on adsorption of Cr^{3+}, Pb^{2+}, and Cd^{2+} onto both unmodified and modified zeolite (phillipsite). The maximum adsorption (mg/kg) onto control soil, soil mixed with SMNZ and UNZ was 67.1, 90.9, 151.5 for Cr^{3+}, 84.8, 120.5, 238.1 for Pb^{2+}, 83.3, 116.3 and 212.8 for Cd^{2+} respectively. Thus, the use of natural zeolite, particularly UNZ has an important role in controlling the mobility of Cr^{3+}, Pb^{2+}, and Cd^{2+} metal ions in the soil system and thus their transfer to plant system.

KEY WORDS: Zeolite, Immobilization, Heavy metals, Column, Pot trial, Batch

INTRODUCTION

The risk of heavy metals contamination in the environment has recently been rising quickly and causing havoc, particularly in the agricultural sector, by accumulating in the soil and plant through uptake [1]. In half a-billion hectares of land, there are five million sites of soil contamination where different heavy metals have contaminated the soil, with current soil concentrations exceeding maximum allowable limits [2]. Global economic costs associated with heavy metal pollution in soil are expected to exceed US$10 billion annually [3]. This shows that heavy metal soil pollution has developed into a serious global issue [4].

The application of chemical fertilizers and pesticides, as well as irrigation with rivers and streams that have been tainted with industrial effluents, are the main causes of heavy metal pollution in Ethiopian agricultural soils [5, 6]. Chromium, cadmium, and lead are among toxic heavy metals identified as a risk to human health through the consumption of vegetable crops [7]. Studies revealed that the levels of heavy metals in soils and plants cultivated around factories and urban areas are above permissible limit. For instance, [6] showed that soil samples under tomato and cabbage cultivation taken from Mojo area (Ethiopia) contains 37.93 and 35.80 mg/kg lead, 4.76 and 5.30 mg/kg cadmium and 36.2 and 35.9 mg/kg chromium, respectively. They also showed that the levels of lead, cadmium and chromium detected in tomato samples were 3.63 0.56 and 1.49 mg/kg, respectively, while the corresponding values in cabbage were 7.56, 1.56 and 4.63 mg/kg.

The quality of water bodies, the atmosphere, the soils, and food crops can all be negatively impacted by heavy metal contamination, which is hidden and persistent. Through buildup in the food chain, it also poses a serious threat to the health and well-being of living things, including humans [8]. They can cause a variety of morphological changes in plants, such as chlorosis, necrotic patches, color changes, curving of the leaves, sugar transfer, and water relations [9]. They can also decline the biomass of above-ground plant components [10]. Even at low doses, they are quickly accumulated in organisms and can result in life-threatening sickness [11].

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Therefore, it is essential to suppress the contamination of soils and plants with heavy metals. Immobilization, soil washing, and phytoremediation are frequently considered as some of the most effective methods for cleaning up heavy metal-contaminated areas [12]. Yet, only industrialized nations are known to have used these technologies in the field. Low cost and ecologically sustainable remedial options, such as immobilization through adsorption process, are needed to restore contaminated lands in developing countries with high population density and limited funding available for environmental restoration. This will lower the associated risks, make the land resource available for agricultural production, improve food security and safety, and lessen problems with land tenure. Immobilization through adsorption process is the most advantageous since it is inexpensive, uses little energy, and is simple to implement in treatment stations after conventional processing stages [13, 14], especially when using low-cost natural sorbents such as clay materials, biomass, and zeolite [15].

Zeolites are natural resources that are believed to present in vast amount in Ethiopia. However, systematic study on these materials at national level is lacking making the tracing of such resources difficult for research undertaking. Despite this problem, previous studies showed abundant resources of mordenite and clinoptilolite near Adama-Nazret, philipsite and clinoptilolite in the Awassa area and several zeolitic phases and highly-pure large deposit of stilbite in the north region of the country [16]. Due to its inexpensive cost, the adsorption and ion exchange approach employing natural zeolites is significantly more trustworthy. Zeolite has enclosed linked spaces that are occupied by water molecules and large metal cations, which is why it is evident that zeolite is renowned for its ability towards ion-exchange [17]. It has the potential to function as chelators and stabilizers [18]. Natural zeolites are also widespread and can be obtained and processed using a low-technology method [19]. Zeolite has been shown to be effective in removing heavy metals in previous studies. However, majority of the studies have concentrated on removing harmful heavy metals from groundwater and wastewater rather than on cleaning up agricultural fields [20, 21]. Additionally, researchers are concentrating on assessing the effectiveness of clinoptilolite zeolite among various zeolites. This indicates the importance of further investigation on the potential application of other types of zeolites such as phillipsite, on remediation of soils contaminated with heavy metals. Despite the fastest growth of small and medium-scale industries in Ethiopia that could be sources of toxic heavy metals, there are no reports in the literature on the use of naturally occurring minerals like zeolites in the detoxification and immobilization of a soil environment contaminated with these metals. Therefore, this study aimed at evaluating (i) the efficiency of Ethiopian natural zeolite (unmodified and surfactant modified) in the immobilization of Cd^{2+}, Pb^{2+} and Cr^{3+} using soil-zeolite columns and pot experiments and (ii) the effect of different parameters on adsorption of these metals using batch experiments.

EXPERIMENTAL

Soil sampling and preparation

The experimental soil sample (sandy clay loam) at a depth of 0-20 cm was collected from Rare research farm of Haramaya University, air-dried, crushed using a pestle and mortar and passed through a 2 mm diameter sieve. The soil used for different applications (column, pot and batch experiments) was then artificially contaminated with cadmium, lead, and chromium as $Cd\ (NO_3)_2 \cdot 4H_2O$, $Pb\ (NO_3)_2$, and $Cr\ (NO_3)_3$ obtained from Sigma Aldrich, (USA). The pH, CEC and organic carbon of the collected soil were 7.67, 0.83%, and 28.80 C mol/kg, respectively.

Zeolite preparation

The natural zeolite collected from Dodota district, Arsi Zone, Oromia Region, Great Rift Valley of Ethiopia was crushed by using laboratory mortar and pestle into fine size (less than 2 mm). The obtained zeolite was washed with double distilled water till its turbidity in water was eliminated and put in an oven and then dried at 105 °C to constant weight. The dried sample was then taken from an oven drier and immediately put in a desiccator to protect it from moisture.

Surfactant-modified zeolite preparation

Surface modification of the zeolite was done using hexadecyl trimethyl ammonium bromide (HDTMABr) surfactant (1000 mg/L). A known amount of zeolite was mixed with HDTMABr solutions in a 1:100 (solid: liquid) ratio. The solution was agitated for 8 h at 150 rpm on an orbital shaker. The solution was then filtered and the solid leftover was washed with double-distilled water and allowed to air dry for 6 h. The finally prepared zeolite (SMNZ) was ground with a mortar and pestle to get uniform powder [22].

Characterization of zeolite samples

The modified and surfactant modified zeolite samples were characterized by using different instruments. The crystalline structure and phase purity was determined by using powder X-ray diffraction (Philips X'PERT) employing Cu Kα radiation (=1.5418) in the 2θ range of 4-90. The fundamental chemical composition of zeolite was studied by using an X-ray fluorescence (Ametek, Germany) device with SDD silicon drift detector with a resolution of 145 eV at 10 000 pulses. The SEM pictures of zeolite samples were studied to get insight into their morphology using scanning electron microscopy (JCM-6000 Plus). A Micromeritics instrument (ASAP 2420) was used to calculate the specific surface area (Brunauer-Emmet-Teller method) and total pore volume of the sample. Thermogravimetric analysis (TGA) was carried out using PerkinElmer TGA7 instrument in the temperature range of 30 to 900 °C under airflow at 20 °C min^{-1} heating rate.

Determination of pH and cation exchange capacity of zeolite samples

A Consort C8C38 pH meter was used to measure the pH of the zeolite samples in a suspension of zeolite and distilled water at a ratio of 1:2.5, and its CEC was determined according to [23]. Five grams of samples were agitated end-to-end on a shaker with 50 mL of 0.5 M NH_4Cl and allowed to stand for 24 h. The contents were combined with 50 mL of 95% denatured alcohol and agitated. The solutions were then centrifuged, decanted and the adsorbed ammonium was removed by using a fresh solution of 0.5 M CsCl to determine the CEC of the zeolite.

Metal solution preparation

A 1000 mg/L stock solution of Cd^{2+}, Pb^{2+}, and Cr^{3+} was prepared from $Cd(NO_3)_2{\cdot}4H_2O$, Pb $(NO_3)_2$ and $Cr(NO_3)_3$, respectively in 1000 mL volumetric flask using deionized water (DIW). All chemicals were analytical grade obtained from Sigma Aldrich, (USA). The other required concentrations were prepared from stock solution by dilution with DIW. All glass wares were thoroughly cleaned with soap, followed by 10% HNO_3, and then with DIW before use [23].

Metal (Pb, Cd, and Cr) leaching study (soil column experiment)

About 2 kg of air-dried and sieved (< 2 mm) soil was mixed with 0%, 10%, 15%, and 20% of modified and unmodified natural zeolites by weight and added to polyvinyl chloride (PVC) tubes (5 cm in diameter and 40 cm in height) in triplicate. The soil-zeolite column was artificially contaminated with aqueous solution of $Cd(NO_3)_2{\cdot}4H_2O$, $Pb(NO_3)_2$, and $Cr(NO_3)_3$ containing 200 mg of Cd^{2+}, Pb^{2+}, and Cr^{3+} of each per kilogram of soil. Then, 200 mL of DIW was added to the column containing the mixture of heavy metals, soil and zeolite and allowed to stand for a month

[25]. A Whatman No. 42 filter paper and a piece of nylon mesh were placed at the bottom of the leaching column to prevent the loss of soil. The treatments included were soil + 200 mg/kg of each metal (T1), soil + 200 mg/kg of each metal + 10% w/w of UNZ (T2), soil + 200 mg/kg of each metal + 15% w/w of UNZ (T3), soil + 200 mg/kg of each metal + 20% w/w UNZ (T4), soil + 200 mg/kg of each metal + 10% w/w SMNZ (T5), soil + 200 mg/kg of each metal + 15% SMNZ (T6), soil + 200 mg/kg of each metal + 20% SMNZ (T7). Each column was then carefully irrigated with distilled water at 60 % (w/w) FC for 10 days. Then each column was separated into 20 cm segments, forming two layers representing different soil depths, and the amount of Pb, Cd, and Cr in each layer was determined according to [26]. Three grams of soil samples were digested with a mixture of 10 mL concentrated hydrochloric acid and 3.5 mL concentrated nitric acid and placed in the fume hood overnight without heating. The content was then heated on the next day for 2 h at 104 °C. The digested sample was diluted with distilled water and then filtered with a Whatman number 42 filter paper. Finally, the volume was topped up to a 100 mL with distilled water. Then concentration of these heavy metals in the soil samples was analyzed using atomic absorption spectrophotometer (Buck Scientific 210VGP FAAS).

Pot experiment

The experiments were conducted in three replications, using a completely randomized design. The experiments were set up by putting 10 kg of soil in plastic pots (30 cm x 15 cm). The amounts of zeolite added were 0, 10, 20, and 30 mg/kg of soil. Soils in each pot were then contaminated with 200 mg of Pb^{2+}, Cd^{2+}, and Cr^{3+} per kg of soil and incubated for 25 days. Maize variety BH-661 was then planted as a test crop. Chemical fertilizer was applied at 100 kg/ha and each pot was irrigated at 60% water holding capacity, which is field capacity. The treatments included are soil + 200 mg/kg of metals (T1), soil + 200 mg/kg of metals + 10 mg/kg UNZ (T2), soil + 200 mg/kg of metals + 20 mg/kg UNZ (T3), soil + 200 mg/kg of metals + 30 mg/kg UNZ (T4), soil + 200 mg/kg of metals + 10 mg/kg SMNZ (T5), soil + 200 mg/kg of metals + 20 mg/kg SMNZ (T6), soil + 200 mg/kg of metals + 30 mg/kg SMNZ (T7).

Plant heavy metals analysis as affected by natural-zeolite

The plant tissue collected at 12 weeks was washed with deionized water and dried in an oven at 100 °C for 24 h and blended to fineness and then allowed to pass through less than 2 mm sieve. One gram of the plant tissue was digested with five mL of 4:1 mixture of concentrated HNO_3:$HClO_4$ at 105°C for 1 h to dryness. The mixture was then cooled and topped up to a 50 mL volumetric flask with 1 M nitric acid. The solution was filtered into the sampling bottles after it was centrifuged for 30 minutes and then analyzed using Atomic Absorption Spectrophotometer [27].

Batch experiment

The effects of pH, sorbent dose, stirring speed, contact time, and initial concentration were studied by shaking solutions containing soil, zeolite (UNZ, SMNZ), and known concentration of metal ions on a mechanical shaker for a fixed time at laboratory ambient temperature. Then the contents were filtered using Whatman number 42 and the equilibrium concentration of each metal was determined by means of atomic absorption spectrophotometer (AAS) using the air-acetylene flame. The soil/solution ratio selected was a 1:5 ratio [28] and adjustment of pH was done using either 0.1 M HNO_3 or 0.1 M NaOH [24], the experiments were done in triplicate. The adsorption (%) and the amount of each metal adsorbed by the zeolite-soil mixture were calculated using equations 1 and 2, respectively [29]:

$$\text{Adsorption (\%)} = \frac{\text{Co}-\text{Ce}}{Co} x100 \quad (1)$$

$$Q_{e(\frac{mg}{g})} = \frac{Co-Ce}{w1} xV \quad (2)$$

where C_o is the initial concentration of metal ions (mg/L), C_e is the concentration in the final solution (mg/L), respectively; V represents the volume of equilibrium liquid (L), and W_1 is the mass of soil (g).

Effect of pH

The influence of pH on the adsorption of Cd^{2+}, Cr^{3+}, and Pb^{2+} was studied by varying pH values from 2-10 (2, 4, 6, 8, 10). For this purpose, 50 mL of these metals solutions (30 mg/L) was added to 250 mL plastic bottles which contain 10 g of soil and 0.5 g of zeolite (5%). The pH value of the solution was adjusted using HCl and NaOH solution and shaken at 200 rpm for 24 hours. The solution was then filtered using the Whatman number 42 filter paper. The equilibrium concentration of metals in the solution was measured by AAS.

Effect of zeolite dose, stirring speed, contact time, and initial concentration

The effects of these parameters were done by varying dose from 0.25 to 2 g (0.25, 0.5, 1, and 2 g), string speed from 50 to 200 rpm (50, 100, 150, and 200), contact time from 1 to 48 hour (1, 4, 8, 16, 24, and 48) and initial concentration from 0 to 50 mg/L (0, 5, 15, 30, and 50 mg/L). The pH value of the solution was adjusted to the optimized value.

Data fitting to adsorption kinetics models

The kinetics of the adsorption data was examined at pre-optimized conditions in the time range of 1 to 48 h to observe the dynamic interactions of metals with solid phases and to predict their fate with time using pseudo-first-and pseudo-second-order kinetics models. The pseudo-first-order and pseudo-second-order equations were given in Equations 3 and 4, respectively [30]:

$$\log (q_e\text{-}q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e 2} + \frac{1}{q_e} t \quad (4)$$

Data fitting to adsorption isotherm models

To fit the equilibrium data of the adsorption of metals onto zeolite-soil mixture under pre-optimized conditions, the Langmuir and Freundlich isotherm models were used. Equations 5 and 6 provided the linear forms of the Langmuir and Freundlich isotherm equations, respectively [31]:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}\text{b}} + \frac{C_e}{q_{max}} \quad (5)$$

$$ln\, q_e = ln\, K_f + \frac{1}{n\, ln\, C_e} \quad (6)$$

Desorption study

The desorption of each metal from the zeolite was measured immediately after adsorption at the greatest initial concentration. Fifty mL of 0.01 M $NaNO_3$ desorption solution (pH = 7) [32] was put in the filtered residue after the adsorption experiment and agitated on the shaker at pre-optimized conditions. The desorbed amount of heavy metals (Q_{de}) and the desorption (%) were calculated based on equations 7 and 8, respectively [29]:

$$Q_{de}\,(\frac{mg}{g}) = \frac{C1xV}{w1} \tag{7}$$

$$\text{Desorption (\%)} = \frac{\text{Qde}}{Qe}x100 \tag{8}$$

where Q_{de} is the desorbed quantity of heavy metals (mg/g), V is volume of solution used for desorption (L), C_1 is metal ion concentration of desorption supernatant (mg/L), and W_1 is the mass of sorbent (g) and Q_e is the adsorption capacity.

Statistical analysis

The data obtained for each treatment was subjected to analysis of variance (ANOVA) using general linear model (GLM) procedures using statistical analysis (SAS Institute 2006, version 9.1.3.). The Tukey test was used to determine the significant differences among treatments at α = 0.05.

RESULTS AND DISCUSSION

Powder X-ray diffraction pattern

Both the unmodified and modified zeolites exhibited diffraction peaks at 2θ values of 12.36, 27.84, and 27.89° corresponding to the reflection planes of (001), (041) and (022) that can be ascribed to phillipsite (ph) structure (024-1046) (Figure 1). Besides, other peaks at 2θ values of 20.86 (100) and 25.62 (112) representing quartz (038-0448) and albite (009-0466) were observed. Phillipsite is identified as the major component of the zeolite with Si: Al ratio of 2.6. The Si:Al ratio of phillipsite generally falls between 1.3 and 3.3 which is in agreement with our result confirming the phillipsite nature of the zeolite material [33]. The surfactant-modified natural zeolite (SMNZ) showed similar diffraction pattern with the unmodified zeolite (UNZ) except diminished peak intensities observed at 2θ value of 25.62 ° and 20.86° revealing the little effect of the surfactant in terms of influencing the zeolite framework.

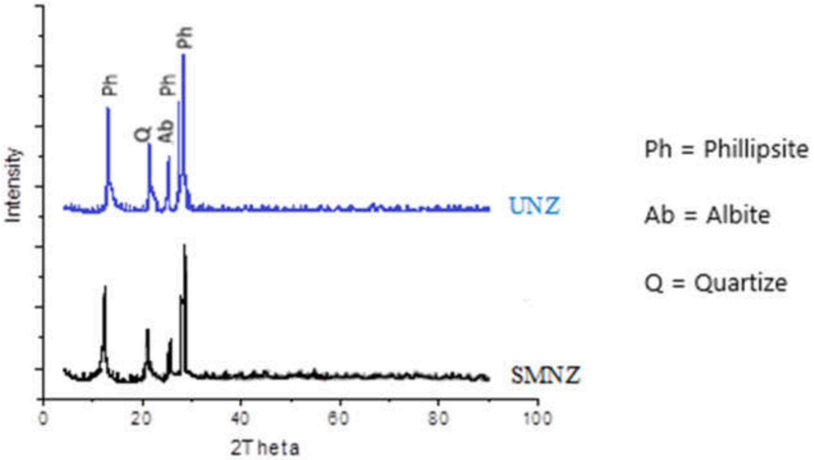

Figure 1. XRD patterns of the unmodified and surfactant-modified natural-zeolite (UNZ = unmodified natural-zeolite, SMNZ = surfactant modified natural-zeolite).

Table 1. Chemical composition of the studied unmodified (UNZ) and surfactant-modified (SMNZ) zeolites.

Samples		Constituents (%)							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	TiO_2
UNZ	70.94	17.38	2.42	0.69	0.16	4.22	3.24	0.08	0.08
SMNZ	70.83	17.01	2.38	0.56	0.16	4.20	3.20	0.06	0.08

UNZ = unmodified natural-zeolite, SMNZ = surfactant modified natural-zeolite.

Chemical composition

The chemical analysis result showed that the zeolite considered in this study (phillipsite) contains SiO_2, Al_2O_3, Fe_2O_3, Na_2O, and K_2O as major components while CaO, MgO, MnO, and TiO_2 are minor components (Table 1).

Scanning electron microscopy (SEM)

The SEM micrographs of UNZ and SMNZ are shown in Figure 2. Surfactant modification resulted in a slight change in morphology. However, both images indicate the presence of pore channels on the surface, which is a characteristic feature of porous materials. Previously documented studies also show that zeolite materials have high pore channels on their surface [34, 35].

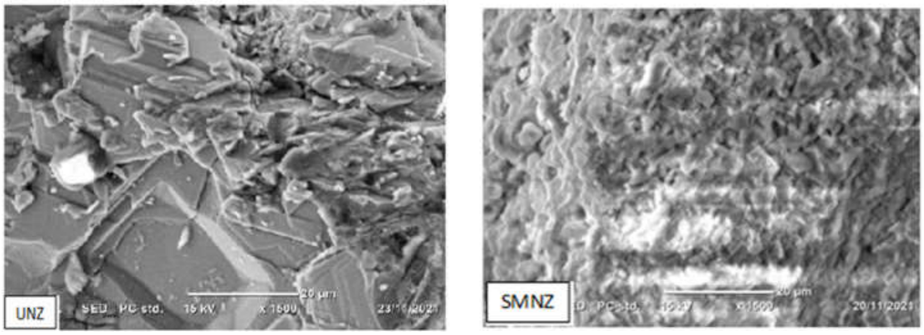

Figure 2. Scanning electron microscopy image of the studied unmodified and surfactant modified natural-zeolite at 20 µm resolution.

BET study

The specific surface area and total pore volume of UNZ, and SMNZ were 25.152 m^2/g and 0.093 cm^3/g, 34.98 m^2/g, and 0.106 cm^3/g, respectively. The increase in specific surface area and total pore volume in the case of SMNZ in comparison to UNZ could be due to the creation of additional pores at the zeolite surface during addition of surfactant. This outcome is consistent with [36] who found that adding a surfactant to clinoptilolite zeolite enhanced its specific surface area from 29 to 140 $m^2\ g^{-1}$ and total pore volumes from 0.1045 to 0.2460 $cm^3\ g^{-1}$.

Thermogravimetric analysis

The TGA profiles of the studied zeolites (UNZ, SMNZ) illustrate three steps of weight loss (Figure 3). UNZ showed about 0.75 % initial weight loss at 150 °C followed by a weight loss of 0.1% at 299 °C and 0.3% at about 570 °C. SMNZ showed an initial weight loss of 0.24% at 80

°C. This was followed by weight loss of 0.02% at 260 °C and 1.744% at 660 °C. The weight loss observed from 50-200 °C and 200-500 °C might be due to loss of surface bonded water (physically adsorbed water) and loss of matrix-bound water [37] The loss of weight observed after 500 °C could be due to the breakdown of hydroxyl ion (hydroxylation process) and oxidation of the organic phase [34, 38]. In general, both samples showed high thermal stability in the studied range. The endothermic peaks observed from derivative weight curves of both samples starting from 50 °C further indicate the elimination of physio-sorbed species. The decrease in mass loss for the surfactant modified zeolite at the initial stage of heating could be ascribed to the increased hydrophobicity of the zeolitic surface. On the other hand, the mass loss of the surfactant modified zeolite is found to be higher than the pristine natural zeolite at higher temperature, possibly due to oxidation of the organic phase on the zeolitic surface [38].

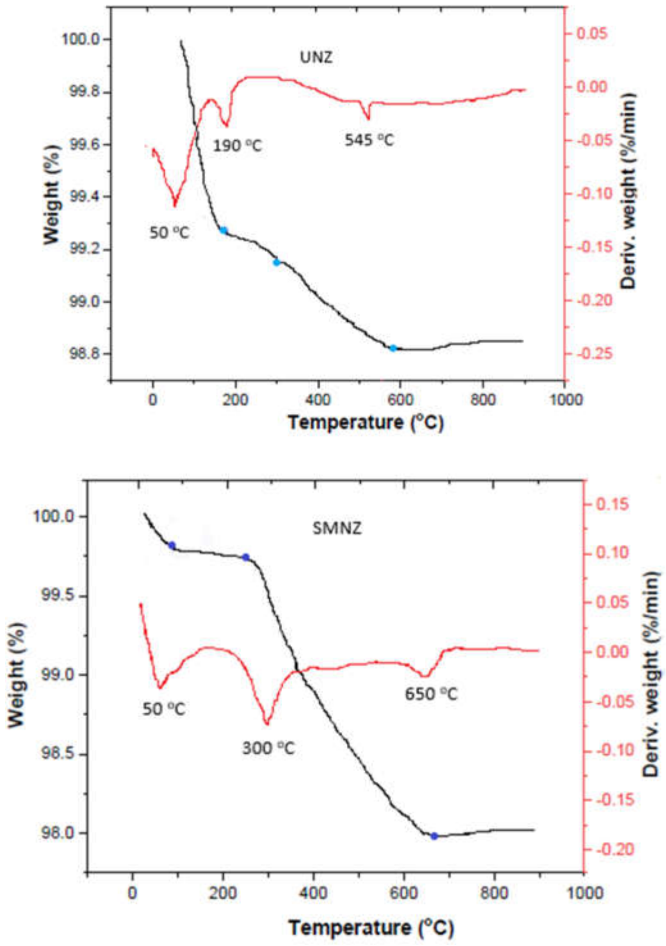

Figure 3. Thermogravimetric analysis (TGA-black/DTA-red color) of the studied unmodified and modified natural-zeolites (UNZ, and SMNZ).

Cation exchange capacity (CEC) and pH of zeolite samples

The pH of unmodified and modified zeolite materials was 7.51 and 7.48, respectively, which indicates that the materials are slightly alkaline. The original zeolite (phillipsite) has a high CEC value (313.7 C mol$_c$/kg). This indicates the ability of the material to hold cationic metals. Surfactant modification decreased the CEC of host zeolite to 53.33 C mol$_c$/kg which might be associated with change in the pore volume, pore diameter, and surface area of the natural zeolites. The reduction in the CEC could be because of the blocking of pore channels of natural zeolites with CEC surfactant [39].

Metals leaching study (column experiment)

The leaching patterns of the studied metals in the soil-zeolite mixture are shown in Table 2. The soils mixed with both modified and unmodified zeolite (phillipsite) decreased the leaching of all metals by retaining on the top layer of the soil column (0-20 cm) in comparison with the control soil. The soil mixed with unmodified zeolite (T2, T3, and T4) retained a higher concentration of each metal in the top layer (0-20 cm) than soil mixed with SMNZ (T5, T6, and T7) and the maximum result was obtained at T4 (20% UNZ). The low retention of SMNZ in comparison with UNZ may be due to the loaded HDTMAB resulted in a charge reversal on the external surface of the silicates from negative to positive. But still, soil mixed with SMNZ significantly retained a high concentration of metals on the top layer in comparison with the control soil. It was previously evidenced that after being modified with HDTMABr, internal pore parts remain negatively charged and serve to absorb cationic metals [40].

Table 2. Lead, cadmium, and chromium leaching pattern as affected by different rates of zeolite at two different soil depths.

Treatments	Pb^{2+} (mg/kg)		Cd^{2+} (mg/kg)		Cr^{3+} (mg/kg)	
	0-20 cm	20-40 cm	0-20 cm	20-40 cm	0-20 cm	20-40 cm
T1	12.33g	47.31a	9.42g	45.84a	7.02g	45.61a
T2	56.09c	15.60e	49.85c	18.79d	39.18c	21.93d
T3	63.12b	14.03e	56.28b	14.51e	47.37b	15.79e
T4	77.71a	6.69f	66.99a	7.82f	60.23a	9.06f
T5	21.37f	39.71b	17.19f	37.00b	17.54f	36.55b
T6	26.47e	33.03e	21.74e	35.13cb	20.76e	33.63cb
T7	32.90d	27.27d	26.02d	31.91c	24.85d	31.87c
CV	3.10	8.93	5.10	7.62	5.59	6.68
LSD	2.24	4.10	3.16	3.64	3.03	3.25

Means within a column with the same letter are not significantly different from each other at $p < 0.05$.

The result (Table 2) further shows that the zeolite material used has a higher affinity towards lead as a high amount was detected on the top of the soil column followed by cadmium and then chromium. The uptake might be ascribed to various mechanisms which include primarily adsorption and ion-exchange processes [41].

Heavy metals transfer into maize tissue

The amount of Cr^{3+}, Pb^{2+}, and Cd^{2+} uptake from soil mixed with both UNZ and SMNZ was significantly ($P < 0.05$) decreased in comparison with the control treatment (T1) at all application rates (Table 3). The result also shows that at the same application rates, soil mixed with UNZ (T2-T4) reduced the uptake of metals more than the one mixed with SMNZ (T5-T7). The amount of Cr^{3+} and Cd^{2+} transferred into maize significantly ($P < 0.05$) decreased with increasing application rates of both UNZ (T2-T4) and SMNZ (T5-T7). Though the amount of Pb^{2+} uptake reduced with increasing application rates of UNZ (T2-T4) and SMNZ (T5-T7), an insignificant difference was observed among T3, T4, and T7. The ionic radius of metal ions is inversely related to the charge density and electrostatic attraction which limits the interaction of the metal ions with the adsorption sites. Thus, metals with higher electronegativity sorb more readily on the surface of the adsorbent. The obtained selectivity series is in agreement with the metal ions electronegativity, namely Pb^{2+} (2.33) > Cd^{2+} (1.69) > Cr^{3+} (1.66). Hydration of metal ion also plays a crucial role in the adsorption process. Absolute value of the enthalpy of hydration increases with increase in ionic size. Enthalpy of hydration indicates that, the Pb^{2+} (aq) ion will have more accessibility to the adsorbent surface, followed by Cd^{2+} (aq) and Cr^{3+} (aq). The less significant difference shown for Pb transfer among the treatments T3, T4 and T7 could be as the result of the strong sorption to the zeolite surface [42].

Table 3. Heavy metals uptake by maize plant as affected by modified and unmodified zeolite.

Treatments	Amount transferred (mg/kg)		
	Cr^{3+}	Pb^{2+}	Cd^{2+}
T1	58.34a	51.34a	53.73a
T2	35.28c	23.55c	31.14c
T3	22.27e	5.84e	18.20e
T4	9.16g	4.81e	7.00g
T5	45.54b	37.63b	40.10b
T6	26.32d	17.39d	21.64d
T7	13.97f	8.19e	10.60f
CV	6.64	9.40	6.69
LSD	3.48	3.50	3.05

Means within a column with the same letter are not significantly different from each other at $p < 0.05$.

Effect of pH

The result showed that Cr^{3+}, Pb^{2+}, and Cd^{2+} uptake increased with the increase of pH up to 6 and then decreased with a further increase in pH (Figure 4) The maximum percent adsorption on soil only, soil mixed with SMNZ and UNZ at pH 6 were 34.2, 44.7, and 63.1 for Cr^{3+}, 36.3, 49.7, 73.2 for Pb^{2+} and 35.5, 47.7, 66.3 for Cd^{2+}, respectively. The rivalry between hydrogen ions for adsorption sites may be the cause of the reduced adsorption of these metals at very low pH [43]. The concentration of hydrogen ions as competitors decreased with increasing pH, which led to an increase in the adsorption of metal ions by the adsorbents [44]. Furthermore, at alkaline pH values, the adsorption of metals decreases due to formation of the metal hydroxides [45].

Effect of adsorbent dose

The effect of increasing modified and unmodified zeolite (phillipsite) dose on adsorption of chromium, cadmium and lead was presented in Fig. S1. When the addition of the adsorbent dose increased, the percentage removal of metal ions also increased. The maximum adsorption of chromium on SMNZ (50.8%) and UNZ (68.7%) was achieved at the highest dose (2 g). The removal of lead and cadmium on the unmodified zeolite (phillipsite) was increased as dose increased from 0.25 to 1 g and become constant beyond this dose. The initial rise in adsorption capacity with the increase in adsorbent dose was anticipated because as the amount of adsorbent particles increases, more surface areas are accessible for metal attachment, which makes it simpler for adsorbate to enter the adsorption sites [46]. The percentage removal obtained at this optimized dose (1 g) were 84.0 for lead and 70.3 for cadmium. However, their maximum adsorption on modified zeolite was obtained at 2 g (57.4% for Pb, and 55.0% for Cd). The relatively higher dose required for the surfactant treated zeolite compared with the pristine rival could be due to the partial blocking of the pores.

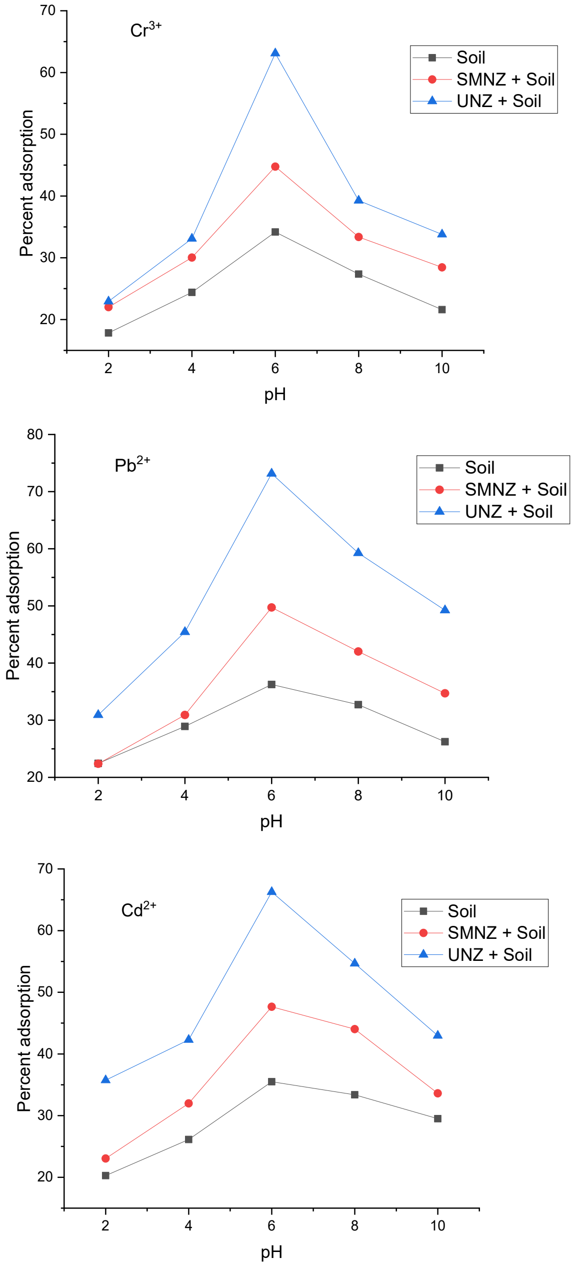

Figure 4. Effect of pH on adsorption of Cr^{3+}, Pb^{2+} and Cd^{2+} on to soil and soil mixed with SMNZ and UNZ at adsorbent dose of 0.5 g, contact time of 24 h, initial metal concentration of 30 mg/L and stirring speed of 200 rpm.

Effect of stirring speed

The effect of stirring speed on the adsorption of the studied heavy metals on the soil mixed with zeolite (phillipsite) was given in Fig. S2. The adsorption of chromium on soil alone, soils mixed with SMZ and UNZ was increased with increasing stirring speed and the maximum was reached at 200 rpm. The corresponding maximum percent removal at indicated speed was 37.9, 70.2, and 52.8, respectively. The maximum adsorption of lead (39.0%) and cadmium (37.2%) on the experimental soil was also achieved at 200 rpm. The percentage removal of cadmium and lead on the soil treated with UNZ and SMNZ also increased with stirring speed with corresponding percent removal reaching maximum at 150 rpm (74.3%) and 200 rpm (53.17%) for cadmium and at 100 rpm (84.3%) and 150 rpm (56.1%) for lead. The stirring speed required to reach maximum for lead on the soil mixed with zeolite (phillipsite) is lower than the speed required for adsorption on the control soil owing to high affinity even at low stirring speed. Because of the increased turbulence and thinner boundary layer surrounding the adsorbent particles, the percentage adsorption increases with agitation speed [47].

Effect of contact time

The adsorption rate of Cd^{2+} and Cr^{3+} was observed as rapid in the first 8 h, followed by a gradual increase in time until equilibrium adsorption was noticed at 16 h for Cd^{+2} and at 24 h for Cr^{+3}. Very rapid adsorption of Pb^{2+} on soil mixed with SMNZ and UNZ was also observed in the first 4 and 8 h, respectively, followed by a gradual increase in time until equilibrium was observed at 16 h. The maximum amounts adsorbed at the indicated time on soil only, soil mixed with SMNZ and UNZ were 46.7, 55.7 and 63.9% for Cr^{3+}, 49.5, 56.3 and 82.4% for Pb^{2+}, 48.3, 52.4 and 70.2% for Cd^{2+}, respectively. After these shaking hours no further increase in the adsorption amount was observed. When the empty sites were eventually filled by the adsorbed metal ions, a repulsive force was created between the adsorbed molecules on the surface of the adsorbent and in the bulk phase, which caused the adsorption rate to drop [48].

Effect of the initial heavy metal ions concentration

The percent removal of all metals was decreased with increasing metals initial concentration (5-50 mg/L). Percentage adsorption on soil, soil mixed with SMNZ and UNZ was decreased from 47.2 to 20.8%, 57.2 to 27.5, 76.1 to 45.6 for Cr^{3+}, 50.9 to 24.9, 55.6 to 32.5, 89.8 to 66.82 % for Pb^{2+} and 47.0 to 23.4, 53.8 to 32.4, 85.4 to 59.1 % for Cd^{2+}, respectively. Since there are few metal concentrations in the solution relative to the available surface area at low metal concentrations, adsorption sites are readily accessible and could be occupied [47].

Adsorption kinetics

Results of the kinetic study according to pseudo-first-order and pseudo-second-order models for the adsorption of Cr^{3+}, Pb^{2+}, and Cd^{2+} on both SMNZ and UNZ under optimum conditions have been presented in Table 4. To evaluate how well the experimental data fits the kinetics models, the values of the correlation coefficient (r^2) and the computed qe were employed. Though the values of r^2 observed in the case of the pseudo-first-order model were in acceptable ranges (> 0.9), the values observed for the pseudo-second-order model were very close to unity (> 0.99) (Table 4). The values of experimental qe ($qe_{exp't}$) also well agreed with the calculated ones (qe_{calc}). This indicates that the adsorption kinetics of the investigated metal ions onto both UNZ and SMNZ at studied initial metal ions concentrations follow the pseudo-second-order model.

Table 4. Kinetic parameters for adsorption of chromium, lead and cadmium onto zeolite-soil mixture according to pseudo-first-order and pseudo-second-order model.

Treatment	Metals	qe $_{\text{exp't}}$ (mg/kg)	pseudo-first-order reaction			pseudo-second-order reaction		
			qe $_{\text{calc.}}$	K_1 (1/h)	R^2	qe $_{\text{calc.}}$	K_2 (kg/mgh)	R^2
Soil	Cr^{3+}	70.00	47.60	0.120	0.9775	74.074	0.003	0.9968
SMNZ + S		83.50	50.84	0.075	0.9692	89.29	0.005	0.9935
UNZ + S		95.85	51.24	0.094	0.9541	100.00	0.006	0.9973
Soil	Pb^{2+}	74.30	32.877	0.208	0.9655	75.76	0.004	0.9998
SMNZ + S		84.50	38.265	0.111	0.9030	86.96	0.009	0.9985
UNZ + S		123.50	104.16	0.235	0.9058	129.87	0.019	0.9959
Soil	Cd^{2+}	72.25	35.27	0.193	0.9891	74.07	0.012	0.9995
SMNZ + S		78.50	39.49	0.171	0.9684	80.65	0.016	0.9991
UNZ + S		105.20	60.42	0.204	0.9982	107.53	9.104	0.9994

Adsorption isotherm

Langmuir and Freundlich isotherm constants for the adsorption of Cr^{3+}, Pb^{2+}, and Cd^{+2} ions onto zeolites under optimum conditions are shown in Table 5. The values of r^2 (correlation coefficient) are considered to predict the applicability and goodness of fit of the experimental data to the models. The values of r^2 obtained (Table 5) are > 0.9 for all metals showing a high significance of the proposed models, as similarly reported by others [48, 49]. This means that both models fit well the adsorption data and may be applicable for the adsorption of metals on zeolite but both models may not equally describe the adsorption of metals. Accordingly, the isotherms of Cr^{3+} ions adsorption better fit the Langmuir model as the values of r^2 in the Langmuir model are higher than that of the Freundlich isotherm model (Table 5). This proves that Cr^{3+} forms monolayer adsorption at the surface of the zeolite adsorbent [50]. Adsorption of Pb^{2+} ions on soil alone and soil mixed with UNZ better fits Langmuir and Freundlich isotherm models respectively but, its adsorption on soil mixed with SMNZ can be described by both models as their r^2 values are almost equal. The suitability of both models indicates that single-layer adsorption might have occurred, with heterogeneous active site energy distribution on the surface. Adsorption of Cd^{2+} on soil alone and soil mixed with UNZ is better described by the Freundlich isotherm model but its adsorption on soil mixed with SMNZ better fitted the Langmuir isotherm model.

Table 5. Freundlich and Langmuir isotherm constants for Cr^{3+}, Cd^{2+}, and Pb^{2+} sorption onto soil and soil mixed with unmodified and modified zeolite.

Treatments	Metals	Langmuir			Freundlich		
		q_{max} (mg/kg)	b (L/kg)	r^2	n	K_f	r^2
Soil	Cr^{3+}	67.11	0.102	0.9569	1.750	7.834	0.9073
SMNZ + Soil		90.91	0.100	0.9592	1.691	10.132	0.9242
UNZ + Soil		151.52	0.120	0.9872	1.675	18.620	0.9637
Soil	Pb^{2+}	84.75	0.082	0.9760	1.650	8.373	0.9411
SMNZ + Sol		120.48	0.066	0.9549	1.490	9.143	0.9545
UNZ + Soil		238.10	0.132	0.9549	1.696	32.840	0.9985
Soil	Cd^{2+}	83.33	0.071	0.9549	1.442	6.405	0.9763
SMNZ + Soil		116.28	0.072	0.9937	1.594	10.13	0.9744
UNZ + Soil		212.76	0.103	0.9043	1.692	25.04	0.9950

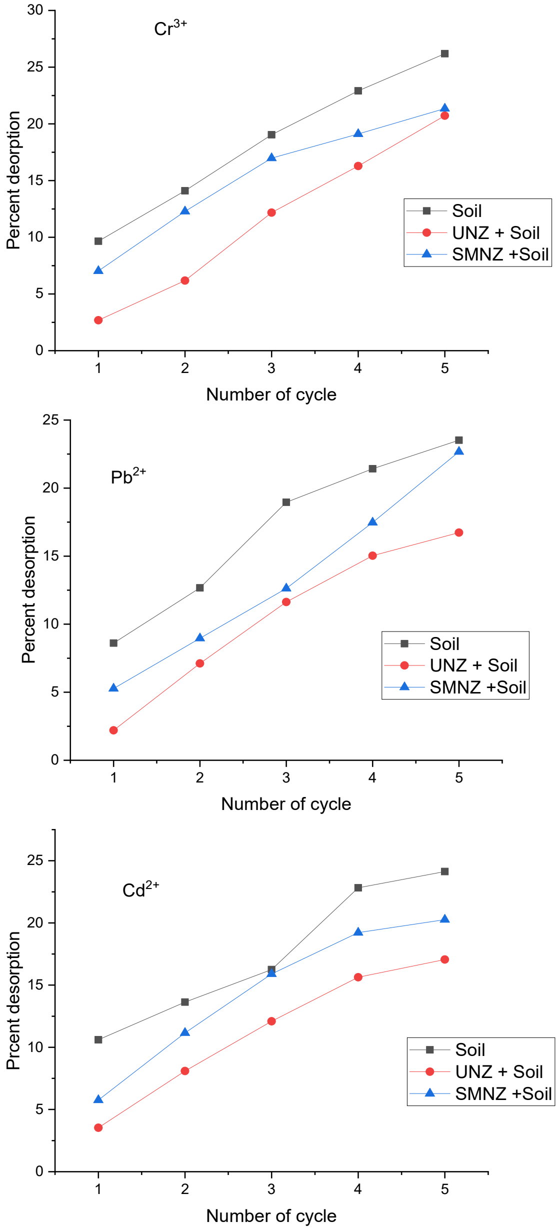

Figure 5. Desorption patterns of lead, chromium and cadmium from control soil, soil treated with UNZ and SMNZ at pH 6, contact time (16 hours for Pb^{2+} and Cd^{2+}, 24 hours for Cr^{3+}) and initial metal ions concentration of 50 mg/L.

The maximal adsorption capacities (q_{max}) of Cr^{3+}, Pb^{2+}, and Cd^{2+} on soil mixed with UNZ were higher than soil mixed with SMNZ and soil alone (Table 5). The Freundlich constant, *n* values for adsorption of all metals on both UNZ and SMNZ lie between 1 and 10 (Table 5) indicating favorable conditions for adsorption [30]. The K_f value observed for the adsorption of Cr^{3+}, Pb^{2+}, and Cd^{+2} on UNZ was higher than the values observed for their adsorption on SMNZ implying the greater adsorption capacity of UNZ in comparison with SMNZ.

The interaction between the sorbent and the adsorbent can be predicted by using separation factor 'R_L' (essential characteristics of the Langmuir isotherm). This dimensionless equilibrium parameter can be calculated using equation 9 [50]:

$$R_L = \frac{1}{1+bCo} \qquad (9)$$

where: b is the Langmuir constant and C_o is the initial concentration of the sorbate. The values of R_L at each initial concentration for all treatments are between 0 and 1 indicating the favorability of adsorption.

Desorption

The total amount of metals desorbed after five cycles from control soil, soil mixed with SMNZ and UNZ followed the order $Pb^{2+} > Cd^{2+} > Cr^{2+}$ (Figure 5). The respective desorbed amount in mg/kg and percent desorption were 47.4 (91.9), 52.7 (76.8) and 66.2 (58.0) for Cr^{3+}, 53.1 (85.2), 54.5 (67.0) and 88.0 (52.71) for Pb^{2+} and 51.2 (87.4), 58.6 (72.3) and 84.5 for Cd^{2+} (56.4). The result shows that the soil treated with UNZ retained a high amount of metals in comparison with the control soil and SMNZ at the end of the desorption cycles and the percentage of lead retained was relatively higher than that of cadmium and chromium.

CONCLUSION

The application of zeolite for the removal of heavy metals in this study shows significant results in the order of $Pb^{2+} > Cd^{2+} > Cr^{3+}$ in all tested parameters. The soil mixed with zeolite significantly ($p < 0.05$) retained a high concentration of these metals in comparison with the control soil. The addition of zeolite also has a significant role in reducing the transfer of metals to maize crops. On the other hand, unmodified zeolite has a high affinity towards all metals in comparison with modified zeolite. The experimental conditions such as pH, dose, stirring speed, contact time, and initial metal ions concentration significantly affected the sorption of Pb^{2+}, Cd^{2+}, and Cr^{3+} onto both modified and unmodified zeolite (phillipsite). The adsorption kinetics result shows that the pseudo-second-order model represented the best fits for the experiments. The maximum adsorption imply that natural zeolite has a significant role in stabilizing toxic heavy metals in polluted soil and in reducing their transfer into plants.

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