



Research article

Effects of natural and modified zeolite based composite fertilizers on slow release and nutrient use efficiency

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ABSTRACT

Excessive use of chemical fertilizers causes serious environmental hazards, as only a fraction is really adsorbed by the soil. As part of the solution, the feasibility of using unmodified (UNZC) and surfactant-modified natural zeolite-based composite (SMNZC) fertilizers as support materials for the provision of nutrients to soil on a slow release basis was assessed using column and pot experiments. The characterization of the zeolite materials was done using powder XRD, XRF, SEM, BET, and TGA instruments. The percentage of cationic nutrients released from soil columns containing UNZC increased over time. Their release from SMNZC initially slowed down and became stable as the number of days increased. The percentage of N-NO₃⁻ and available P released from UNZC has constantly decreased with time. Their release from SMNZC increased as the number of days increased. The maximum P uptake by maize was observed for the soil treated with SMNZC, and there was no significant difference at all rates. The maximum uptake of Ca (3663.40 ppm), Mg (2617.34 ppm), and Fe (222.83 ppm) was observed at 250 kg/ha of UNZC. The highest uptake of K, Zn, and Cu was also observed for the soil amended with UNZC, irrespective of its application rate. Application of UNZC and SMNZC at the same rate equally affected total nitrogen uptake. Thus, this finding showed that UNZC is a better carrier of cationic nutrients, while SMNZC is preferable for the slow release of NO₃⁻ and available P. In conclusion, both the modified and unmodified support forms showed better performance than conventional fertilizer in delivering nutrients slowly and sustainably.

1. Introduction

Conventional fertilizers, which are used in agriculture to increase crop yield, are currently popular in commerce. However, the widespread use of commercial fertilizers reduces how well soil nutrients are used [1]. The large-scale use of fertilizers has contributed more to environmental problems because of their high solubility, which causes leaching losses of between 40 and 75 percent [2]. In Ethiopia, boosting agricultural output is one of the biggest obstacles to realizing food security and poverty reduction. An obvious approach to overcome the soil fertility problem is to increase fertilizer application and enhance good agronomic practices to increase agricultural productivity. Because of this, the amount of fertilizer used nationally each year increased from 3500 t to roughly 140,000 t by the early 1990s, and then to roughly 200,000, 400,000, and 550,000 t in 1994, 2005, and 2010, respectively [3]. However, according to Ethiopian Soil Information System [4], most of the cultivated soils in Ethiopia were low levels of total nitrogen (N),

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phosphorous (P), potassium (K), sulfur (S), copper (Cu), zinc (Zn) and boron (B) [5]. It is also reported that in Ethiopia, the depletion rate of macronutrients N, P, and K was 122, 13, and 82 kg/ha year⁻¹, respectively which is estimated to be the highest in sub-Saharan Africa. As a result, studies on how to use efficient methods to reduce nutrient losses while increasing crop yield and improving nutrient use efficiency using low cost materials are imperative.

In the past, it was reported that the use of slow release fertilizers (SRFs) which deliver nutrients more gradually than commercial fertilizers is very crucial to boost nutrient use efficiency and minimize environmental effects. This slow release encourages improved nutrient delivery to the plants, which speeds up early germination, rapid development, and a high nutritional level [6,7]. In this regard, the use of natural zeolites (crystalline hydrated aluminosilicates) is crucial not only to increase the fertilizer use efficiency of crops but also to combat the adverse effects of chemical fertilizer on agriculture ecosystems [8,9]. Their high surface area, large porosity, ion exchange property, and high nutrients loading capacity make them important materials in agriculture as nutrient carriers and slow releaser. Zeolites, with or without surfactant modification, have a special porous structure that allows them to efficiently hold nutrients and water [10,11]. While almost all of naturally occurring zeolites do not possess high affinity for trapping anionic species such as NO₃⁻ and PO₄³⁻, modifying their surfaces via cationic surfactants can enhance their capabilities to trap anions [12]. The use of the quaternary amine hexadecyl trimethyl ammonium (HDTMA); a long-chain surfactant with a permanent positive charge for such purpose was frequently reported in the past. The surfactant molecules form bilayers on zeolite surfaces. The surfactant loading on the zeolite is a function of the external CEC of zeolite and the chain length of the cationic surfactant [13]. The use of natural zeolite (clinoptilolite) as nitrogen, phosphorus and potassium SRFs (as single element fertilizer) have been carried out in the past to facilitate plant growth [14, 15]. [16] also prepared synthetic zeolite incorporated with macronutrients (Ca²⁺, Mg²⁺, PO₄³⁻, NO₃⁻) to enhance nutrient availability in the soil. However, employing naturally occurring zeolites and/or the surfactant modified form as support for both macro and micro-nutrients for the slow release application is still not well studied. Due to the simultaneous introduction of many nutrients, which saves money over applying each fertilizer separately, these fertilizers are advantageous economically. Furthermore, there is a paucity of information related to the applicability of other types of zeolites such as phillipsite as slow-release fertilizers.

Previous studies showed abundant resources of mordenite and clinoptilolite near Adama-Nazret [17], phillipsite and clinoptilolite in the Awassa area, several zeolitic phases and a highly pure large deposit of stilbite in the north region of the country [18]. However, systematic study on these materials at the national level is lacking, making the tracing of such resources difficult for research undertaking. [19] also indicated that despite scattered findings of zeolite deposits around Ethiopia, no efforts have been made to explore deeply the presence and potential importance of zeolites in this country, and no follow-up work appears to have been carried out so far on it. According to Ref. [20], the soils of the studied area (Haramaya district, Eastern Ethiopia), face a wider set of soil fertility issues, which have historically been the major focus for extension workers, researchers, policymakers, and donors. In addition to soil fertility issues, a shortage of rainfall is also frequently observed in Haramaya district. This suggests the importance of using such low-cost and locally available porous material that might improve soil nutrient availability, water holding capacity, and nutrient uptake by plants. Therefore, the present work aimed to: i) prepare and characterize the slow-release fertilizers based on natural and surfactant-modified zeolite; and ii) evaluate their effect on the slow and sustainable release of nutrients (N, P, K, Ca, Mg, Fe, Zn, and Cu) to soil using maize (*Zea mays* L) as a test plant.

2. Materials and methods

2.1. Experimental soil sampling, preparation and analysis

The samples of Fluvisols were collected from Haramaya district (Rare research site of Haramaya University) which is located at 510 km from Addis Ababa toward the Eastern part of the country. The site locates at 09° 24' 91" N latitude and 42° 01' 35" E longitude. The collected soil samples were air-dried, crushed using a pestle and mortar, and passed through a 2 mm diameter sieve for laboratory analysis. A 0.5 mm diameter sieve was used for organic carbon and total nitrogen determination. Soil particle size distribution was determined by the hydrometer method [21]. Analysis of soil pH was done using a pH meter with a solution at 1:2.5 soils to water ratio. Analysis of total nitrogen was done by using the Kjeldahl method [22]. Available phosphorus was extracted by 0.5 N sodium bicarbonate solution as described by Ref. [23] and analysis of organic carbon was done according to the method described in Ref. [24]. One molar neutral ammonium acetate (pH = 7) was used to extract the exchangeable bases (Ca, Mg, K). CEC was also determined by using the ammonium acetate method [22]. Available micronutrients (Cu, Fe, and Zn) were extracted with ammonium bicarbonate di-ethylene tri-amine penta-acetic acid (AB-DTPA) as described by Ref. [25].

2.2. Zeolite collection and preparation

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

2.3. Surfactant-modified zeolite preparation

Hexadecyl trimethyl ammonium bromide (HDTMABr) was used for surfactant modification of the host zeolite. A known quantity of washed zeolite sample was mixed with HDTMABr solutions (1000 mg/L) in a 1:100 (solid: liquid) ratio. The content was stirred for 8 h

at 150 rpm on an orbital shaker. After filtering the solution, the solid leftover was cleaned with double-distilled water and allowed to air-dry for 6 h. Using a mortar and pestle, the produced surfactant-modified zeolite (SMZ) was mechanically ground to fine particle size [26].

2.4. Preparation of zeolite based composite fertilizers (UNZC, and SMNZC)

The zeolite-based composite fertilizers were prepared by simple impregnation of nutrients into both modified and unmodified natural zeolite. Two hundred grams of zeolite sample was added to 1 L distilled water. To achieve the best possible impregnation of these nutrients into zeolite, 5 % solutions of macro (P, N, K, Ca, Mg) and micro-nutrients (Fe, Zn, Cu) in the form of their salts ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, KNO_3 , $\text{Ca}_3(\text{PO}_4)_2$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were added subsequently and the contents were stirred for 3 h. The resulting suspension was vacuum filtered, oven dried at 105 °C, and fine ground with pestle and mortar. The synthesized zeolite based fertilizers was stored in an air-tight container till further use [27].

2.5. Characterization of zeolite samples

The materials prepared were characterized by various techniques. In order to determine the crystalline structure and phase purity, powder X-ray diffraction (PXRD) patterns were registered in a Philips X'PERT diffractometer outfitted with an X'Celerator detector and employing Cu K α radiation ($\lambda = 1.5418$). The data were gathered in the 2 θ range of 4–90. The fundamental chemical composition of zeolite was studied by using X-ray fluorescence (Ametek, Germany) device with SDD silicon drift detector with a resolution of 145 eV at 10,000 pulses. The scanning electron microscopy (JCM-6000 Plus) was used to analyze the morphology of the zeolite samples. In a Micromeritics instrument ASAP 2420 device, N₂ sorption-desorption characteristics were tested at –196 °C. Normally, 100 mg of each sample was outgassed for 16 h under a high vacuum before the isotherms were recorded. Thus, the materials' surface areas were calculated using the Brunauer-Emmet-Teller (BET) method. The total pore volume was taken from the relative pressure close to unity ($p/p_0 = 0.98$). Utilizing a PerkinElmer TGA7 instrument, thermogravimetric analysis (TGA) was carried out. The analyses were performed in the 30 °C–900 °C temperature range under airflow at 20 °Cmin^{–1} heating rate.

2.6. Water absorbance capacity (WAC)

The percentage of water that a plant can absorb (the optimum amount of moisture) for a specific period was calculated using the term “water absorption capacity” (WAC). These studies were done by taking 1.0 g zeolite samples: unmodified natural zeolite (UNZ), surfactant-modified natural zeolite (SMNZ), unmodified zeolite based composite fertilizer (UNZC), and surfactant-modified zeolite based composite fertilizer (SMNZC) (W1) in pre-weighted beakers (W2). These beakers were put in desiccators under a moist environment for 5 days and reweighed (W3). Their WAC was checked by using Eq. (1) [27].

$$\text{WAC} = \frac{W_3 - W_2}{W_1} * 100 \quad (1)$$

2.7. Swelling ratio (SR) and equilibrium water content (EWC) study

To determine the increased weight of the zeolite samples owing to water soaking, the swelling ratio (SR) was determined. Zeolite samples weighing 1.0 g were dissolved in 200 mL of distilled water and left to stand for 24 h at room temperature and pressure. The contents were filtered to calculate SR and EWC using Eqs. (2) and (3), respectively [28].

$$\text{SR} = \frac{W_s - W_d}{W_d} \quad (2)$$

$$\text{EWC \%} = \frac{W_s - W_d}{W_s} * 100 \quad (3)$$

where W_s and W_d are the wet and dry weights of zeolite samples respectively.

2.8. Water retention capacity (WRC)

To measure how much water a soil can retain over time, the water retention capacity (WRC) was calculated. Utilizing pre-weighed beakers A (WA) and B (WB), the WRC of zeolite samples (UNZ, SMNZ, UNZC, and SMNZC) was determined (WB). 50.0 g of soil was taken in beaker A (the control) and 2.0 g of zeolite samples were mixed with 50 g of soil in beaker B in triplicate. All beakers then received 30 mL of distilled water. After allowing water to permeate the samples for 24 h, the weights of the beakers (WA1 and WB1) were retaken. The beakers were then kept in a glass box and weighed (WA2 and WB2) daily for the next 5 days allowing 24 h intervals between the readings then at 15 days [29]. The WRC was then calculated using Eq. (4).

$$\text{WRC} = \frac{W_2}{W_1} * 100 \quad (4)$$

Were, W1 is the weight of the beaker with soil, zeolite, and water after 24 h, and W2 is the weight of the same content taken after the next days in 24 h intervals between readings.

2.9. 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 Ref. [30]. Five grams of samples were agitated end-to-end on a shaker with 50 mL of 0.5 M NH₄Cl 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.

2.10. Nutrients release pattern study from zeolite based composite fertilizers

The study was conducted for 10 days by uniformly mixing 400 g of soil and 10 g of zeolite based composite (NZC) in a PVC column (62 cm height x 5 cm diameter) in triplicate. Homogenization of the soil and NZC was done by shaking on a rotary shaker for 24 h using locked plastic bottles and being allowed to stand for 30 days. To prevent soil loss, a piece of nylon mesh and a Whatman No. 42 filter paper was positioned at the base of the leaching column. Following this, 180 mL of deionized water was applied to the column and about 50 mL of the filtrate was collected for 10 days. The collected filtrates were analyzed to determine how the composite fertilizers released nutrients in the soil per day [27]. The treatments included are control soil column (T1), soil + UNZC (T2), and soil + SMNZC (T3). The filtrates collected were analyzed for N-NO₃⁻ and available P by UV Visible Spectrophotometer (T80+UV/VIS spectrometer, PG instrument), K by Flame Photometer (corning, 410), and the other nutrients (Zn²⁺, Ca²⁺, Mg²⁺, Fe²⁺, Cu²⁺) by Flame Atomic Absorption Spectrometer (Buck Scientific 210VGP FAAS). The result was presented as the average percentage of nutrients released out of total available nutrients present in zeolite based composite fertilizers. The measured values were next compared to the untreated soil's nutrient release patterns.

2.11. Pot experiments

To test the applicability of the prepared fertilizers, maize plants were treated with UNZC and SMNZC at different application rates. Furthermore, other experiments were carried out with commercial fertilizer (NPK, blended form) according to the recommended rate (100 kg/ha) set by the Ministry of Agriculture of local government in order to evaluate and compare the effect of both the commercial and proposed fertilizers on plant nutrient uptake. The experiments were performed by putting ten kg of soil into each experimental pot (surface area 1602.97 cm²) in the main season. The soil pots were then amended with the prepared composite and commercial fertilizers. Maize variety BH-661 was planted as a test crop at a depth of 4 cm and irrigated to field capacity (60 % w/w). The experiments were laid out in a completely randomized design (CRD) consisting of eight independent treatments in triplicate. The treatments included are unfertilized condition (T1), fertilized with commercial fertilizer but no zeolite (T2), UNZC 100 kg/ha (T3), UNZC 200 kg/ha (T4), UNZC 250 kg/ha (T5), SMNZC 100 kg/ha (T6), SMNZC 200 kg/ha (T7), and SMNZC 250 kg/ha (T8). The exact amounts of the commercial and composite fertilizers used for 100 kg/ha, 200 kg/ha, and 250 kg/ha were 1.600, 3.205, and 4.070 g respectively.

2.12. Plant nutrient analysis and biomass estimation

Leaves collected at 12 weeks were washed with distilled water, oven-dried at 70 °C to a constant weight, crushed, passed through a 2-mm sieve, and put in paper bags. Wet-acid digestion method was adopted to extract N, P, K, Ca, Mg, Cu, Fe, and Zn [31]. The Kjeldahl method was used to determine the total nitrogen in plants [32]. Ca, Mg, Cu, Fe, and Zn in plant digests were analyzed using Atomic Absorption Spectrophotometer (Buck Scientific 210VGP FAAS), K using Flame Photometer (corning, 410), and P with a

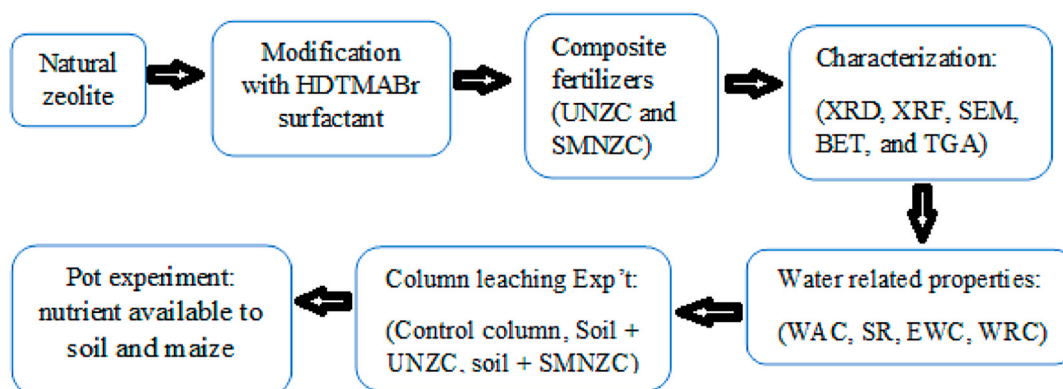


Fig. 1. Flow chart for the experimental procedure.

spectrophotometer (T80+UV/VIS spectrometer, PG instrument) using required standard solutions. The dry biomass of the maize plants (above the ground) was determined by using an oven dryer. The procedures depicted above are all summarized in the flow diagram depicted on Fig. 1.

2.13. Statistical analysis

The data collected for each treatment were subjected to analysis of variance (ANOVA) using general linear model (GLM) procedures SAS version 9.0. Treatment means were compared using the least significant difference (LSD) test at $P < 0.05$. Origin 2018 software was used for drawing graphs.

3. Results and discussion

3.1. Powder X-ray diffraction pattern

The diffraction data of all zeolite materials before (UNZ, SMNZ) and after impregnated with nutrients (UNZC, and SMNZC) showed peaks at 2θ values of 12.36, 27.84, and 27.89° corresponding to the reflection planes of (001), (022), and (041) that can be ascribed to phillipsite (ph) structure (024–1046) (Fig. 2). In addition, other peaks are observed at 2θ values of 20.86 (100) and 25.62 (112) representing quartz (038–0448) and albite (009–0466) associated with the natural zeolite. The surfactant-modified natural zeolite (SMNZ) showed a similar diffraction pattern with the host zeolite (UNZ) except diminished peak intensity observed at 2θ value of 25.62° and 20.86° exhibiting the little effect of the surfactants in terms of influencing the zeolite framework. This demonstrated the material's structural stability before and after the surfactant treatment, which is consistent with earlier findings. For instance, while comparing the diffraction patterns of surfactant-modified forms of clinoptilolite zeolite with their corresponding unmodified counterparts, [33] found a close similarity. Moreover, doping the zeolite with nutrients didn't affect the zeolite structure. Furthermore, no peak representing the dopants is observed in the nutrient-loaded zeolites perhaps due to the lower concentration of the dopants. But, the peak intensities observed around 2θ values of 12.36°, 25.62°, and 20.86° get declined in the case of UNZC and SMNZC possibly due to the incorporation of nutrients.

3.2. Chemical composition

According to the results of the chemical analysis, the investigated zeolite (phillipsite) contains CaO, MgO, MnO, P_2O_5 and TiO_2 as trace components along with SiO_2 , Al_2O_3 , Fe_2O_3 , Na_2O and K_2O as main constituents (Table 1). Previous studies also showed that zeolites can accommodate sodium, calcium, magnesium, potassium or other cations which can be removed or exchanged without destroying the aluminosilicate framework [8]. The Si: Al ratio made by the major component of this zeolite material (phillipsite) is 3.6 as observed from XRF analysis. The increment in Ca, Fe, Mg, Na, K, Cu, P and Zn oxides in the case of UNZC and SMNZC shows the adsorption of these nutrients onto zeolite (phillipsite) during the preparation of composite fertilizers. The decreasing tendency of Al_2O_3 and SiO_2 might be also related to incorporation of nutrients into the material.

3.2.1. Scanning electron microscopy

The SEM micrographs of UNZ, SMNZ, UNZC, and SMNZC are shown in Fig. 3. The micrograph of UNZ revealed the prismatic aggregates of the host zeolite (phillipsite). Surfactant modification and the addition of dopants (nutrients) resulted in a slight change in morphologies. The images indicate the presence of pore channels on the surface, which is a characteristic feature of porous materials. Pores and cavities are key characteristics of zeolite materials. SEM images from previously documented studies also show the spongy nature of zeolite materials [34,35].

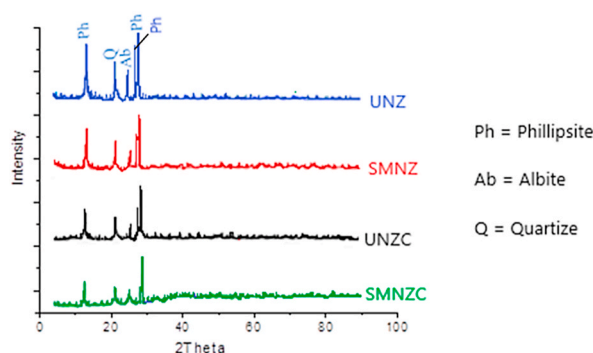


Fig. 2. XRD patterns of zeolite samples before (UNZ and SMNZ) and after (UNZC and SMNZC) impregnated with nutrients. UNZ = unmodified natural zeolite, SMNZ = surfactant-modified natural zeolite, UNZC = unmodified natural zeolite based composite fertilizer, SMNZC = surfactant-modified zeolite based composite fertilizer.

Table 1

Chemical composition of zeolite samples before (UNZ and SMNZ) and after impregnated with nutrients (UNZC and SMNZC).

Samples	Constituents (mass %)											
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	ZnO	CuO	P ₂ O ₅	TiO ₂
UNZ	70.94	17.38	2.42	0.69	0.16	4.22	3.24	0.08	–	–	0.05	0.08
SMNZ	70.83	17.01	2.38	0.56	0.16	4.20	3.20	0.06	–	–	0.03	0.08
UNZC	53.33	10.18	5.14	3.73	3.96	7.98	6.41	0.03	2.68	2.10	3.05	0.05
SMNZC	54.04	12.00	4.71	3.69	3.34	6.74	6.01	0.04	2.41	1.32	3.89	0.03

UNZ = unmodified natural zeolite, SMNZ = surfactant-modified natural zeolite, UNZC = unmodified natural zeolite based composite fertilizer, SMNZC = surfactant-modified zeolite based composite fertilizer.

3.3. BET study

The specific surface area and total pore volume of UNZ, SMNZ, UNZC, and SMNZC were 25.152 m²/g and 0.1093 cm³/g, 34.98 m²/g and 0.2106 cm³/g, 12.35 m²/g and 0.075 cm³/g, 14.83 m²/g and 0.081 cm³/g respectively. The outcome showed that the specific surface area and porous properties of the zeolite phase are affected by surfactant modification. The cause of 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 a secondary pore structure at the zeolite surface after modification. This finding is in accordance with [15] who showed surfactant modification of clinoptilolite zeolite increased the specific surface area from 29 to 140 m² g⁻¹ and the total pore volumes from 0.1045 to 0.2460 cm³ g⁻¹. On the other hand, the doping of nutrients decreased the specific surface area and pore volume in the unmodified and surfactant-modified zeolites based composites owing to the pore filling by the nutrients introduced into the zeolite structure.

3.4. Thermogravimetric analysis

Three steps of weight loss are shown in the TGA profiles of UNZ, SMNZ, and UNZC, while four steps of weight loss are shown for SMNZC (Fig. 4). UNZ displayed about 0.75 % initial weight loss at 150 °C followed by a loss of 0.1 % at 299 °C and 0.3 % at about 570 °C. SMNZ showed a weight loss of 0.24 % at 80 °C, 0.02 % at 260 °C, and 1.744 % at 660 °C. About 0.72, 0.53, and 1.52 % weight loss were shown by UNZC at 71.5 °C, 262.3 °C, and 590 °C respectively. Similarly, SMNZC showed weight losses at 100 °C (0.27 %), 150.6 °C (0.46 %), 275 °C (0.04 %), and 700 °C (1.49 %). The weight loss seen between 50 and 200 °C and 200 and 500 °C, respectively, may

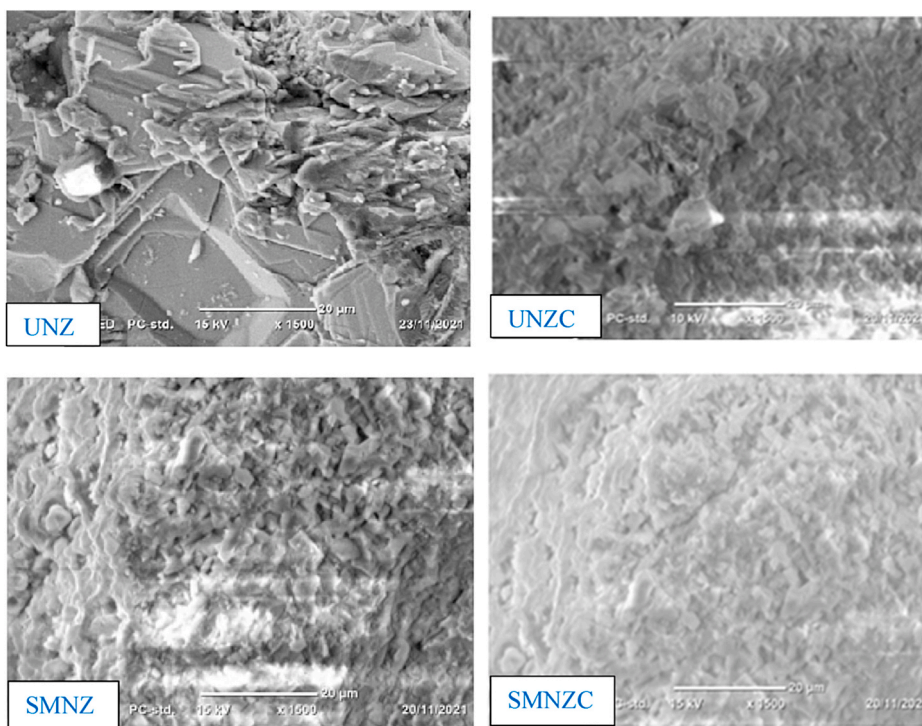


Fig. 3. Scanning electron microscopy image of zeolite samples before (UNZ and SMNZ) and after impregnated with nutrients (UNZC and SMNZC) at 20 μm resolution. UNZ = unmodified natural zeolite, SMNZ = surfactant-modified natural zeolite, UNZC = unmodified natural zeolite based composite fertilizer, SMNZC = surfactant-modified zeolite based composite fertilizer.

be caused by the loss of surface-bonded water (physically adsorbed water) and the loss of matrix-bound water [36]. Weight loss after 500 °C may be caused by the breakdown of the hydroxyl ion (hydroxylation process). Earlier studies also showed that the breakdown of hydroxyl ions increases as temperature increases but the overall de-hydroxylation process of zeolite is slow and takes place between 500 and 800 °C [36]. In the studied range, all of the samples displayed high thermal stability. The endothermic peaks observed from the derivative weight curves of all samples starting at 50 °C further indicate the evaporation of physically or chemically absorbed water (dehydration) [37] or elimination of other physically adsorbed species. The major part of the dehydration was completed at about 545, 650, 600 and 690 °C for UNZ, SMNZ, UNZC and SMNZC respectively. The presence of one extra endothermic peak on SMNZC shows the elimination of additional species from the material that might be introduced into the zeolite during modification with HDTMABr and doping with nutrients.

3.5. Water absorbance capacity, swelling ratio, and equivalent water content of zeolite samples

These parameters are essential features for the slow release fertilizers [27]. The WAC, SR, and EWC of the zeolite samples before and after doping with nutrients are given in Table 2. Though all the samples hold moisture greater than half of their weight, surfactant-modified zeolite samples (SMNZ and SMNZC) showed improved content. This improvement might be due to the creation of additional pores at the phillipsite surface during modification. Zeolite is a porous medium with open pore network channels into its structure, which can also play an important role in water retention. The presence of great porosity can facilitate entry of moisture into the zeolite structure [11]. The availability of more water in the pore channel of zeolite can improve the slow delivery of nutrients to the plant. This unique quality of zeolite is crucial during times of water scarcity, which reduces biomass output, especially in regions where water availability is restricted or where there are large water losses [38].

3.6. Water retention capacity (WRC) of zeolite samples

Another important characteristic of slow release fertilizer is water retention ability, which is crucial for agriculture in arid and desert regions in order to conserve water and enhance plant health. It measures how well the soil retains water after being mixed with zeolites [39]. In comparison to the soil without zeolite, which had a water retention capacity of 91.58 on the first day and dropped to

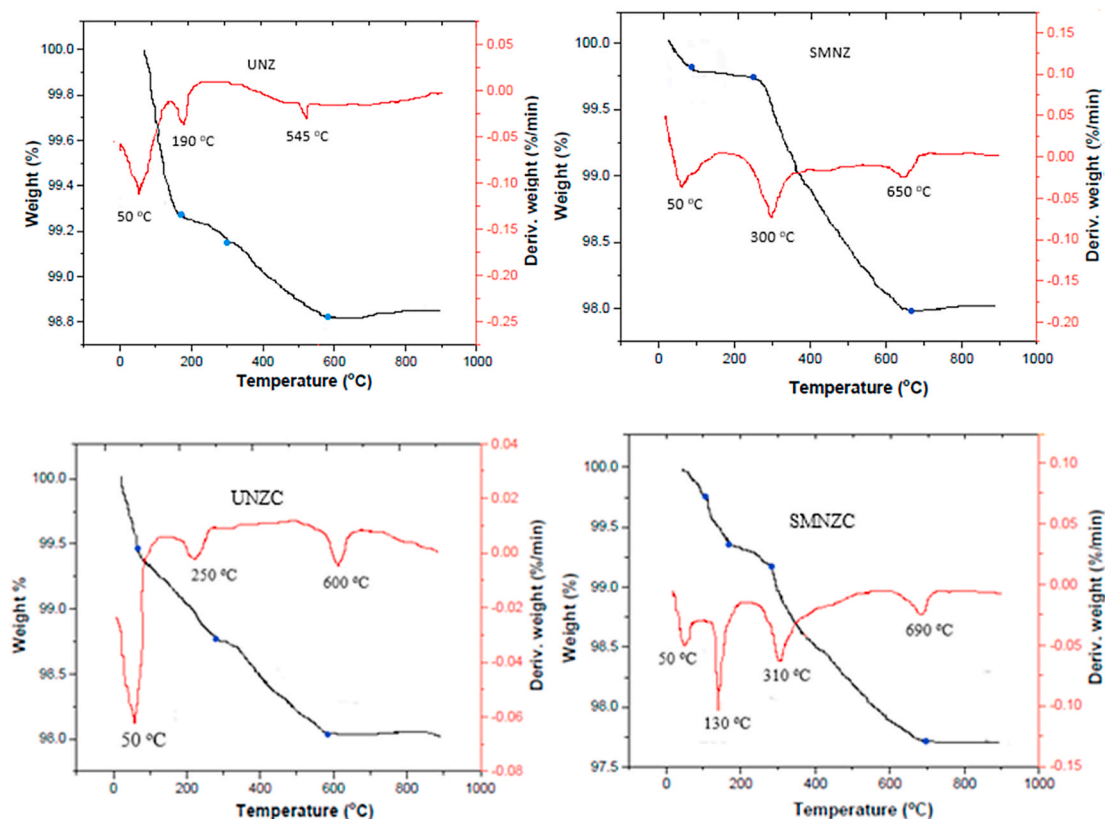


Fig. 4. Thermogravimetric analysis (TGA) spectra of the studied zeolite samples before (UNZ, SMNZ) and after impregnated with nutrients (UNZC, SMNZC). UNZ = unmodified natural zeolite, SMNZ = surfactant-modified natural zeolite, UNZC = unmodified natural zeolite based composite fertilizer, SMNZC = surfactant-modified zeolite based composite fertilizer.

Table 2Water absorbance capacity (WAC), swelling ratio (SR), and equivalent water content (EWC) of zeolite samples (mean \pm SD).

Zeolite Sample	WAC (%)	SR (g/g)	EWC (%)
UNZ	57 \pm 1.00	2.05 \pm 0.09	68.25 \pm 0.75
UNZC	56 \pm 2.65	2.07 \pm 0.18	68.45 \pm 1.95
SMNZ	63 \pm 3.61	2.14 \pm 0.2	73.26 \pm 2.08
SMNZC	61 \pm 3.00	2.18 \pm 0.19	74.87 \pm 0.83

UNZ = unmodified natural zeolite, UNZC = unmodified natural zeolite based composite fertilizer, SMNZ = surfactant-modified natural zeolite, SMNZC = surfactant-modified natural zeolite based composite fertilizer.

75.19 % on day 15, soil mixed with all zeolite samples (phillipsite) had a water retention capacity greater than 90 % on all days (days 1–15) (Table 3). On the other hand, soil mixed with surfactant treatment had a considerably higher WRC than soil with unmodified zeolite ($P < 0.05$). Zeolite can decrease the bulk density and increase total porosity, which consequently increase soil water content. Its application changes the inter-particle porosity of soil. This held water can increase the amount of water that is available to the soil and then to the plants as needed [11]. The present result is in accordance with previous results. For instance Ref. [27], revealed that the soil mixed with synthetic zeolite based SRFs had WRC of 94.04 and 69.14 % on the 3rd and 20th day while soil without SRFs retained 75.01 and 55.5 %, respectively (the rate of water retained in the case of soil alone is approximately 18 % less than that of soil with SRFs). [39] also showed that WRCs of the soil without SRFs (hybrid nano-fertilizer, HNF) were calculated to be 82, 69, and 51.3 % on the 5th, 10th, and 15th days, respectively. However, in the case of HNF, the water retention capacities of the soil for the same reference days were found to be 97, 75.6, and 57.8 %, respectively.

3.7. Cation exchange capacity (CEC) and pH of zeolite samples

As indicated in Table 4, the unmodified (UNZ) and modified (SMNZ) zeolite materials used were slightly alkaline materials as observed from their pH values (Table 4), but there is a small decrease in pH of UNZC and SMNZC probably due to the incorporation of non-metallic moieties [24]. The original natural zeolite (UNZ) has a high CEC value (313.67 Cmol_c/kg) which is comparable with previously reported values. For instance Ref. [40], determined the CEC values of two natural zeolite (mordenite, and clinoptilolite) and three synthetic zeolite (zeolite Na-PI, zeolite A, and zeolite X) and reported 266, 211, 325, 615 and 556 Cmol_c/kg values for each respectively. [41,42] also reported the CEC values of natural clinoptilolite zeolite (155 Cmol_c/kg) and mordenite zeolite (136.35 Cmol_c/kg) respectively, which are lower than the values reported in this study. Surfactant modification decreased the CEC of zeolite samples which might be associated with a decrease in the negativity of the surface. Similarly, a decrease in CEC of zeolite based composite fertilizers (UNZC and SMNZC), was observed as compared to UNZ and SMNZ which could be attributed to the incorporation of cations into the NZ matrix.

3.8. Characteristics of the experimental soil

The selected properties of the experimental soil are given in Table 5. The soil is classified as sandy clay loam depending on the levels of sand, silt, and clay content. According to the ratings of soil test values set by Ref. [43], the experimental soil contains a very low amount of total nitrogen and organic carbon. The low values of these parameters are comparable to OC and total nitrogen levels in the majority of Ethiopian cultivated soils, which may be explained by past land use practices such as the total removal of biomass from the field and the quick rate of mineralization after cultivation. According to the rate set by the same authors, the contents of iron, zinc, and copper in the soil were also below a critical level (5 mg/kg for Fe, 1.5 mg/kg for Zn, and 0.5 mg/kg for Cu). The accessible P concentration of the soil is within the range of medium (10–17 mg/kg). This shows that applying P in the form of DAP fertilizer over 15 years did not significantly increase the soil's P levels to a high range. The levels of exchangeable K, Ca, and Mg in the soil fall in the range of high, which might be related to K, Ca, and Mg-rich minerals [44].

Table 3

Water retention capacity (WRC) of the studied zeolite samples (in percent).

Treatment	Days					
	D1	D2	D3	D4	D5	D15
UNZ + Soil	95.25 ^c	94.31 ^c	94.13 ^c	94.05 ^c	93.03 ^c	90.67 ^c
UNZC + Soil	97.90 ^b	96.74 ^b	96.07 ^b	95.62 ^b	95.41 ^b	90.22 ^d
SMNZ + Soil	99.13 ^a	98.53 ^a	97.93 ^a	97.76 ^a	97.41 ^a	93.14 ^a
SMNZC + Soil	99.19 ^a	98.62 ^a	97.91 ^a	97.85 ^a	97.36 ^a	92.65 ^b
Soil (control)	91.58 ^d	84.08 ^d	81.02 ^d	80.30 ^d	76.28 ^d	75.19 ^e
CV	0.32	0.20	0.134	0.65	0.22	0.17
LSD	0.56	0.35	0.23	1.10	0.36	0.27

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

Table 4
Cation exchange capacity and pH of zeolite samples before and after impregnated with nutrients.

Zeolite sample	pH	CEC (Cmolc/kg)
UNZ	7.51 ± 0.31	313.67 ± 13.54
UNZC	7.18 ± 0.03	255.00 ± 7.60
SMNZ	7.48 ± 0.06	53.33 ± 6.50
SMNZC	7.10 ± 0.17	26.80 ± 1.64

Table 5
Selected properties of the experimental soil (mean ± SD).

Properties	Values	Properties	Value
Textural class	Sand clay loam	CEC (Cmolc/kg)	28.80 ± 2.00
Clay	26 ± 1.05	K (Cmolc/kg)	0.82 ± 0.10
Silt	18 ± 0.97	Ca (Cmolc (+)/kg)	18.62 ± 2.75
Sand	56 ± 2.01	Mg (Cmolc (+)/kg)	6.09 ± 0.02
pH	7.67 ± 0.08	Fe (mg/kg)	4.85 ± 0.52
OC (%)	0.83 ± 0.03	Zn (mg/kg)	1.47 ± 0.13
N (%)	0.04 ± 0.01	Cu (mg/kg)	0.45 ± 0.04
P (mg/kg)	16.83 ± 0.28		

3.9. Nutrients slow release study

The release pattern of nutrients from the prepared zeolite (phillipsite) based composite fertilizers per day is presented in Fig. 5. The release of all nutrients from control soil shows a sequential decrease with an increasing number of days. This indicates that these nutrients might not be available after certain days. According to Fig. 5, Cu^{2+} , Mg^{2+} , Zn^{2+} , Ca^{2+} , K^+ , and Fe^{2+} are released from UNZC at an increasing rate over time. After 4 days, the rate of release of Ca^{2+} , K^+ , and Fe^{2+} increased more quickly than it did at first. But, except for zinc which released at a constant rate in the first seven days, the release of these nutrients from SMNZC initially slowed down over time and became stable. The lower initial release rate of these cationic nutrients from UNZC in comparison to SMNZC suggests that UNZC has a stronger affinity for the investigated cations. However, because the amount of cationic nutrients released each day is not drastically reduced as it is in control soil, SMNZC is still a superior slow releaser than control soil. This might be the case because surfactant only adheres to the zeolite's exterior surface, leaving the cation-exchange sites inside the pores open [45]. The current results are well in accord with previous findings, and the pattern observed indicates the presence of a continuous supply of nutrients to plants, thereby preventing leaching losses that are commonly observed with traditional fertilizers [45]. The higher affinity of the studied zeolite to all cationic nutrient is probable due to its high CEC value. These studies ensure the long-term accessibility of nutrients to the plants, which enhances the healthy growth of plants that is lacking in the traditional fertilizer.

Unlike cationic nutrients, the patterns of nitrate and available phosphorus released from UNZC and SMNZC per day were different. The amount of N-NO_3^- and accessible P that was released from UNZC over time declined steadily, showing that these nutrients were only weakly bound to the unmodified natural zeolite (phillipsite). The release of N-NO_3^- from SMNZC increased as the number of days increased but the release of available P became constant after 8 days. The result shows that surfactant-modified zeolite is a better slow releaser of nitrate and available phosphorus as the amount released per day increased with time. This could be due to the loaded HDTMAB having resulted in charge reversal on the outer surface of the silicates from negative to positive or might be due to the formation of bilayer coverage on the modified zeolite which increases affinity for anions [13], [46]. [33] also showed that surfactant-modified clinoptilolite was a better slow releaser of nitrate when compared with their unmodified form. They further showed that in the case of soil, and unmodified clinoptilolite there is no release of nitrate after 12 days. On the other hand, even after 15 days, there was a release of about 7 % of nutrients from Surfactant-modified SRFs. This may be because nitrate ions have some ligand ability to form inner-sphere complexes with oxide particles of iron (III) [47]. [15] further studied the influence of the Fe (III)-modified clinoptilolite on phosphorus leaching from soil and obtained a reduction of phosphorus leached from the sample of sandy soil compared with untreated soil. [26] also observed that the P loading on SMZ increased by a factor of 4.9 as compared to the unmodified zeolite and control soil.

3.10. pH, organic carbon, and CEC of the soil as affected by UNZC and SMNZC

The pH, OC and CEC of the soils collected from each pot were given in Table 6. Regardless of UNZC (T3-T5) and SMNZC (T6-T8), the pH values of the soil were increased significantly ($P < 0.05$) with increasing application rates, but there was no significant difference ($P < 0.05$) in pH among applications at the same rates. The pH of soils (T1 and T2) had no significant difference ($P < 0.05$) but less than soils treated with zeolite (phillipsite) based composites. Our result concurs with past findings which reported increased soil pH with the addition of zeolite [48,49]. This increase in pH may be due to the increase in CEC by zeolite, which also increases the capacity of retention of exchangeable bases. [50] also indicated that increment of soil pH could be due to the exchange between NH_4^+ and cations such as Ca^{2+} and Na^+ , with the soil solution and the release of OH^- . The CEC Values of soils treated with zeolite based

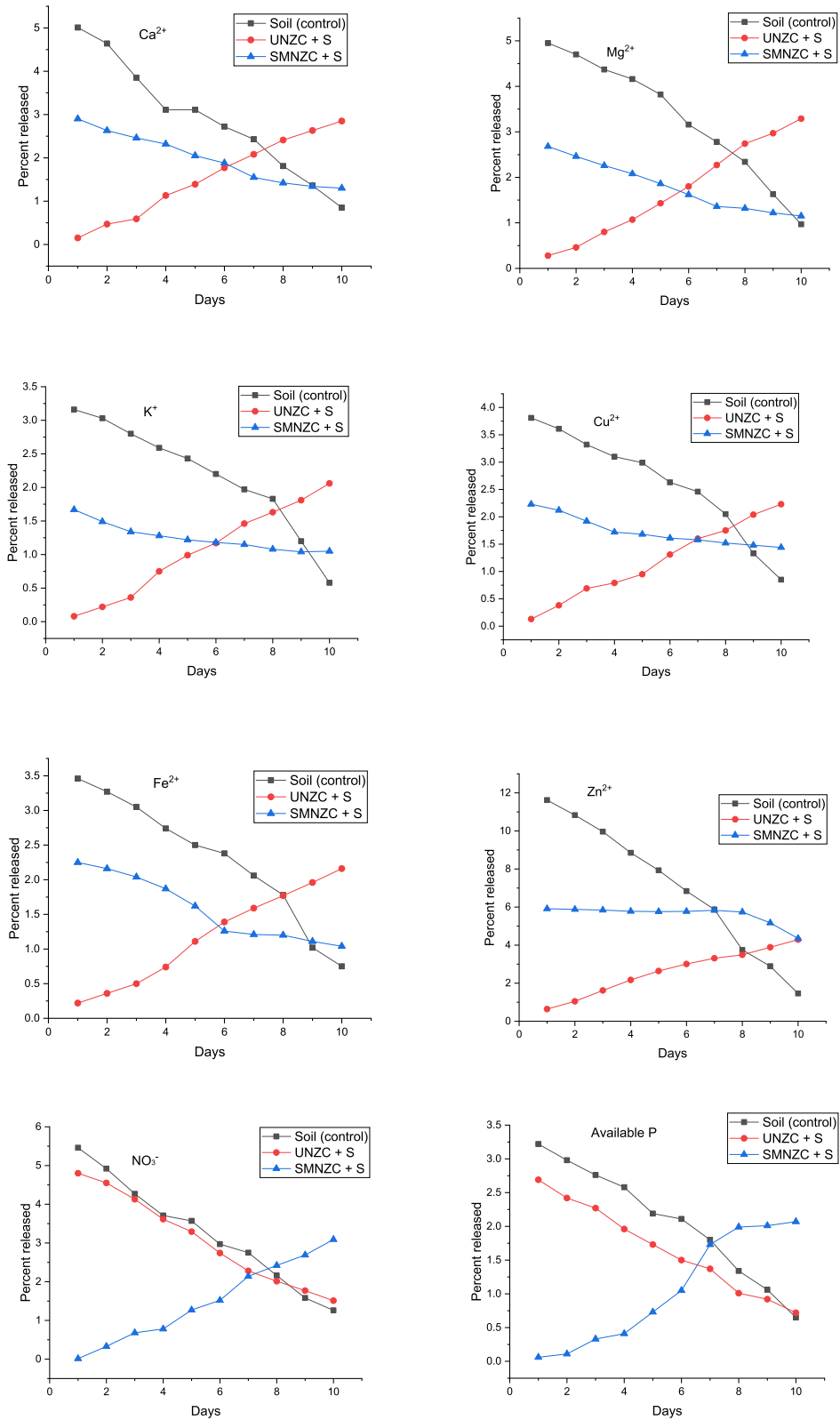


Fig. 5. Slow release pattern (%) of nutrients (NO₃⁻, P, K⁺, Fe²⁺, Zn²⁺, Cu²⁺, Ca²⁺, and Mg²⁺) from UNZC and SMNZC in the soil during ten days study. UNZC + S and SMNZC + S represent soil mixed with unmodified and modified zeolite based composite fertilizers respectively.

Table 6
Organic carbon, cation exchange capacity, and pH of the soil as affected by zeolite (phillipsite) based composite fertilizers.

Treatments	pH	OC (%)	CEC (Cmolc/kg)
T1	7.63d	0.81c	28.07e
T2	7.65d	0.83c	28.67e
T3	7.85c	0.85c	47.47b
T4	7.98b	0.84c	54.13a
T5	8.13a	0.86c	55.80a
T6	7.81c	1.16b	36.2d
T7	7.99b	1.35a	38.67dc
T8	8.14a	1.40a	42.80c
CV	0.64	6.19	5.99
LSD	0.02	0.11	4.30

Means within a column with the same letter are not significantly different from each other at $p < 0.05$. T1 (neither SRF nor commercial fertilizer was added), T2 (commercial fertilizer only), T3 (UNZC 100 kg/ha), T4 (UNZC 200 kg/ha), T5 (UNZC 250 kg/ha), T6 (SMNZC 100 kg/ha), T7 (SMNZC 200 kg/ha), and T8 (SMNZC 250 kg/ha).

composite fertilizers (T3-T8) were significantly ($P < 0.05$) higher than that of unamended soils (T1 and T2) and the maximum value was obtained at T5 (250 kg/ha of UNZC) though it is at par with T4. On the other hand, at all application rates, the CEC of soils treated with UNZC (T3-T5) was significantly ($P < 0.05$) higher than that of SMNZC (T6-T8). This could be due to decreased negativity of the surface upon surfactant modification. Application of UNZC did not improve the organic content of the soil. The effect was seen on only soils treated with T6-T8 (SMNZC) and the maximum result was observed at T8 though it is at par with T7. This indicates that the HDTMAB surfactant added during modification might be a source of carbon as indicated by Ref. [26]. Previous study also revealed that cationic surfactant can sorb nonpolar organics and increase the organic content of the zeolite [12].

3.11. Macro and micronutrients status of the soil as affected by zeolite based composites

The amount of nitrogen, available phosphorus, potassium, calcium, magnesium, iron, copper and zinc detected in the soil amended with zeolite (phillipsite) based composite fertilizers after harvest were given in Table 7. Almost nutrient contents in all soils treated with the composite fertilizers (T3-T8) are significantly ($P < 0.05$) higher than that of T1 and T2. The total nitrogen in the soil amended with zeolite was marginally increased with increasing application rates (irrespective of UNZC and SMNZC) but there were no differences among applications at the same rates indicating the capacity of the studied zeolite (phillipsite) to retain nitrate and ammonium in the soil. According to the findings of the field study on zeolite-assisted maize cultivation given by Ref. [51], the amount of nitrate (NO₃-N) in the soil increased when the zeolite (clinoptilolite) dose was increased from 0 to 125, 250, and 500 t ha⁻¹. These values were 15.4, 16.4, 18.5, and 19.3 mg/kg, respectively. [52] also showed that zeolites' selectivity for the ammonium cation (NH₄⁺) enables them to extract it from manure, composts, or other fertilizers that include the ammonium form of nitrogen, minimizing losses. On the other hand, the amount of available P content obtained in the soils treated with UNZC (T3-T5) are statistically equal and lower than that of soils treated with SMNZC (T6, T7, and T8) at all application rates. The maximum result was recorded at T8 (SMNZC 250 kg/ha). The content of potassium in the soils treated with UNZC (T3-T5) increased with application rates and was significantly higher than that of T6-T8 (SMNZC) at all application rates. In line with this study, [53] used a synthetic zeolite, made from fly ash, as a potassium fertilizer in wheat production and showed the excellent efficiency of potassium release from zeolite, which increased the pool of bioavailable K in the soil solution which is lacking in chemical fertilizers. High calcium content was also recorded in the soils treated with UNZC (T5). Insignificant differences ($P < 0.05$) were recorded among T3, T4, T7 and T8. The maximum amount of magnesium, iron, zinc, and copper was also observed in the soils treated with the highest rate of unmodified phillipsite based

Table 7
Nutrient status of the soil as affected by zeolite (phillipsite) based composite fertilizers.

Nutrient status									
Treat.	N (%)	A.P (mg/kg)	K (Cmolc/kg)	Ca (Cmolc/kg)	Mg (Cmolc/kg)	Fe (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	
T1	0.04e	10.63e	0.70g	17.52e	5.85e	4.26e	1.21g	0.33fd	
T2	0.10d	18.42d	1.60f	18.62ed	6.02e	4.95e	1.65f	0.44d	
T3	0.19c	20.99dc	3.67c	27.32b	9.30b	13.82b	6.57b	3.66b	
T4	0.24b	21.13c	3.90b	29.52b	11.70a	13.89b	7.46a	4.28a	
T5	0.28a	21.17c	4.37a	34.48a	12.01a	15.81a	7.53a	4.32a	
T6	0.20c	24.65b	2.26e	22.36cd	6.69d	7.42d	2.91e	2.41c	
T7	0.24b	28.37a	2.24e	26.33 cb	7.68c	7.81d	3.45d	2.57c	
T8	0.27a	29.32a	2.99d	27.30b	7.77c	10.15c	4.00c	3.63b	
CV	6.19	7	4.28	9.67	4.10	6.81	5.01	3.51	
LSD	0.02	2.65	0.20	4.51	0.60	1.15	0.38	0.16	

Means within a column with the same letter are not significantly different from each other at $p < 0.05$. Were Treat. = treatments, A.P = available phosphorus. T1 (neither SRF nor commercial fertilizer was added), T2 (commercial fertilizer only), T3 (UNZC 100 kg/ha), T4 (UNZC 200 kg/ha), T5 (UNZC 250 kg/ha), T6 (SMNZC 100 kg/ha), T7 (SMNZC 200 kg/ha), and T8 (SMNZC 250 kg/ha).

composite (T5). But, the contents of magnesium, zinc, and copper in T4 and T5 had no significant differences ($P < 0.05$). The result of this study is in line with the principles of slow-release formulation studied previously. For instance Ref. [16] observed that synthetic zeolite incorporated with macronutrients (Ca^{2+} , Mg^{2+} , PO_4^{3-} , NO_3^-) enhanced nutrient availability in the soil in comparison with chemical fertilizer (NPK).

3.12. Maize nutrient uptake as affected by zeolite based (phillipsite) composite fertilizer

The amount of nutrients taken up from the soils amended with unmodified and modified zeolite (phillipsite) based composite fertilizers at different application rates are presented in Table 8. Images of maize plants with control soil, commercial fertilizer, UNZC and SMNZC fertilizer treatments are given in Fig. 6 (a, b, c and d respectively). The result shows that the addition of zeolite improved the amount of nutrients up taken by maize in comparison with the control soil. The addition of the same application rates of UNZC and SMNZC equally affected nitrogen uptake and the highest uptake was observed at an application rate of 200 and 250 kg/ha indicating 200 kg/ha was the optimum rate. The P uptake increased with the application rates of UNZC, though an insignificant difference was observed among T4 and T5. The maximum P uptake was observed on soils treated with SMNZC, regardless of its application rates. Increasing the application rates of the composite fertilizers did not change the amount of K up taken by maize. But, the highest uptake was observed for the soil amended with UNZC (T3-T5). The maximum Ca, Mg and Fe uptake was observed at T5 (UNZC 250 kg/ha). Increasing application rates of SMNZC (T6-T8) did not show a significant change in the uptake of Ca and Fe. The amount of Mg up taken increased with increasing application rates of both UNZC and SMNZC. Similar to the case observed in potassium uptake, no significant differences ($P < 0.05$) were observed in Zn and Cu uptake from soils amended with UNZC, though maximum uptake was observed at T5. This indicates that a low application rate can facilitate the uptake of these nutrients. Increasing application rates of SMNZC (beyond T7) did not show a significant ($P < 0.05$) effect on the uptake of Zn and Cu.

The present finding confirms that when loading is done nutrients enter into the pores, guaranteeing more binding of nutrients and therefore improved accessibility to the crops. These nutrients can be delivered from zeolite based composite depending on the pore size, adsorption level, and binding capacity [54,55]. The beneficial effects of the proposed fertilizers treatment on maize plants compared to chemical fertilizer could be due to the improved soil's physical, chemical and biological properties, and also the continues nutrient availability, as evidenced by decreased leaching and water retention in addition to the availability of elements to be absorbed by plant roots. In line with our finding [16], revealed that application of synthetic zeolite SRFs increased the availability of N, P, K, and Ca in the soil and to lettuce plant when compared to chemical fertilizer. [56,57] also showed that soils mixed with zeolite (unspecified), improved N, P, and K uptake and use efficiency of maize in comparison with the control treatment (chemical fertilizer). They also observed that the highest zeolite dose significantly increased N, P, and K use efficiency. Further, [49] showed that the addition of zeolite (unspecified) improved the number of nutrients such as nitrogen, phosphorus, potassium, and calcium in the leaves of Rhodes grass in comparison with chemical fertilizer.

In addition to nutrient uptake, the amendment of the soils with zeolite improved the biomass production of the maize in comparison with the control soil. The difference in biomass of maize amended with T3, T7, and T8 was insignificant ($P < 0.05$), and the highest value was obtained at T5 (UNZC 250 kg/ha) though an insignificant difference was observed in comparison with T4 (Table 8). This implies that the quantities of nutrients supplied at these rates (T4 and T5) were sufficient to produce similar biomass. The result further indicates that at the same application rates of UNZC and SMNZC, the biomass of maize amended with UNZC was significantly ($P < 0.05$) higher than that of SMNZC (T6-T8). The improved biomass are due to the significant increase of CEC by zeolite, which helps retain more nutrients and favoring the availability and solubility of essential elements such as P, which participates in the radical growth and benefits the absorption of water and nutrients [58]. In line with our result [49], observed that as zeolite doses became larger, so was the dry matter content of the plants harvested from each pot. Furthermore, application of SRFs increased the dry biomass of capsicum and kale plants in comparison with control and chemical fertilizers probably due to utilization of nutrients from SRFs [59, 60].

4. Limitation of the material

Though the applicability of the material for plant production is confirmed, it needs continuous work with the concerned government officials to develop the awareness of the farmers towards the material at the national level since this kind of work is new to our country. The second limitation is related to its production in a huge amount (beyond the laboratory), indicating the need to plant an industry or sophisticated machine to prepare it in a huge amount that may require additional costs. In addition, though the use of composite fertilizer is advantageous for the simultaneous introduction of many nutrients, it is not appropriate to use such fertilizers when we want to apply each nutrient separately at the required rate. This forces us to use a common rate for both macro and micro nutrients, and field optimization of such fertilizers is a must.

5. Conclusion

The present results indicate the applicability of both modified and unmodified zeolite based composite fertilizers for plant growth. The porous structure of the studied zeolite was effectively utilized to incorporate essential macro and micronutrients that are released slowly and sustainably to the plant depending upon their affinity to the zeolite. The major component of the zeolite material used was phillipsite as observed from XRD analysis. Surfactant modification increased the specific surface area and total pore volume of the zeolite material. UNZC showed better efficiency in carrying the studied cationic nutrients (Ca, Mg, K, Cu, Zn, and Fe) whereas SMNZC

Table 8

Amount of nutrients up taken by maize as influenced by zeolite (phillipsite) based composite fertilizers.

Treat.	N (%)	P (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)	Fe (ppm)	Zn (ppm)	Cu (ppm)	Biomass mg/ha
T1	0.16d	1058.90d	1628.16c	1580.10c	1220.82h	28.89e	12.24d	6.15e	0.27e
T2	0.59c	1852.60c	1661.17c	1643.20c	1299.80g	41.01e	14.26d	7.44e	0.77d
T3	1.21b	1958.40c	3102.31a	2211.40b	1741.37d	121.82c	44.52a	18.30ba	1.11b
T4	1.65a	2328.70b	3135.32a	2463.90b	2050.12b	150.10b	47.21a	18.56ba	1.22a
T5	1.63a	2540.40b	3201.32a	3663.40a	2617.34a	222.83a	49.23a	20.12a	1.30a
T6	1.14b	3016.60a	1958.20b	2274.50b	1454.17f	89.49d	28.38c	13.65d	0.92c
T7	1.60a	3069.50a	1991.20b	2337.70b	1536.74e	93.54d	32.42 cb	16.23c	1.07b
T8	1.63a	3122.40a	2002.20b	2527.10b	1802.41c	101.62dc	35.78b	16.75BCE	1.05b
CV	4.88	8.21	3.13	8.59	1.70	12.33	9.70	7.56	6.57
LSD	0.1	336.49	126.67	347.71	49.76	22.66	5.52	1.92	0.11

Means within a column with the same letter are not significantly different from each other at $p < 0.05$. where, Treat. = treatments. T1 (neither SRF nor commercial fertilizer was added), T2 (commercial fertilizer only), T3 (UNZC 100 kg/ha), T4 (UNZC 200 kg/ha), T5 (UNZC 250 kg/ha), T6 (SMNZC 100 kg/ha), T7 (SMNZC 200 kg/ha), and T8 (SMNZC 250 kg/ha).

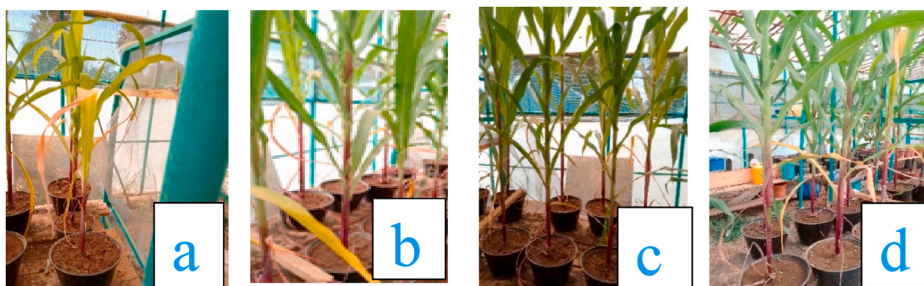


Fig. 6. Images of maize plants with (a) control soil; (b) commercial fertilizer treatment; (c) UNZC fertilizer treatment and (d) SMNZC fertilizer treatment.

is found to be a better slow releaser than control soil. SMNZC is a better carrier of nitrate and soil-available phosphorus than UNZC. The surfactant-modified zeolite can simultaneously sorb both inorganic cations and inorganic anions. The prepared SRFs also enhanced the moisture content of the soil, as observed from the WAC, SR, and WRC studies. Furthermore, it was observed that both SRFs enhanced nutrient availability in the soil and delivery to maize plants in comparison with the chemical fertilizer. The highest uptake of Ca (3663.40 ppm), Mg (2617.34 ppm), and Fe (222.83 ppm) was observed when 250 UNZC kg/ha was applied. Maximum uptake of K, Zn, and Cu was also observed for the soils amended with UNZC, and no significant difference was observed at all rates. The highest total nitrogen uptake (1.65 %) was observed when both forms of SRFs were applied at 200 and 250 kg/ha, indicating 200 kg/ha was the optimum rate for both forms. The highest accessibility of phosphorus to plants was facilitated on the soils amended with SMNZC regardless of its application rate. The outcome also revealed the applicability of the proposed SRFs at lower rate in comparison with the commercial fertilizer. In conclusion, the studied zeolite can be used as carriers of nutrients and also as a medium for their slow release to improve soil nutrients and crop nutrient uptake.

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Data availability

Data will be made available on request.

CRediT authorship contribution statement

Wubishet Legese: Software, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation. **Abi M. Tadesse:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Kibebew Kibret:** Writing – review & editing, Supervision, Funding acquisition. **Lemma Wogi:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to

influence the work reported in this paper.

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