Assessment of natural and calcined starfish for the amelioration of acidic soil

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RESEARCH ARTICLE

Assessment of natural and calcined starfish for the amelioration of acidic soil

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Abstract Quality improvement of acidic soil (with an initial pH of approximately 4.5) with respect to soil pH, exchangeable cations, organic matter content, and maize growth was attempted using natural (NSF) and calcined starfish (CSF). Acidic soil was amended with NSF and CSF in the range of 1 to 10 wt.% to improve soil pH, organic matter content, and exchangeable cations. Following the treatment, the soil pH was monitored for periods up to 3 months. The exchangeable cations were measured after 1 month of curing. After a curing period of 1 month, the maize growth experiment was performed with selected treated samples to evaluate the effectiveness of the treatment. The results show that 1 wt.% of NSF and CSF (700 and 900 °C) were required to increase the soil pH to a value higher than 7. In the case of CSF (900 °C), 1 wt.% was sufficient to increase the soil pH value to 9 due to the strong alkalinity in the treatment. No significant changes in soil pHs were observed after 7 days of curing and up to 3 months of curing. Upon treatment, the cation exchange capacity values significantly increased as compared to the untreated samples. The organic content of the samples increased upon NSF treatment, but it remains virtually unchanged upon CSF treatment. Maize growth was greater in the treated samples rather than the untreated samples, except for the samples treated with 1 and 3 wt.% CSF (900 °C), where maize growth was limited due to strong alkalinity. This indicates that the amelioration of acidic soil using natural and calcined starfish is beneficial for plant growth as long as the application rate does not produce alkaline conditions outside the optimal pH range for maize growth.

Keywords Acidic soil · Starfish · Soil pH · Cation exchange capacity · Maize growth

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Introduction

Acidic soil is a serious problem in Republic of Korea and other industrial countries around the world causing a variety of adverse effects including decreased soil productivity and suboptimal plant growth. For the most part, the soil in Republic of Korea originates from granite and granite gneiss parent materials that are more likely to be acidic in comparison to calcareous shale or limestone. This condition is further intensified by atmospheric deposition containing SOx and NOx, common atmospheric pollutants of urban and/or industrial origin. Lime, in the form of finely ground agricultural lime, is the most common amendment to remedy acidic soils, but this practice raises two issues: (a) use of a nonrenewable resource and (b) increased costs issues (Adams 1984). In this

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study, two forms of a renewable resource, namely, natural and calcined starfish, were used as amendments to improve soil quality with respect to soil pH, cation exchange capacity, and organic content. Starfish as an invasive species may cause serious problems in the marine environment, often leading to degradation of natural marine ecosystems. Moreover, since starfish feed on bivalves (ear shell, short-necked clam, scallop, etc.), they represent a serious threat to the commercial viability of the shellfish cultivation industry. To control outbreaks of these invasive species, fishermen capture great numbers of starfish. This practice, often accompanied by uncontrolled or improper disposal, generates nuisance and environmental degradation of coastal areas. A limited quantity of starfish is used for beneficial applications including as a fertilizer (Park 2003) and for removal of heavy metal ions (Hong et al. 2011). The major inorganic phase in starfish is calcite ($CaCO_3$), and this can be transformed into quicklime (CaO) by the calcination process. Evidently, starfish can provide not only a calcium source but also a variety of other minor and trace elements (e.g., Mg, P, K, Zn, etc.) that can improve the quality of acidic soil (Lebrato et al. 2013). In this study, the beneficial reuse of starfish was explored as a conditioner for acidic soil. The effectiveness of treatment was evaluated for three different types of starfish (natural, calcined at 700 °C, and calcined at 900 °C). Maize growth experiments were conducted after the acidic soil was ameliorated with natural and calcined starfish to assess the potential benefit of the ameliorated acidic soil for plant growth. Maize is known as a very important crop for humans and animals and has been reported to grow well in the pH range of 6.5–8 (International Institute for Tropical Agriculture 1982). Soil pH outside the optimal range is expected to affect maize growth adversely.

The objective of this study was to investigate the effectiveness of the ameliorated acidic soil treated with natural and calcined starfish. Soil pH, exchangeable cations, organic content, and maize growth upon treatment were used as parameters which indicate the effectiveness of amelioration of the acidic soil.

Experimental methodology

Acidic soil

Acidic soil was collected from a fruit garden in the Chungcheongnam do Province, Republic of Korea at a depth of 0–30 cm below the ground surface. The acidic soil was then sieved through a #10 mesh (2 mm) to remove coarse materials and provide a homogeneous sample. Physicochemical and mineralogical characterization information of the acidic soil is presented in Table 1. The bulk chemistry of the acidic soil measured using the X-ray fluorescence (XRF) spectrometer is presented in Table 2.

Table 1 Physicochemical and mineralogical properties of the acidic soil

Soil properties	Acidic soil
Soil pH	4.5±0.15
Organic matter content (percent)[a]	7.6
Cation exchange capacity (centimoles of positive charge per kilogram)[b]	3.29
Composition (percent)[c]	
Sand	97.5
Silt	1.6
Clay	0.9
Texture[d]	Sand
Mineral compositions	Quartz
	Kaolinite
	Muscovite
	Microcline
	Cristobalite

[a] Organic matter content (%) was calculated from measured loss-on-ignition (LOI; Ball 1964; FitzPatrick 1983)

[b] Cation exchange capacity (CEC) measured by USEPA method 9081 (USEPA 1986)

[c] Sand 50–2,000 μm, silt 2–50 μm, clay<2 μm

[d] Soil texture suggested by the US Department of Agriculture (USDA)

Amelioration agent

Starfish were collected from Tong-young, Republic of Korea and rinsed several times with deionized water to remove impurities and a salty layer. The starfish were then air-dried. Following the drying process, the dried starfish were pulverized manually using a mortar and pestle to pass through a #20 sieve (0.853 mm). The starfish calcination process was performed at 700 and 900 °C for 2 h to evaluate the transformation of the calcite into quicklime. The calcined starfish at 700 °C reached a metastable state which exists in the middle of calcite and quicklime due to the incomplete transformation of calcite to quicklime. The complete calcination process was achieved at 900 °C. This is in agreement with the thermal

Table 2 Physicochemical properties of the acidic soil, NSF, CSF (700 °C), and CSF (900 °C)

Chemical properties	Soil	NSF	CSF (700 °C)	CSF (900 °C)
SiO_2	61.0	8.11	22.9	4.67
Al_2O_3	19.8	2.51	6.93	1.08
TiO_2	0.72	0.08	0.3	0.03
$Fe2O_3$	4.56	0.65	3.70	0.50
MnO	0.07	0.12	0.09	0.10
MgO	0.70	3.83	0.8	9.33
CaO	0.21	64.4	61.6	71.3
Na_2O	0.22	4.13	0.28	3.75
K_2O	4.67	2.62	1.6	1.47
P_2O_5	0.24	1.88	0.18	1.22
SO_3	0.04	5.15	0.73	1.87
pH (1:5)	5.02	7.14	12.48	12.52

Oxide values expressed in percentages by mass

Table 3 Test matrix for the control and treated samples

Sample ID	NSF (weight%)	CSF (700 °C) (weight%)	CSF (900 °C) (weight%)	L:S ratio
Control	–	–	–	0.2
1NSF	1	–	–	0.2
3NSF	3	–	–	0.2
5NSF	5	–	–	0.2
10NSF	10	–	–	0.2
1CSF_700	–	1	–	0.2
3CSF_700	–	3	–	0.2
5CSF_700	–	5	–	0.2
1CSF_900	–	–	1	0.2
3CSF_900	–	–	3	0.2

decomposition temperature of 848 °C found in the literature at which the standard Gibbs free energy of the reaction is zero (Gilchrist 1989).

The physicochemical properties of the acidic soil, natural starfish, and calcined starfish at two different temperatures (700 and 900 °C) as analyzed by the XRF spectrometer are presented in Table 2.

Treatment

The acidic soil was treated with natural and calcined starfish in the range of 1 to 10 wt.%. All treatments were cured for 7 days, 14 days, 21 days, 1 month, and 3 months. A liquid-to-solid ratio of 0.2 was used to ensure full hydration. A specific treatment matrix is presented in Table 3. The sample IDs are denoted as NSF for natural starfish, CSF_700 for starfish calcinated at 700 °C, and CSF_900 for starfish calcinated at 900 °C.

Maize growth experiment

After the acidic soil was treated with natural and calcined starfish, the treated soils were cured for 1 month, and then the maize (miniheukchal, lot no. 124201) growth experiment was performed. The soil pH was increased above 7 from the original soil pH of 4.5. Maize seeds, collected from the Jinheoung nursery (Republic of Korea), were sown in a small pot containing the following samples: control, 1NSF, 1CSF_700, 1CSF_900, and 3CSF_900. The soil pH varied in the range of 7 to 9 for the 1NSF, 1CSF_700, and 1CSF_900 samples, while the sample, 3CSF_900, showed a soil pH value of approximately 10.5. The small pots had three holes of about 7-mm diameter on the bottom with a plastic screen positioned over them to prevent soil loss. In addition, the pot had the following dimensions: height of 7 cm, top inner diameter of 5 cm, and bottom diameter of 4.8 cm.

Physicochemical analyses

The pH values of the acidic soil treated with NSF and CSF were obtained after curing in accordance with the Korean standard test (KST) method with a liquid (DI water)-to-solids (L:S) ratio of 5 to 1. The bulk chemistry of the acidic soil, NSF and CSF were measured using X-ray fluorescence (XRF; ZSX100E, Rigaku). The exchangeable cations were measured using a 1 N ammonium acetate extraction method at pH 7 in

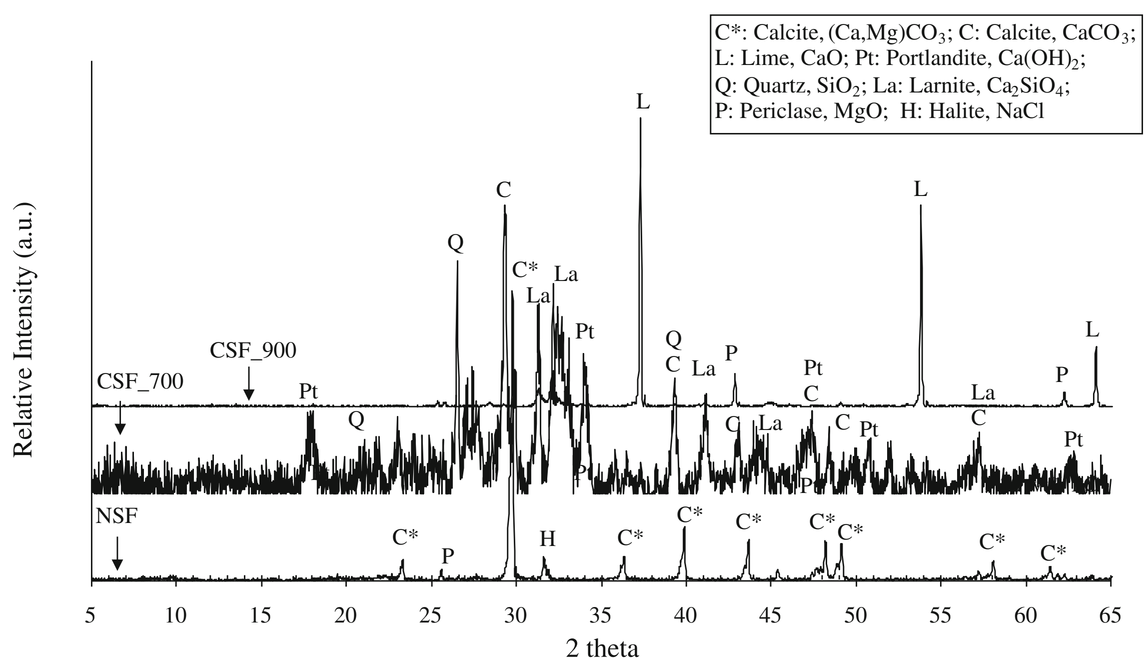

Fig. 1 XRD patterns of the NSF, CSF_700, and CSF_900 samples

accordance with the KST method, and the extracted solutions were analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500CE, USA). All sample analyses were performed in triplicate, and the averaged values were reported only if the individual measurements were within an error of 10 %. Two different quality control standards and recovery spikes were used to monitor the accuracy and performance of the equipment.

X-ray powder diffraction (XRPD) analyses

The mineralogy of the acidic soil was analyzed by XRPD analyses. The acidic soil was air-dried and pulverized to pass through a #200 sieve. Step-scanned X-ray diffraction patterns were collected using a PANalytical X-ray diffraction (XRD) instrument (X'Pert PRO MPD). XRPD analyses were conducted at 40 kV and 30 mA using a diffracted beam graphite monochromator with Cu radiation. The XRPD patterns were collected at 2θ values in the range of 5 to 65°, with a 2θ step size of 0.03° and a count time of 3 s/step. The qualitative analyses of the XRPD patterns were performed using the Jade software version 7.1 (Material's Data Inc 2005) with reference to the patterns present in the International Centre for Diffraction Data database (ICDD 2002).

Scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM-EDX) analyses

SEM-EDX analyses were conducted on samples NSF and CSF_900. SEM-EDX analyses were performed using a Hitachi S-4700 (Hitachi, Japan) equipped with energy-dispersive X-ray (EDX) spectroscopy, Energy EX-200 (Horiba, Japan). Prior to SEM analyses, the air-dried samples were coated with platinum (Pt).

Results and discussion

Characteristics of the acidic soil and amelioration agents

The initial soil pH was 4.5 and the acidic soil was classified as sand in accordance with the United States Department of Agriculture (USDA; Table 1). The results of the major chemical composition of the acidic soil, NSF, CSF_700, and CSF_900 performed by XRF analyses are listed in Table 2. The acidic soil is mainly composed of 61 wt.% SiO_2 and 19.8 wt.% Al_2O_3. The NSF, CSF_700, and CSF_900 additives mainly consisted of CaO with a CaO content ranging from 61.6 to 71.3 wt.%. The main phases of the acidic soil identified by XRPD analysis are quartz (SiO_2, PDF# 46-1045), kaolinite ($Al_2Si_2O_5(OH)_4$, PDF# 29-1488), muscovite ($KAl_2Si_3AlO_{10}(OH)_2$, PDF# 07-0025), microcline ($KAlSi_3O_8$, PDF# 19-0932), and cristobalite (SiO_2, PDF# 39-1425; Table 1).

The XRPD patterns for the amelioration agents NSF, CSF_700, and CSF_900 are presented in Fig. 1. It was evident that calcite, the main phase in the NSF sample, was transformed into quicklime in CSF_900 sample. In CSF_700

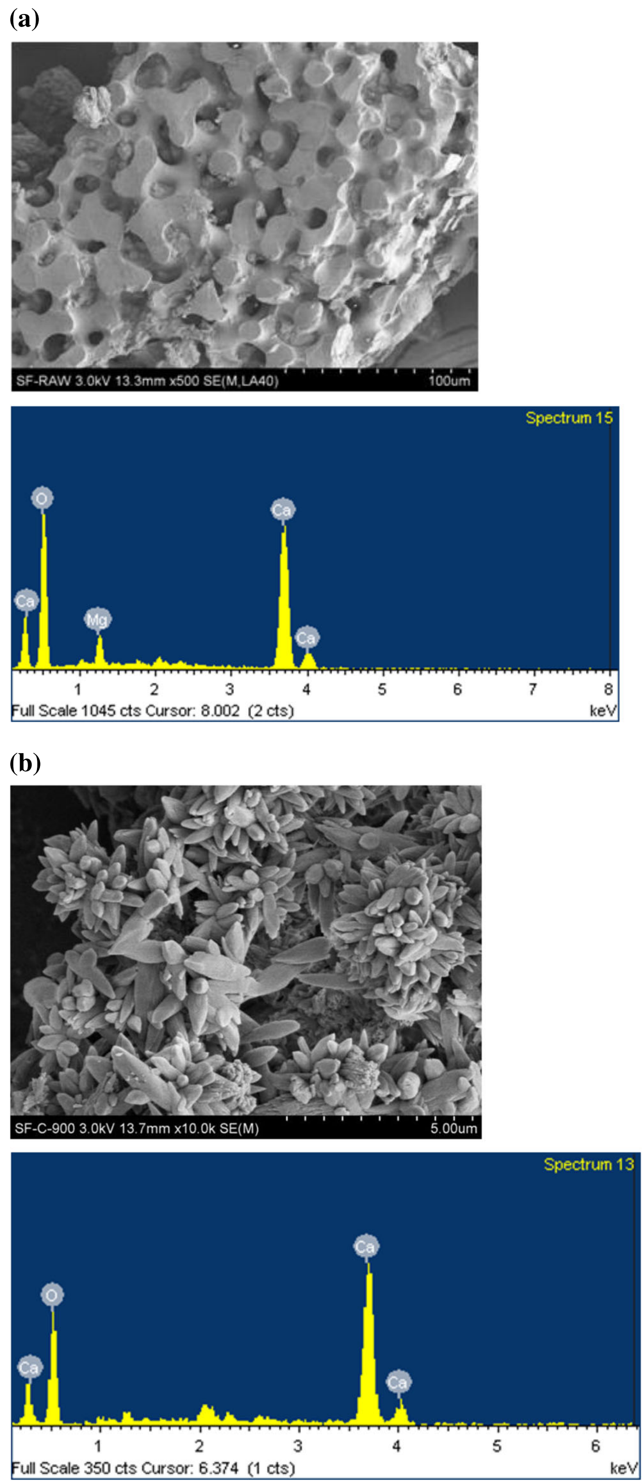

Fig. 2 SEM-EDX results of the NSF (**a**) and CSF_900 (**b**) samples

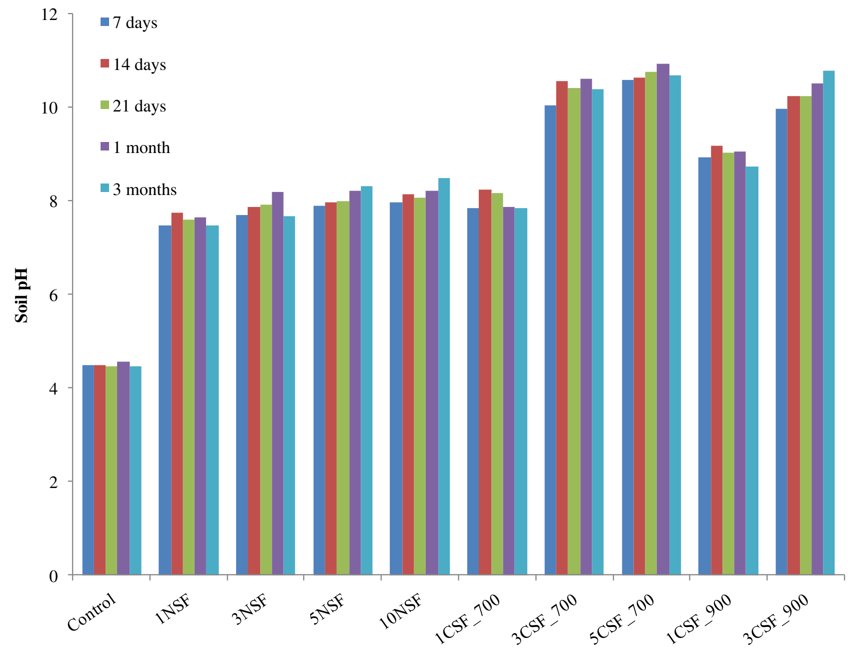

Fig. 3 Soil pH improvement upon treatment using starfish

sample, calcite and portlandite coexisted, indicating incomplete transformation of calcite to quicklime.

The SEM-EDX results show that calcite with Mg impurities was observed in the NSF sample (Fig. 2a). Fig. 2b illustrates the transformed quicklime in the CSF_900 sample.

pH improvement of the acidic soil

The improvement of soil pH upon addition of starfish amendments is presented in Fig. 3. The starfish treatment was beneficial in increasing soil pH. The initial soil pH of 4.5 in the control sample was increased in the range of 7 to 8 upon all NSF treatments. Addition of NSF above and beyond 1 wt.% did not contribute significantly to the improvement of soil pH, indicating that 1 wt.% was sufficient in elevating the soil pH value to neutrality. In the case of the CSF_700 treatment, it showed a soil pH value of 7.9 after 3 months of curing in the 1 wt.% CSF_700 treatment; however, 3 and 5 wt.% CSF_700 treatments increased the soil pH higher than 10. Therefore, the 1 wt.% CSF_700 treatment could be recommended to improve soil pH in the range of 7 to 8 (beneficial for plant growth). In the case of the CSF_900 treatment, treatments of 1 and 3 wt.% CSF_900 showed soil pH values of 8.7 and 10.8 after 3 months of curing, respectively. This indicated that less than 1 wt.% CSF_900 should be recommended to achieve a soil pH in the range of 7 to 8. It has been reported that soil pH was significantly increased from 3.8 to 5.2 upon agricultural lime treatment at an application rate of 2,400 kg/ha (Blamey and Chapman 1982). These researchers indicate that precipitated $CaCO_3$ (the main phase in starfish) had an influence on changing the soil pH. Another study using oyster shell as a $CaCO_3$ source reported soil pH increases in the range of 5.21 to 6.64 at a rate of 8 t/ha (Onwuka et al. 2009).

The soil pH values remained virtually unchanged with increasing curing times up to 3 months for all samples, except for the 3CSF_900 sample, where the reaction seems to be on

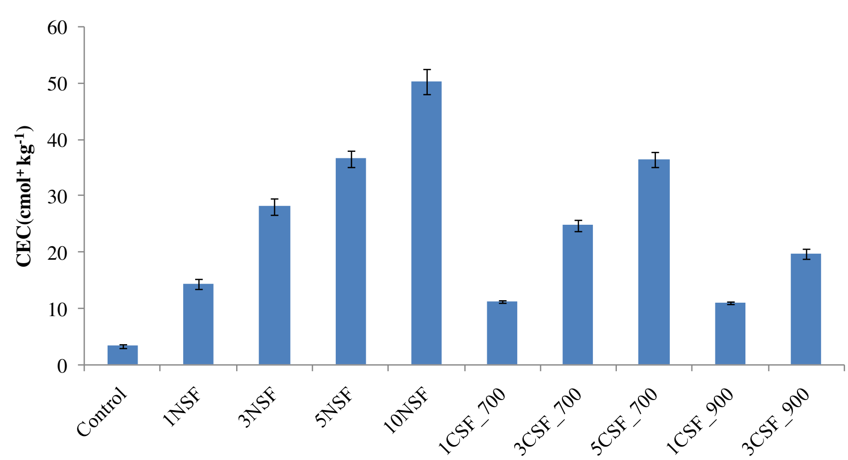

Fig. 4 Changes in exchangeable cations upon treatment using starfish

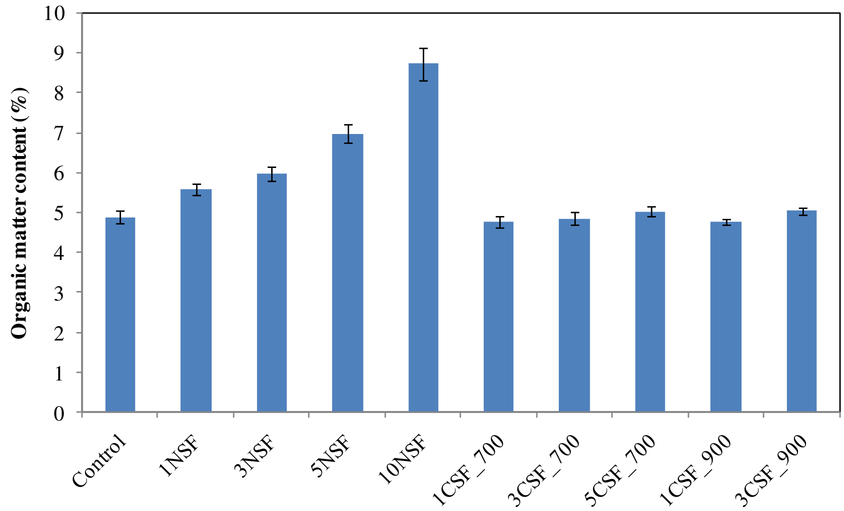

Fig. 5 Changes in organic content upon treatment using starfish

going. This indicates that a curing period of 7 days is sufficient to improve the soil pH using starfish.

Increase in exchangeable cations upon treatment

Exchangeable cations for the control and treated samples were monitored after 1 month of curing. This data is presented in Fig. 4. The exchangeable cation value for the control sample was 3.29 cmol$^+$/kg, which is similar to the value for sandy soil that supports USDA classification. The exchangeable cation levels for the treated samples significantly increased in comparison to those of the control sample. The highest exchangeable cation value of approximately 34 cmol$^+$/kg, typical for clay soil types was attained in the 3NSF sample. It has been reported that once amelioration agents are introduced to an acidic soil, their exchangeable cations are released into the soil and occupy soil exchange sites (Yuan et al. 2011). Therefore, upon addition of the amendment, the exchangeable cations in starfish become available to the acidic soil and contribute to the increase in the exchangeable cation value of the soil. For treated samples 1NSF, 1CSF_700, and 1CSF_900, the exchangeable cation values ranged from 11 to 14.4, typical

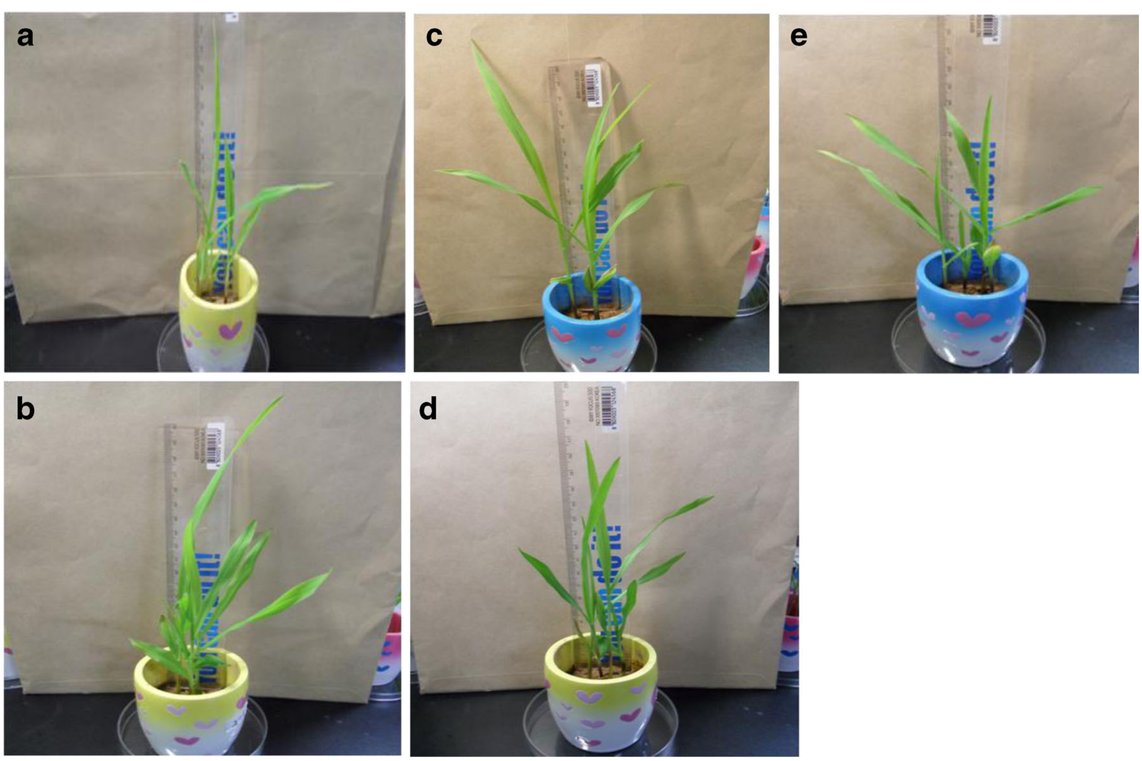

Fig. 6 Maize growth after 20 days of seeding in the following samples: control (**a**), 1NSF (**b**), 1CSF_700 (**c**), 1CSF_900 (**d**), and 3CSF_900 (**e**)

Table 4 Maize plant growth results

Sample ID	Germination rate (percent)	Height (centimeter)
Control	66.7	17.5
1NSF	66.8	23
1CSF_700	50	22
1CSF_900	66.7	16.8
3CSF_900	100	14.5

for loam and silt loam soils. Exchangeable cation values in the clay loam region (15–30 $cmol^+/kg$) were also obtained from the samples, 3CSF_700 and 3CSF_900. Evidently, the addition of starfish, contributed to a significant increase in the exchangeable cations of the amended soil. This increase, brought about by the starfish amendment, results in soil quality improvement that is beneficial for plant growth.

Changes in organic matter content

The organic matter content for the control and treated samples were monitored after 1 month of curing as shown in Fig. 5. The organic matter content of the control sample was approximately 5 %. A gradual increase of organic matter content was observed upon NSF treatment. The highest organic matter content value of 8.5 % was obtained upon the 10 wt.% NSF treatment. On the other hand, the organic matter content did not change noticeably upon CSF treatment. This indicated that the organic matter content that existed in the NSF was removed during the calcination process. There are several benefits of organic matter in soil. Organic matter is a reservoir of nutrients that can be supplied to the soil. Also, organic matter can hold water that can be adsorbed by plants. Moreover, organic matter can cause soil aggregation and clumping that enhances the soil structure. Therefore, the samples treated with NSF are better for planting applications than the samples treated with CSF with respect to organic matter.

Maize growth experiment

Maize growth experiments, conducted using the following samples control, 1NSF, 1CSF_700, 1CSF_900, and 3CSF_900 for a growth period of 20 days after seeding, are presented in Fig. 6. Maize growth in the soil pH range of 7 to 8 was simulated with samples 1NSF and 1CSF_700. The sample 1CSF_900 was used to investigate maize growth in the soil pH value of approximately 9. Moreover, the sample 3CSF_900 was used to simulate maize growth in soil pH values of higher than 10. In all of the treated samples, germination varied from 50 to 100 % (Table 4). The longest height of the maize plants in the control sample was approximately 17.5 cm, which was lower than the 1NSF and 1CSF_700 samples. The longest maize height (23 cm) was observed upon the 1 wt.% NSF treatment (Table 4). Moreover, the plants grown on treated soils appeared healthier and richer than the plants grown on the control sample, except for samples 1CSF_900 and 3CSF_900, where the plant height was smaller than the control sample. This indicated that maize growth was limited at soil pH values higher than 8. This finding is in agreement with the reported pH range of 6.5–8 for optimal maize growth found in the literature (International Institute for Tropical Agriculture 1982). Also, the increase of exchangeable cations may contribute to the growth of maize in ameliorated acidic soil. However, the pH effect on maize growth is more pronounced than the effects of exchangeable cations. This was noticed in sample 3CSF_900, which has a higher exchangeable cation value than the 1NSF samples. However, the maize growth in the 3CSF_900 sample was not favorable. Therefore, the optimum use of NSF, CSF_700, and CSF_900 in acidic soil could be beneficial to the growth of maize.

Conclusions

Natural and calcined starfish (700 and 900 °C) were used as renewable resources for the amelioration of acidic soil. The soil pH and exchangeable cations were monitored upon treatment. Maize growth experiments were also conducted in order to evaluate the effectiveness of the treated ameliorated acidic soil. The treatment results showed that 1 wt.% of natural and calcined starfish (700 and 900 °C) were sufficient for increasing the soil pH to higher than 7 values. Curing periods of 7 days are deemed adequate for the treated soil samples as indicated by the absence of notable changes in soil pH for longer curing periods up to 3 months. Moreover, a significant increase in exchangeable cations was observed upon treatment. Unlike calcined starfish treatments in which the organic content remained virtually unchanged, natural starfish amendments, resulted in increased organic content. Maize growth was improved in all treated samples, except for samples, 1CSF_900 and 3CSF_900, where maize growth was limited due to alkaline pH conditions outside the optimal range for maize growth. Overall, starfish proved to be an effective and efficient renewable resource amendment for the treatment of acidic soil capable of improving soil quality with respect to soil pH, exchangeable cations, organic content, and maize growth.

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