Eurasian Journal of Soil Science 2023, 12(3), 277 - 281

Eurasian Journal of Soil Science

Journal homepage : http://ejss.fesss.org

The effects of clinoptilolite type of zeolite and synthesised zeolite-enriched fertilizer on yield parameters of Cucumber (*Cucumis sativus*) plant and some chemical properties in dark chestnut soil

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Article Info

Received : 15.09.2022
Accepted : 12.04.2023
Available online : 17.04.2023

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Abstract

Zeolites have been used in agriculture since the 1960s, due to the effectiveness of these crystalline microporous solids as soil amendments for plant growth, their cation exchange capacity (CEC) and slow-release fertilizer properties. Most work on slow-release fertilizers has focused on natural Clinoptilolite, Phillipsite and Chabazite. The aim of this study was to synthesize clinoptilolite type of zeolite-enriched fertilizer study their effectiveness as soil amendments. Greenhouse experiments were performed to study the effects of clinoptilolite type of zeolite, synthesised zeolite-enriched ammophos fertilizer and ammophos fertilizer (12% N, 52% P_2O_5) on yield parameters of Cucumber (Cucumis sativus) plant and some chemical properties in dark chestnut soil. According to greenhouse experiment results, there were significant differences among the treatments in relation to yield parameters (weight of one cucumber, shoot length, number of leaves, area of 10 leaves, number of fruits and fruit weight per plant) of cucumber and available nutrient contents of soil. It was determined that the yield parameters of cucumber plant, available nutrient contents (N, P and K) and cation exchange capacity were increased the most by synthesised zeolite-enriched fertilizer application.

Keywords: Zeolite, clinoptilolite, synthesis of zeolite enriched fertilizer, cucumber, nutrient,

Introduction

Zeolites are hydrated aluminosilicates with an infinite three dimensional crystal structure, containing cations of alkaline elements and alkaline soil elements or, less frequently, other cations (Jarosz et al., 2022). Zeolites are important materials with very broad applications in agriculture and environmental engineering. One of the most important applications of zeolites in agriculture is the slow/controlled-release fertilizer aspect. Slow release is a term that is interchangeable with delayed-release, controlled-release, controlled-availability, slow acting and metered-release (Ming and Allen, 2001). Some of the natural zeolites that have been studied for slow-release fertilizer aspects are Clinoptilolite, Chabazite, Phillipsite and Mordenite. The widespread abundance of these zeolites in nature and their selectivity for certain cations (i.e. NH_4^+ and K^+) makes them suitable for this purpose. Zeolite incorporation in soil was found to increase crop yields and to promote nutrient use efficiency. Other possible uses being investigated include applications as a carrier of slow-release fertilizers, insecticides, fungicides, and herbicides, and as a trap for heavy metals in soils (Ramesh and Reddy, 2011).

: https://doi.org/10.18393/ejss.1284506
: http://ejss.fesss.org/10.18393/ejss.1284506
Publisher : Federation of Eurasian Soil Science Societies
e-ISSN : 2147-4249

Kazakhstan has significant deposits of clinoptilolite, which is a natural zeolite with a high cation exchange capacity and a wide range of applications. Karatau, Kounrad, Kokshetau, Terekty and Shankanai deposits are the the main clinoptilolite deposits in Kazakhstan. Clinoptilolite from Kazakhstan is used in a variety of applications, including agriculture, animal feed, water filtration, and soil remediation. The high-quality and abundance of clinoptilolite in Kazakhstan make it an important source of this valuable mineral (Sadenova et al., 2016; Sultanbayeva et al., 2022). Natural clinoptilolite type of zeolite deposits in Kazakhstan have been used in agriculture without any enrichment with fertilizers until today.

Dark chestnut soil is an important soil type in Kazakhstan (Saparov, 2014; Maxotova et al., 2021; Nasiyev et al., 2021) , as it covers a significant portion of the country's agricultural land and it's an important resource such as fertile soil for agriculture, supports food security, economic importance and biodiversity in Kazakhstan. The aim of this study was to determine if synthesised zeolite-enriched fertilizer are better than natural clinoptilolite type of zeolite at increasing yield and yield parameters of cucumber *(Cucumis sativus)* plant and available nutrient status in dark chestnut soil.

Material and Methods

Experimental Materials

The surface dark chestnut soil (0-20 cm) used in this experiment. Soil texture can accordingly be classified as loamy. The pH in water was 7.25, the humus content was 2.15%, the total N was 0.098%, available P was 40 mg kg^{-1}, available potassium was 280 mg kg^{-1} and the soil C:N ratio was 21,94. The soil was bulked, all tones, visible roots and fauna removed, sieved to less than 2 mm and stored at room temperature until used. Cucumber variety, "F1 Gerasim", was selected as the experiment material.

Synthesis of zeolite enriched fertilizer

In this study, clinoptilolite, which is a natural zeolite with a high cation exchange capacity from Shankanai deposits of Kazakhstan and Ammophos fertilizer which is a complex mineral fertilizer (12%N, 52%P_2O_5) were used for the synthesis of zeolite-enriched fertilizer. The procedure applied for the synthesis of zeolite and fertilizer is given below in general terms.

- Clinoptilolite and Ammophos fertilizer are preliminarily colloidally ground to a fraction with sizes less than 300 nm in a planetary ball mill, thereby having sufficient energy for mechanical alloying
- Weigh out the desired amount of clinoptilolite and Ammophos fertilizer according to the desired ratio.
- Mix the clinoptilolite and fertilizer together in a beaker or flask, and add enough deionized water to create a slurry.
- Stir the slurry for several hours at room temperature to allow for ion exchange to occur between the clinoptilolite and fertilizer.
- Filter the slurry through a filter paper to separate the solid clinoptilolite-fertilizer complex from the liquid solution.
- Rinse the complex with deionized water to remove any residual impurities.
- Dry the complex at 60°C for 12 hours, and then crush it into a granular form suitable for use as a fertilizer.

X-ray diffractometer (Rigaku MiniFlex 600) in a scanning electron microscope was used to determine the elemental composition of zeolite, Synthesis of zeolite-enriched fertilizer and ammophos fertilizer (van Koningsveld and Bennett, 1999). Energy dispersive spectroscopy of all samples was carried out at shooting parameters with an accelerating voltage of 15 keV and a working distance of 15 mm.

Experimental procedure

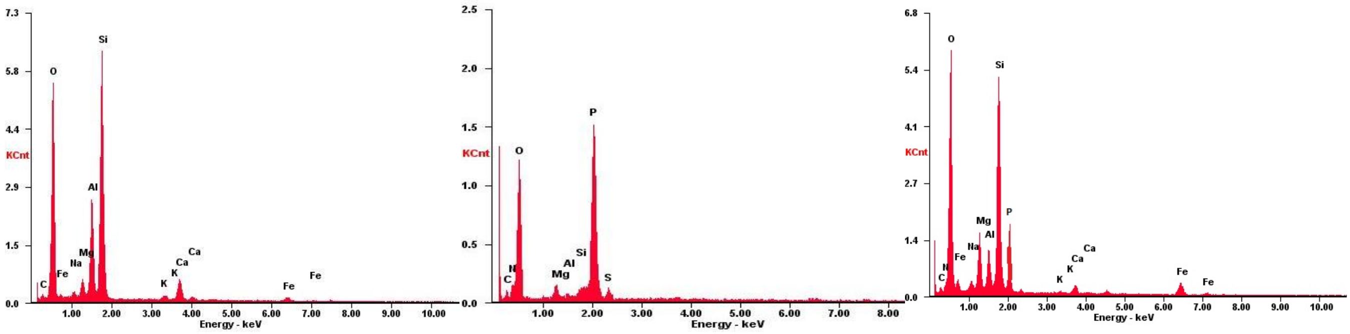
A pot experiment was carried out in the greenhouse of the Kazakh National Agricultural Research University with the cucumber variety "F1 Gerasim" in order to investigate the effects of clinoptilolite type of zeolite (ZEO), synthesised zeolite-enriched ammophos fertilizer (SZF) and ammophos fertilizer (AMF) on yield parameters of cucumber and some soil chemical properties. The experiment consisted of 4 treatments and three replications, and the pots were distributed in completely randomized design. There were ZEO (2 gr/kg soil), AMF (0,4 gr/kg soil), SZF (4 gr/kg soil) and a control treatment without zeolite and fertilizer application. Dark chestnut soil was filled in 5L pots. One cucumber seedling was planted in each pot. The pots were regularly irrigated to maintain a proper moisture level. Plants in pots were harvested 48 days after planting.

Data collection

After the harvest, the cucumber plants evaluated individually to determine the weight of one cucumber (WEC), shoot length (SLE), number of leaves (NUL), area of 10 leaves (ALE), number of fruits (NUF), fruit weight per plant (FWP). Soil samples were taken from each pots at the end of the harvest and the soil samples were air dried and passed through a sieve with 2 mm size opening, some soil characteristics were determined as follows; total soil organic matter contents (SOM), total carbonates contents ($CaCO_3$), soil reaction (pH), mineral-N, available phosphorus and available potassium as described by GOST 26213-2021, ISO 10693:1995, GOST 26423-85, GOST R 53219-2008 and GOST 26205-91.

Results and Discussion

The chemical composition of ZEO is the most important indicator of its quality. Thus, their ion-exchange properties, thermal and acid resistance, and other technological characteristics depend on the ratio of Si to Al and the cationic composition of zeolites. Zeolites with a high content of K give the greatest effect in crop production (Jarosz et al., 2022). According to XRD data, the main phase of the original ZEO from the Shankanai deposit is clinoptilolite, the SiO_2/Al_2O_3 ratio is 3.8. Na^+, K^+, Ca^{2+}, Mg^{2+} and Fe^{3+} were found in the composition of exchange cations, with large amounts of Ca^{2+}. Clinoptilolite /$KNa_2Ca_2(Si_{29}Al_7)O_{72}.32H_2O$/ has a monoclinic lattice with parameters: a=17.64 Ǻ; c=17.88 Ǻ; c=7.40 Ǻ; β=116.300. Other constituents are plagioclase, quartz, hematite, talc and muscovite. According to the results of studies of the elemental composition of the samples (Figure 1), it can be noted that the SZF did not lose its nutritional properties after chemical and thermal treatments. Clinoptilolite was a powerful reserve for the replenishment of potassium and silicon. It was determined that the weight and atomic content of the main nutrients like N and P have been preserved in SZF (Figure 1b).



A B C

Figure 1. The elemental composition of zeolite (A), ammophos fertilizer (B) and synthesised zeolite-enriched (C)

The changes in some of the chemical properties of the dark chestnut soil in the soil samples taken at the end of the harvest of the cucumber plant are given in Table 1. According to the results, it was determined that ZEO, AMF and SZF applications made to the soils compared to the control application did not cause a change in the SOM, soil pH and $CaCO_3$ of the soil. On the other hand, it was determined that the treatments had a significant effect on the cation exchange capacity (CEC), mineral nitrogen (min.N), available phosphorus (Av.P_2O_5) and available potassium (Av.K_2O) content of the soil. In this study, it was determined that the min.N, Av.P_2O_5, Av.K_2O contents and CEC of the soils were increased the most by SZF application. Because zeolites have high CEC, ion selectivity, unique physical characteristics and chemical stability they may be effective as soil conditioners. As reported by Soca and Daza-Torres (2016), the application of zeolite significantly increased the contents of available nutrients and increased soil pH. An increase in soil pH and exchangeable potassium content was observed by Filcheva and Tsadilas (2002), who conducted an experiment to evaluate the effect of clinoptilolite on soil properties. On the other hand, the results of de Campos Bernardi et al. (2013) indicated that application of concentrated natural zeolite, stilbite, enriched with nitrogen, phosphorus, and potassium on sandy soil reduced ammonia volatilisation, increased available phosphorus contents.

Table 1. The changes in some of the chemical properties of the dark chestnut soil

Treatments	SOM, %	pH	$CaCO_3$, %	Min. N, mg kg^{-1}	Av. P_2O_5, mg kg^{-1}	Av.K_2O, mg kg^{-1}	CEC, meq 100 g^{-1}
Control	2.27	8.36	1.23	56.6	32	240	13.8
ZEO	2.27	8.42	1.28	61.9	41	320	17.8
AMF	2.27	8.39	1.30	64.4	68	238	14.1
SZF	2.27	8.40	1.28	69.4	88	380	18.1

The effects of ZEO, AMF and SZF added to dark chestnut soil on the yield parameters of the cucumber plant are given in Table 2. According to the results obtained from the experiment, it was determined that ZEO, AMF and SZF applications increased the yield parameters (WEC, SLE, NUl, ALE, NUF, FWP) of the cucumber plant. In addition, it was determined that the WEC, SLE, NUl, ALE, NUF and FWP were increased the most by SZF application. Plant growth and plant yield parameters might be directly influenced by the amount of nutrients present in soil and available for the plants to complete its life cycle. Plant growth and plant yield parameters results had to be related to available soil nutrient results uptake by cucumber plants for their metabolism. In this study, it was determined that ZEO, AMF and SZF added to the soil also increased the yield parameters of the cucumber plant due to the increase in the min.N, Av.P_2O_5, Av.K_2O and CEC of the soil.

The effects of natural zeolites and enriched zeolites with fertilizer amendment on cucumber (*Cucumis sativus*) seed germination, plant growth, and development were examined. Researchers have reported that germination was faster with ammonium sulfate, diamonium phosphate, and superphosphate (18% P_2O_5) amendment than with enriched zeolites with these fertilizer amendments. Although fertilizers suddenly affect media at initial irrigation after the sowing, zeolites work slowly due to slowly released N from their colloidal sites (Yılmaz et al., 2014). Similarly, a field experiment to investigate the effect of zeolite in the form of clinoptilolite as a supplement to mineral fertilization was conducted by Tsintskaladze et al. (2017), who used maize as a test crop. As per the results, the application of ammonium nitrate alone allowed to obtain a maize grain yield of 7.4 t ha^{-1}, while for the variant combining zeolite and ammonium nitrate, the obtained maize grain yield was 8.8 t ha^{-1}, constituting an 18.9% increase.

Table 2. The changes in yield parameters of cucumber plant

Treatments	WEC, g	SLE, cm	NUL, pcs	ALE, cm^2	NUF, pcs	FWP, g
Control	28,5	138	35	294,0	2	101
ZEO	47,4	159	34	305,3	2	144
AMF	45,3	143	22	309,0	4	183
SZF	71,7	227	36	314,3	4	184

Conclusion

In this study, greenhouse experiment on pot grown cucumber plants demonstrated that zeolitic soil amendments (clinoptilolite type of zeolite from the Shankanai deposit, Kazakhstan and synthesised zeolite-enriched ammophos fertilizer) could be effective alternatives to conventional ammophos fertilizer, providing cucumber plants with both improving soil chemical properties and plant yield parameters. Comparisons of plant growth with controls showed synthesised zeolite-enriched fertilizer amended soils at lower loadings, to be a potential source of providing plants with all the essential nutrients during all stages of growth cycle, thereby increasing plant yield parameters. In soils amended with higher cation exchange capacity of both synthesised zeolite-enriched fertilizer and natural clinoptilolite type of zeolite, plant growth was significantly increased. Higher available N, P and K in the soil may cause plant yield parameters. This study covered a broad range of issues, many of which merit further investigation. Listed below are some recommendations for further investigation.

(i) As the greenhouse experiment was carried out under controlled greenhouse conditions on pot-grown plants, it would be beneficial to compare the effects of zeolite and zeolite-enriched fertilizer addition to different type of soil under field conditions to evaluate the effectiveness of different plant growth.

(ii) The major hurdle in using synthetic zeolites as fertilizer amendments is their cost. Calculating the cost for producing zeolites on a laboratory scale it was valued to be three times an expensive product than its natural counterpart. However, based on the effectiveness of synthesised clinoptilolite type of zeolite-enriched ammophos fertilizer from the Shankanai deposit, Kazakhstan, in particular as a controlled release soil amendment, it would be worth exploring the possibilities of manufacturing zeolites on a large commercial scale under pilot conditions.

Acknowledgements

Funding for this research was provided by Kazakhstan Science and Higher Education Ministry (Project No. AP13068349). We would like to thank for in kind contribution and anonymous reviewers for their constructive comments.

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