EFFECT OF AMMONIUM-CLINOPTILOLITE ON THE GROWTH OF *Amaranthus gangeticus*

[1]NIZA SYAFIQAH HAMZAH, [2]NOOR HIDAYAH DZKULFLI,[3]W MOHD MADHI W ABDULLAH, [4*]NIK AHMAD NIZAM NIK MALEK AND [5]SALEHHUDDIN HAMDAN

Faculty of Biosciences and Medical Engineering, Universiti Teknologi Malaysia, Johor.

[1] haqifays_13@yahoo.com, [2]noorhidayahdz@yahoo.com,[3]madhiabdullah@gmail.com,[4*]niknizam@fbb.utm.my, [5]saleh@fbb.utm.my

*Corresponding author

Abstract. The use of ammonium-clinoptilolite as fertilizer for *Amaranthus gangeticus* offers an option to reduce the environmental pollution problems such as nitrogen contamination in the air and water. In addition, nitrogen from ammonium plays important role in the growth of the plant especially on the leaf growth. High surface area and cation exchange capacity of zeolite type clinoptilolite was used as carrier to control ammonium release. In this study, the effect of ammonium-clinoptilolite (zeolite pre-load with ammonium (NH_4^+)) on *Amaranthus gangeticus* growth was studied. The study indicated that the results of plant heights and leaf number obtained fertilized with ammonium-clinoptilolite were higher compared to control sample (without ammonium).The result shows that the ammonium-clinoptilolite was a good carrier of nitrogen for *Amaranthus gangeticus*.

Keywords Ammonium-Clinoptilolite; *Amaranthus gangeticus*; zeolite; clinoptilolite; modification

1.0 INTRODUCTION

Loss of important nutrients from soil and fertilizer due to leaching, volatilization and fixation are among the reasons why plants did not grow well [1]. Nitrogen is one of the most limiting nutrients for plant growth therefore it can

influence the yields and quality of the plants. There are many studies have been performed mostly on nitrogenous fertilizer in order to reduce any possible unfavorable environmental effects [2]. Around 40-70% of the nitrogen that is commonly used in fertilizer, release to the environment since the plants do not fully absorb all the fertilizer. This situation may cause serious environmental pollution and also huge economic and resources losses [3]. In addition, there is also previous research stated that ammonia volatilization from urea and ammonium containing compound fertilizers contribute in higher cost of fertilization in agriculture [4]. Thus, with the advantages that zeolite possesses which is the ability to hold and slowly release the cation [5], these problems can be solved.

Recently, zeolite has been used in industries especially in the field of agriculture [6]. It has been reported previously that the used of zeolite in amendment of soil with manure can be a beneficial approach for decreasing chemical fertilizer application rate. It also improved the sustainability of agricultural systems as it decreased the nutrient leaching such as phosphate and nitrate [7]. Zeolites are a family of crystalline, hydrated alumino silicates and alkaline earth cations that have three-dimensional crystal structures such as clinoptilolite [8]. Clinoptilolite is one of the most plentiful zeolite in several soil types and it also has the highest charged minerals occurring in soil and because of this, it can enhance soil Cation Exchange Capacity (CECs) [9,10].

There was a previous research that study about ammonium-loaded clinoptilolite and tested on sweet corn but there is no differences in corn growth were observed. However results show fertilization with ammonium-clinoptilolite decreased N leaching from sandy soils while remained the normal corn growth [11]. There are different types of zeolite-fertilizers approach used before and one of it was a zeolite mixed with chemical fertilizer by physically mixing [12] and the other one nutrient loading of ammonium into the zeolite by the process of ion exchanges [13].

In this study, *Amaranthus gangeticus* was selected as a model plant due to highly resistance to weather condition, fast growth and most important thing is *A. gangeticus* is a nutrient responsive crop especially on the leaf growth [14,15]. This plant is a leafy plant, thus it is appropriate to study the plant responses to

ammonium exchanged clinoptilolite because nitrogen from ammonium plays important role in the growth of the plant especially in the leaf growth [16].

2.0 EXPERIMENTAL

2.1 Materials

Zeolite (clinoptilolite) used in this study was imported from Indonesia and was supplied by Provet Group of Companies Sdn. Bhd., Selangor. Ammonium acetate from Fisher Scientific was used as ammonium source for the preparation of ammonium-clinoptilolite.

2.1.1 Preparation and Characterization of Ammonium-Clinoptilolite

100 g of clinoptilolite was mixed with 500 ml ammonium acetate (20 g/L) in a 1000 mL beaker. The suspension was stirred overnight. The suspension was then filtered through a filter paper and the residual Ammonium-Clinoptilolite was dried in an oven at 80 ºC overnight. The dried Ammonium-Clinoptilolite was then ground by using mortar and pestle.This experiment was repeated for five times using the dried Ammonium-Clinoptiloliteto make sure the clinoptilolite was enriched with ammonium cation (NH_4^+).

The structure of clinoptilolite before and after exchanged with ammonium was characterized using X-ray Diffraction (XRD) (Bruker AXS GmbH (Germany)) machine and Fourier Transforms Infrared (FTIR) spectroscopy (NICOLET Is5 FT-IR Spectrometer). XRD patterns were recorded with CuK_α radiation at λ = 1.5418 Å at 40 kV and 20 mA in the range of 2θ = 5°to 50°with a scanning speed of 0.05°per second. For the FTIR spectroscopy, the KBr method was used with the ratio of KBr to sample was 100:1.The proximate analysis of total nitrogen was analyzed by using Kjeldahl method according to the standard method from Association of Official Analytical Chemists (AOAC Official Method 2001.11).

2.2 Performance Study of Ammonium-Clinoptilolite as Fertilizer

The experiment for the study of performance of Ammonium-Clinoptilolite as fertilizer was carried out in semi greenhouse at Unit Pertanian Fakulti Pendidikan, Universiti Teknologi Malaysia. Propagating substrate for sowing the plant was imported from Holland, (Stender). 500 g of soil was added in the polybag size 8 × 8 cm which has pH 6. The soil's ratio content was 3:2:1 (soil, rice husk and coconut fibre).

Ammonium-Clinoptilolite (5g) was applied on day 15 to the plants on soil surface to compare the growth of plants with the control plant which is only soil without any added fertilizer in five replicates. The height (cm) and number of leaf were measured before they were harvested on day 28.

3.0 RESULTS AND DISCUSSION

By Kjeldahl method, total percentage of nitrogen contained in Ammonium-Clinoptilolite was 1.52% and there was no ammonium in the parent clinoptilolite. This method proved the enrichment of ammonium into the clinoptilolite.

The preparation of Ammonium-Clinoptilolite does not affect the clinoptilolite structure because the process of the modification is based on ion exchange [13]. During the loading of ammonium into clinoptilolite, ion-exchange process will occurs where other cation in the clinoptilolite are replaced by the ammonium, NH_4^+. Additionally, the natural zeolite was chosen on the basis of its good ammonium-ion selectivity and potentially low cost [17]. To study the effect of modification of clinoptilolite on its structure, XRD and FTIR were used to characterize them. Figures 1 and 2 show XRD diffractogram and FTIR spectra of clinoptilolite and Ammonium-Clinoptilolite.

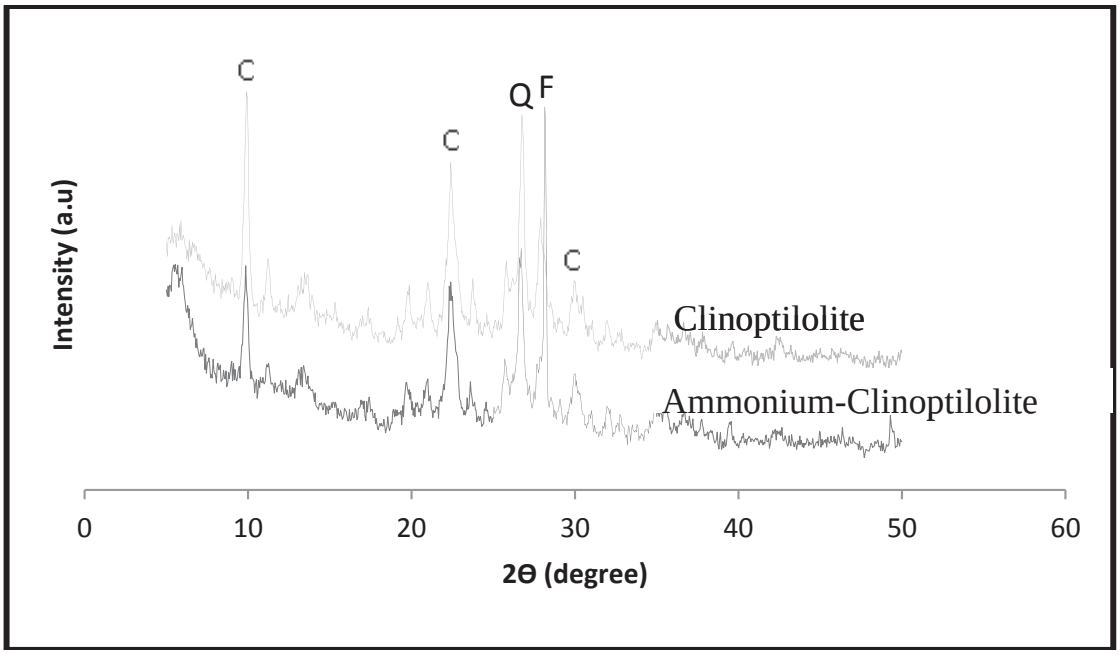

Figure 1 X-ray diffraction pattern of clinoptilolite and Ammonium-Clinoptilolite

Figure 1 shows the characteristics peaks of clinoptilolite were found on the XRD pattern. Based on previous study, the peaks represent natural clinoptilolite in XRD diffractogram were found at about2Θ: 9.92°, 22.43° and 30.50°[18]. While the other strong peaks represent impurities such as quartz and feldspar [19,20]. It also shows that there are no changes in the XRD pattern of the modified zeolite (Ammonium-Clinoptilolite) compared to that of parent clinoptilolite. The result from XRD concludes that the structure of Ammonium-Clinoptilolite was not altered during the ion exchange process and remains stable after loading with ammonium.

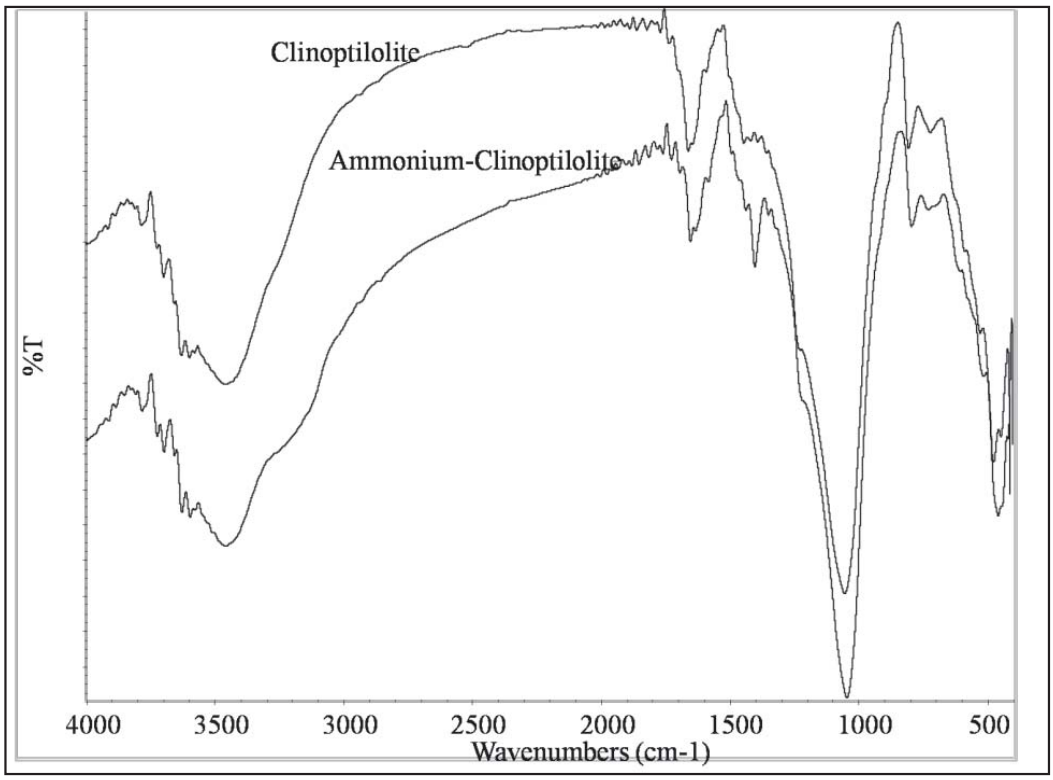

Figure 2 FT-IR spectra of parent clinoptilolite and Ammonium-Clinoptilolite

The FT-IR spectrum of Ammonium-Clinoptilolite in Figure 2 confirms the structural stability of zeolite after loading with ammonium. It can be compared with the FTIR spectrum of original clinoptilolite [21]. From the previous study, the peak in FTIR for clinoptilolite at about 1067 cm^- corresponds to asymmetric stretching vibration modes of internal T-O bonds in TO_4 tetrahedral (T = Si and Al) while the other peaks at 769 and 469 cm^- correspond to the stretching vibration modes of O-T-O groups and the bending vibrations of T-O bonds, respectively [22].

The performance study of Ammonium-Clinoptilolite as fertilizer was carried out against *Amaranthus gangeticus* in 28 days. The ammonium-clinoptilolite was applied on day 15 when the plant was observed to be fresh and strong enough to absorb nutrient from the fertilizer. Figures 3 and 4 showed average leaf number and plant height of the plant after fertilized by clinoptilolite and Ammonium-Clinoptilolite.

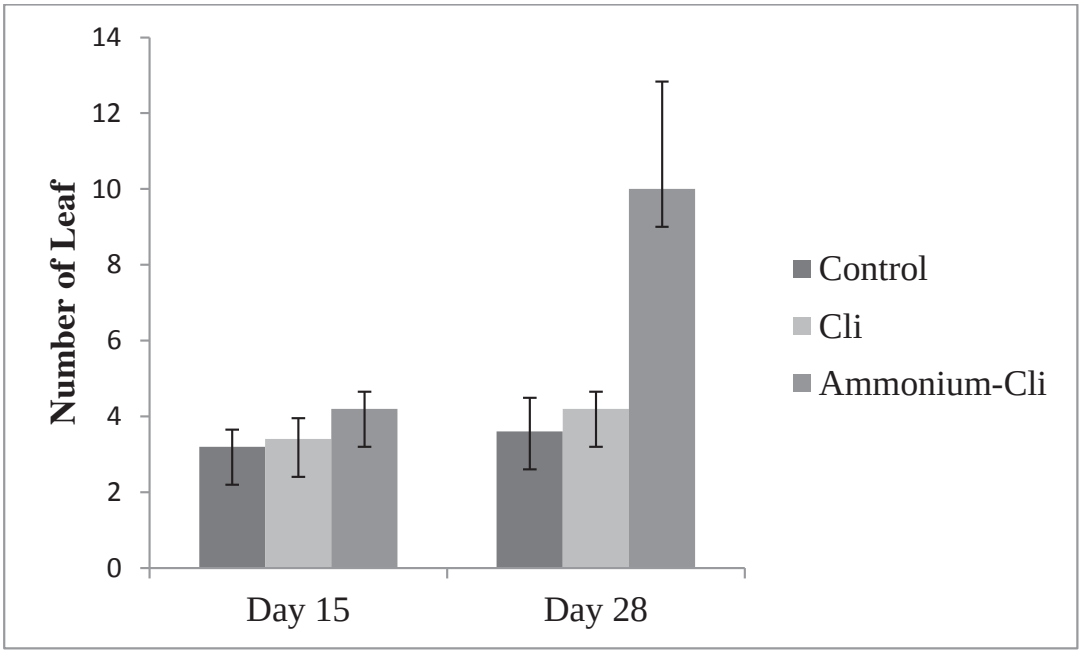

Figure 3 Average of leaf number for day 15 and 28 after fertilized by clinoptilolite and Ammonium-Clinoptilolite

The result in Figure 3 show the average of leaf number of *Amaranthus gangeticus* on day 28 was higher after applying Ammonium-Clinoptilolite as fertilizer. The leaf treated by Ammonium-Clinoptilolite shows more than 100% percentage increased on day 28which produce more leaf compared to the control sample (without fertilizer). Ammonium-Clinoptilolite could be a good N fertilizer because it has been mentioned before in previous studies that many macro-nutrients such as nitrogen can be supplied to the plants by exchanging ammonium into clinoptilolite [23]. Furthermore, nitrogen can stimulate vegetative growth by increasing the number of leaves [24]. In other previous study also reported that increments in the nitrogen rate of the fertilizers would increased the number of leaves [25]. There was a slight increase in the number of leaves when clinoptilolite was applied. This is probably because after clinoptilolite could enhance both the soil cation exchange capacity (CEC) and pH [26].

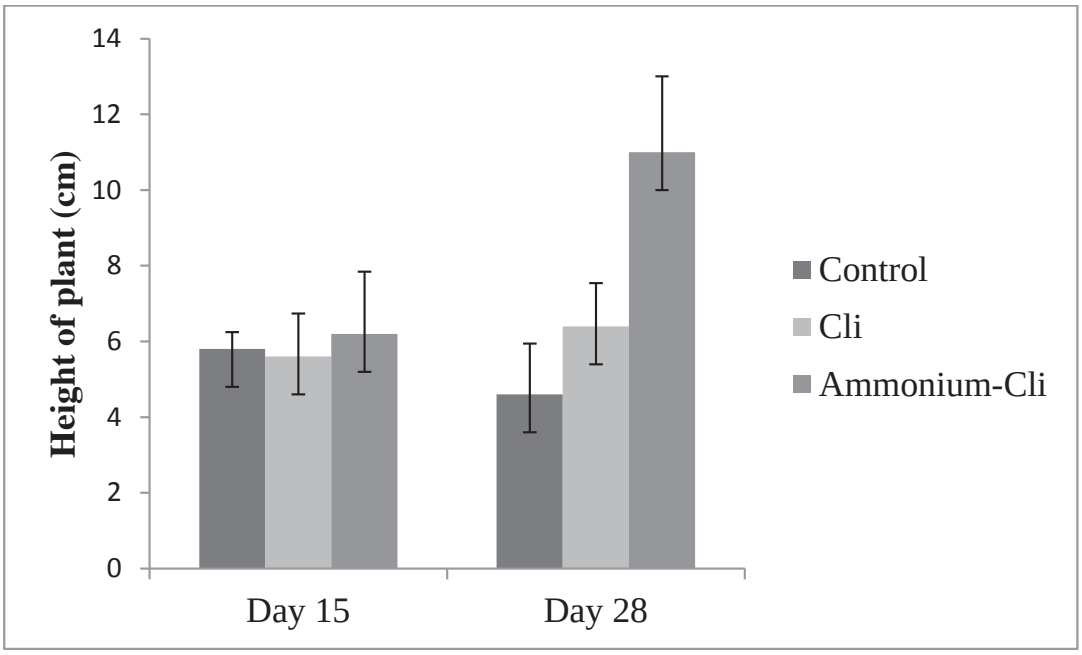

Figure 4 Average of height of plant (cm) for day 15 and 28 after fertilizer with clinoptilolite and Ammonium-Clinoptilolite

As can be seen in Figure 4, the used of Ammonium-Clinoptilolite as fertilizer increased the growth by nearly 80% compared to control. This is because the plant obtained N element from Ammonium-clinoptilolite which is macronutrients for the plant growth. In addition, it also helps in controlling and managing nutrient, by decreasing the release rate of ammonium and loss to the environment [27]. However, slight rises when clinoptilolite was applied might be due the increase of the soil's water holding capacity while slightly decreasing the saturated hydraulic conductivity [26]. As stated by Li and friends, the main use of natural zeolites in agriculture is for ammonium exchange, storage, slow-release and decrease losses of nitrogen through nitrification [28].

4.0 CONCLUSIONS

It can be concluded that clinoptilolite could act as a carrier for major nutrient such as ammonium that gives N element. It was proven that the loading of ammonium into clinoptilolite was proven by several characterization techniques and also the excellent growth of *Amaranthus gangeticus*. As a result, Ammonium-Clinoptilolite could be one of the controlled release fertilizers that could improve

nitrogen release efficiency and results in positive growth of *Amaranthus gangeticus*.

REFERENCES

[1] Cassman, K. G., Dobermann, A. and Walters, D. T. 2002. Agroecosystems, Nitrogen-use Efficiency, and Nitrogen Management. *Ambio*, 31, 132–140.

[2] Trenkel, M. D. 2010. *Slow and controlled-release and stabilized fertilizers: An option forenhancing nutrient efficiency in agriculture*. (2nd Ed). International Fertilizer Industry Association, France.

[3] Wu, L., and Liu, M. Z. 2008. Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention. *Carbohydrate Polymer*, 72 (2) 240–247.

[4] Rabai, K. A., Ahmed, O. H., and Kasim, S. 2012. Improving formulated nitrogen, phosphorus and potassium compound fertilizer using zeolite. *African Journal of Biotechnology*, 11(65), 12825-12829.

[5] Ayan, S., and Tufekcioglu, A. 2006. Growth responses of scots pine seedlings grown in peat-based media amended with natural zeolite. *Journal of Environmental Biology*, 27 (1)

[6] Hayawin, Z. N., Astimar, A. A., Ridzuan, R., Syirat, Z. B., Ravi Menon, N., and Jalani, N. F. 2014. Study on the Effect of Adding Zeolite and other Bio-Adsorbance in Enhancing the Quality of the Palm Based Vermicompost. *Applied Mechanics and Materials*, 472, 926-934.

[7] Gholamhoseini M., Ghalayand A., Khodaei-Joghan A., Dolatabadian A., Zakikhani H., and Farmanbar E. 2013. *Soil and Tillage Research*, 126, 193-202.

[8] Sand, L. B. and Mumpton, F. A. 1976. Natural Zeolites Occurrence, Properties, Use.

[9] Rehakova, M., Cuvanova, S., Rimarand, M.and Gavalova, Z. 2004. Current Opinion in Solid State and Material. Science, 8 397-404.

[10] Ming, D. W., and Dixon, J. B. 1987. Quantitative determination of clinoptilolite in soils by a cation-exchange capacity method. *Clays and Clay Mineral*, 35(6), 463-468.

[11] Perrin, T. S., Drost, D. T., Boettinger, J. L., and Norton, J. M. 1998. Ammonium-loaded clinoptilolite: a slow-release nitrogen fertilizer for sweet corn. *Journal of plant nutrition*, 21(3), 515-530.

[12] Welson Blue, M. L., Haruna, A. O., and Kasim, S. 2013. Maize (*Zea mays* L.) nutrient use efficiency as affected by formulated fertilizer with Clinoptilolite Zeolite. *Emirates Journal of Food and Agriculture*, 26 (2).

[13] Nezamzadeh-Ejhieh, A., and Raja, G. 2012. Modification of nanoclinoptilolite zeolite with hexadecyltrimethylammonium surfactant as an active ingredient of chromate-selective membrane electrode. *Journal of Chemistry*, 2013, 13.

[14] Sakr, W. R., and Husein, M. E. 2012. Response of Amaranthus tricolor L. Plants to Bio and Chemical Nitrogenous Nutrition and their Role in Remediating Some Polluted Soils with Lead and Cobalt. *Agriculture and Environmental Science*, 12 (10) 1377-1394.

[15] Preetha, D., Sushama, P. K., & Marykutty, K. C. 2005. Vermicompost + inorganic fertilizers promote yield and nutrient uptake of amaranth (Amaranthus tricolor L.). *Journal Tropical Agriculture*, 42 (1-2) 87-89

[16] Amaranthus 2010. Production guideline, Department of Agriculture, Forestry and Fisheries, Republic of South Africa, 6-7

[17] Demir, A., Gunay, A., and Debik, E. 2002. Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite. *Water SA*, 28(3), 329-336.

[18] Arcoya, A., Gonzalez, J. A., Travieso, N., and Seoane, X. L. 1994. Physicochemical and catalytic properties of a modified natural clinoptilolite. *Clay Minerals*, 29(1), 123-131

[19] Chmielewska, E., Samajova, E., and Kozac, J. 2009. A comparative study for basic characterization of three Clinoptilolite specimens. *Turkish Journal of Chemistry*, 26(2), 281-286.

[20] Tomasevic-Canovic, M. R. 2005. Purification of natural zeolite-clinoptilolite for medical application: Extraction of lead. *Journal of the Serbian Chemical Society*, 70(11), 1335-1345.

[21] Peter, A., Mihaly-Cozmuta, L., Mihaly-Cozmuta, A., Nicula, C., Indrea, E., and Tutu, H. 2012. Calcium-and ammonium ion-modification of zeolite amendments affects the metal-uptake of Hieraciumpiloselloides in a dose-dependent way. *Journal of Environmental Monitoring*, 14(10), 2807-2814.

[22] Mansouri, N., Rikhtegar, N., Panahi, H. A., Atabi, F., and Shahraki, B. K. 2013. Porosity, characterization and structural properties of natural zeolite- clinoptilolite- as a sorbent. *Environment Protection Engineering*, 39(1), 139-152.

[23] Allen, E. R., Hossner, L. R., Ming, D. W., and Henninger, D. L. 1996. Release rates of phosphorus, ammonium, and potassium in clinoptilolite-phosphate rock systems. *Soil Science Society of America Journal*, 60(5), 1467-1472

[24] Boroujerdnia, M., and Ansari, N. A. 2007. Effect of different levels of nitrogen fertilizer and cultivars on growth, yield and yield components of romaine lettuce (Lactuca sativa L.). *Middle Eastern and Russian Journal of Plant Science and Biotechnology*, 1(2), 47-53.

[25] Gulser, F. 2005. Effects of ammonium sulphate and urea on NO_3^- and NO_2^- accumulation, nutrient contents and yield criteria in spinach. *Scientia Horticulturae*, 106(3), 330-340.

[26] Ming, D. W., and Allen, E. R. 2001. Use of natural zeolites in agronomy, horticulture and environmental soil remediation. *Reviews in Mineralogy and Geochemistry*, 45(1), 619-654.

[27] Jakkula, V. S., Williams, C. D., Hocking, T. J., and Fullen, M. A. 2011. High selectivity and affinity of synthetic Phillipsite compared

with natural Phillipsite towards ammonium and its potential as a slow release fertilizer. *Archives of Agronomy and Soil Science*, 57(1), 47-60.

[28] Li, J., Wee, C., and Sohn, B. 2013. Effect of ammonium-and potassium-loaded zeolite on Kale (Brassica alboglabra) growth and soil property. *American Journal of Plant Sciences*, 4(10).