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Composite Zeolite/ NPK Fertilizer: Performance Evaluation of Papaya Plant Growth and Nutrient Uptake in Semi-Arid Environment

Omaima M. Hafez[1], M. F. El-Dahshouri [2], Hassan A. Hamouda [2] and H.F. Youssef [3]

[1]Pomology Research Department, National Research Centre, Dokki, P.O. Box 12622, Cairo, Egypt.
[2]Fertilization Technology Department, National Research Centre, Dokki, P.O. Box 12622, Cairo, Egypt.
[3]Ceramic, Refractories and Building Materials Department, National Research Centre, Dokki, P.O. Box 12622, Cairo, Egypt.

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ABSTRACT
The present research was conducted to prepare a zeolite-based fertilizer composite containing different rates of zeolite-A (Z) and NPK (19 N: 19 P_2O_5: 19 K_2O) fertilizer (F) to grow papaya seedlings in the Pomology greenhouse of the National Research Centre in Egypt, under the semi-arid conditions of Egypt during the 2014 summer season. Combined mixtures were designed by adding 8.0, 6.0, 4.0, 2.0, 1.0 and 0.0 (g/ pot/ plant) rates of zeolites to the respective NPK amounts of 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 (g/ pot/plant). The macro- and micronutrients in the leaves, stems and roots were analyzed using spectrophotometer and Atomic Absorption Spectrophotometer (Perkin-Elmer 100 B). The whole results were statistically analyzed. The results of Z/F composite application revealed that, the optimum enhanced plant nutrition values were obtained when zeolite contents increased at the expenses of NPK mineral fertilizer. The highest performance was recorded for T_5 (6.0 g Z +1.0 g F) and T_4 (4.0 g Z+2.0 g F), meanwhile T_1 (0.0 g Z+5.0 g F) and T_6 (8.0 g Z+ 0.0g F) implied the lowest values of all treatments. Applying (Z/ F) seemed to positively influence the plant growth by increase the fresh and dry weights, macro and micronutrient uptake by using lower rates of NPK to the extent of 1.0-2.0 g/ pot/ plant. Better plant growth was achieved with 60 to 80% reduction in the fertilizer cost.

Keywords: Combined fertilizer, Zeolite-A + NPK, Papaya growth, Nutrient uptake.

1. Introduction

The inappropriate use of commercial fertilizers caused deterioration in the soil fertility and some inorganic/organic disturbances in the land properties. In semi-arid conditions (as in Egypt), huge areas of sandy soil with low clay fraction, very poor nutrient availability and insufficient water retention for plant growth prevailed. For amending and cultivating such areas and even for expanding the already exist agricultural soil performance, unwise fertilizer consumption is not excluded. This uncontrollable fertilizers use resulted in an increase in the soil salinity, decrease in organic matter content and intern deplete the microbial activity, all of which negatively affect the soil productivity, crops yield and cause serious harmful impacts on both environment and health (Moeskops *et al.,* 2010, Savci, 2012 and Krasilnikov *et al*., 2022). The previous problem was partially overcome by replacing parts of the fertilizers by the naturally- sourced manures (wastes of human, animal and plant) which proved effective (Yadav *et al.,* 2013).

It is well known that, crop production depends on the soil fertility, including its chemical, mineralogical and structural compositions which are presumably translated by its clay fraction content. In the soil structure, clay fine materials with its cationic adhering and water swilling nature are responsible for holding the nutrients, water, microorganisms and organic matter for plants, thus the clay content are directly proportional to soil fertility. Clays and aluminosilicate zeolites are two groups of phyllosilicate hydrated minerals that have relatively similar composition containing alumina, silica and

Corresponding Author: Omaima M. Hafez, Pomology Research Department, National Research Centre, Dokki, P.O. Box 12622, Cairo, Egypt. E-mail: omimahafez@yahoo.com

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different cations, but different internal structures. Where, clay minerals have silica and alumina sheets in a loose layered construction, zeolites show outstanding microporous crystal nature. Both materials have important industerial applications, besides their role played as media for agriculture.

Zeolite ores are not mined in many countries such as Egypt, thus their production from available resources, as clay rocks, is of economic value. As being the world's only negatively charged minerals in existence, zeolites have distinguished identity and performance and implied breakthrough many applications containing agriculture, water softening and purification, catalysis, detergency, oil refining, absorbency etc... (Breck, 1974; Barrer, 1982 and Szostak, 1998).

There are more than 40 different natural types with very complex three-dimensional porous frameworks, "open structures", and a high specific surface area and cation exchange ability in their internal cavities (Anderson, 2001). Thus, different cations can be hosted as calcium, magnesium and sodium with the availability of their exchange with other cations or anions with valuable importance to plant growth like ammonia and/or potassium (Barros *et al*., 2003). On the other hand, owing to their elevated charged external and internal surfaces and cavities they are good adsorbents and behave as "molecular sieves" (Sersale, 1985 and Ramôa, 1993 and Pérez-Botella *et al*., 2022). For the previous reasons, they have been used in agricultural applications (Boettinger and Ming, 2002). Many satisfactory results were recorded on applying different zeolites for amending soil (Lai *et al*., 2000 and Al-Busaidi *et al*., 2008) and in using them as component of growing media in containerized seed propagation and seedlings growth (Ayan and Tillki, 2007). Furthermore, zeolites promoted plant growth by fertilizer improving value; retaining valuable elements as nitrogen, enhancing quality of resulting manures, enriching plant yield and quality (Ayan, *et al*., 2006). In addition, it caused soil temperature restore (Kazemian, 2005). In Japan, natural clinoptilolite was applied as amendment tool in sandy soil to promote sufficient nutrition and elevated water retention necessary for better plant growth and high yields of different crops (Mumpton, 1999).

Papaya (*Carica papaya* L.) is a commercially important tropical fruit with high value in nutrition and medicine that utilized all parts of the plant (Karuna and Kaushal, 2014). In its first six growing months, the plant needs extensive nutrition with appreciable amounts of N, P and K. This eager for nutrients is hindered by the superficial roots of the plant that seemed unable to extend deeply into soil to afford the necessary nutrient elements and water. Thus, plentiful nutrition and sufficient irrigation are required for its plantation (Mohamed, 1995). In addition, Papaya is highly responsive to both organic fertilizer and inorganic manures and its growth, yield and fruit quality is dependent on the balanced nutrition (Krishi, 2015).

In the present paper, growing papaya is targeted due to its vigorous needs for nutrients and water, thus its growth state will be representative to the actual zeolite effect. The sandy soil choice in here was ment to monitor the improvement of its nutrients and water holding ability when conditioned by zeolite/NPK combined fertilizer of different rates. In a previous work, the same research team conducted a separate investigation to evaluate the effect of the prepared combined fertilizer (Z/F) on the physico-chemical parameters of the sandy soil (Youssef *et al*., 2022). Whereas, the specific aims of the present study are; the preparation and application of a composite fertilizer model (Z/ F) containing different rates of zeolite-A, prepared from local clay source, and a widely used commercial fertilizer (NPK), to serve as a better plant growth promoter. The effects of adding different Z/ F rates on the vegetative growth, dry and fresh weight, chlorophyll contents and nutrients uptake were investigated.

1. Experimental

2.1. Materials

2.1.1. Zeolite Synthesis

In the present work, "Kalabsha kaolin" from Aswan utilized as the starting material in zeolite preparation for economic reason and because of its chemical composition resemblance to that of zeolite-A (Rosha *et al.*, 1991 and Dongeard *et al.*, 2000). The chemical analysis of the parent rock as given by X-Ray Fluorescence analysis included (in Wt%); 53.23 SiO_2, 41.58 Al_2O_3, 2.25 TiO_2, 1.83 Fe_2O_3 and other minor oxides of MgO, Na_2O, K_2O, MnO and CaO. Zeolite is prepared following the method of (Youssef, *et al*., 2008). The used very well crystalline zeolite-A was prepared from metakaolin at 80 °C for 2 hours under hydrothermal conditions.

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2.1.2. Zeolite/ Fertilizer/ Soil Preparation

The composition of the starting soil (SS) contained mixture of sand and peat moss at 2:1 ratio, respectively; one seedling per pot is applied. Six treatments with five replicate (seedling/pot/replicate) were prepared, using zeolite-A powder (Z) and NPK fertilizer compound (F) 19 N; 19 P_2O_5: 19 K_2O in the following admixture rates given in Table 1. Each treatment is signed in the form of (Z/ F/ Pot/ plant) as follows:

Table 1: The applied Z/ F admixture rates

Treatments	**Zeolite/ Fertilizer Mixture(Z/ F) in grams**	
	Zeolite-A	**Fertilizer (NPK)**
T_1 (Z_0F_5)	0.0	5.0
T_2 (Z_1F_4)	1.0	4.0
T_3 (Z_2F_3)	2.0	3.0
T_4 (Z_4F_2)	4.0	2.0
T_5 (Z_6F_1)	6.0	1.0
T_6 (Z_8F_0)	8.0	0.0

During the whole duration of the experiment, the monthly fertilizer's addition is stabilized, whereas foliar application with micronutrients compound (3.0% Fe, 3.0% Zn and 3.0% Mn) at 5 g L^{-1} was twice added (April and June) after the soil fertilization.

2.1.3. Plant Material

Papaya seedlings of Solo cultivar (2 months old) were used in this work with uniform seedlings of similar vigor, age and size to be transplanted (late of February). This research was conducted during 2014 season in pots (45 cm) and started from March 1^{st} to the end of August.

2.2. Methods

2.2.1. Nutrient concentration

Nutrient elemental compositions in the leaves (the 4^{th} top leave of plant), stems and roots were analyzed for the macro- and micronutrient contents. Nitrogen (N) was detected by using the Kjeldahl method, Phosphorous (P) by spectrophotometer (Chapman and Pratt, 1978). Potassium (K) and micronutrients (Fe, Mn and Zn) were measured in the suspension using (Perkin-Elmer 100 B) Atomic Absorption Spectrophotometer (Lindsay and Norvell, 1978).

3. Statistical Analysis

The whole results were submitted to analysis of variance according to (Snedecor and Cochran, 1967). Differences among treatments means were determined by using the LSD test at a significance level of 0.05 (Waller and Duncan, 1969).

4. Results and Discussion

4.1. Growth Parameters

Growth parameters such as plant length, stem thickness, Leaf area (cm^2), Chlorophyll, fresh and dry weights Content were affected by applying different Z/F mixtures.

4.1.1. Plant Length and Thickness

Figures 1a & b gave the graphical presentation of the monthly growth rates (%) for both papaya stem length (Fig.1a) and thickness (Fig.1b) on applying different Z/F mixtures. The stem is normally representing the whole plant. The configured data implied different degrees of growth rates for both parameters (length and thickness); treatments T_1 (high F) and T_6 (high Z) showed no differences, T_2 (Z_1F_4) and T_3 (Z_2F_3) presented the highest rates, whereas T_4 (Z_4F_2) and T_5 (Z_6F_1) showed the moderate rates of all treatments.

The graphed data indicated that, the best vegetative growth period for papaya plant occurred during April – May, through which a plentiful convenient nutrition is necessary for plant growth.

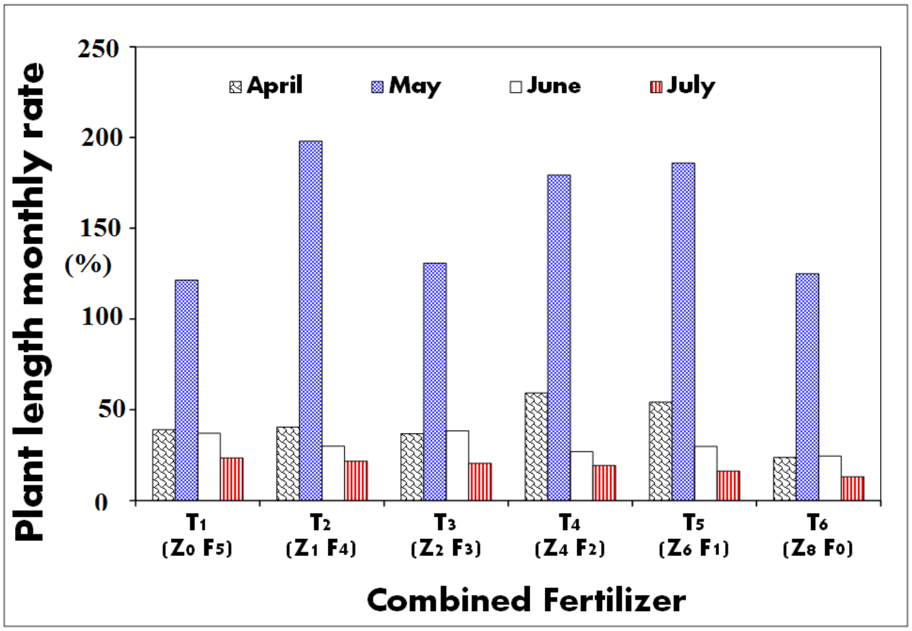

Fig.1a: Effect of applying combined **Z/ F** on stem length monthly growth rate (%).

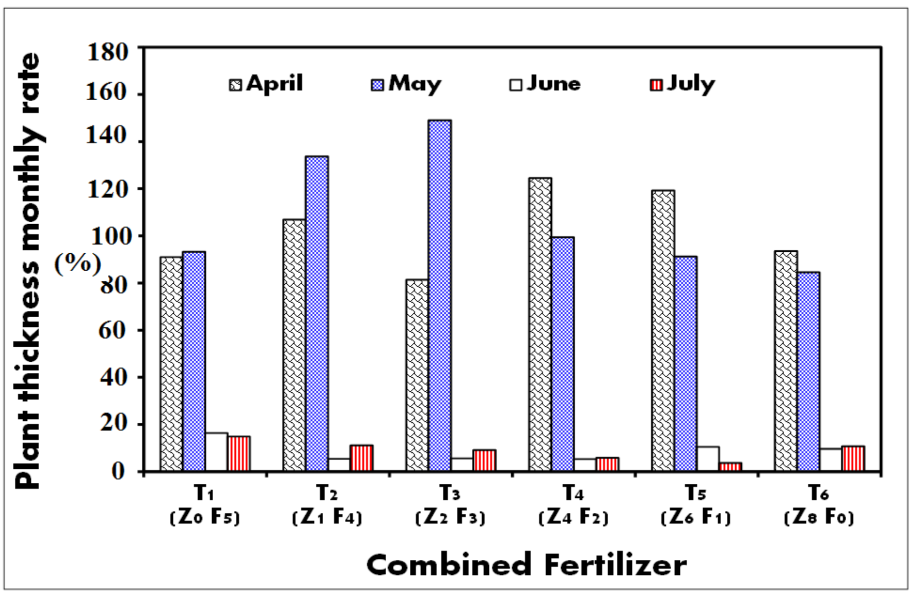

Fig. 1b: Effect of applying combined **Z/ F** on stem thickness monthly growth rate (%)

4.1.2. Leaf area (cm^2) and Chlorophyll Content

Figure 2 presents the effect of adding different Z/F mixtures on the plant leaf area (cm^2) and chlorophyll content parameters. In general, both parameters witnessed decrease in amount with increasing zeolite content at the expense of fertilizer.

The figure showed that, the highest significant leaf area obtained from treatments T_1 to T_4 without any internal differences between them. T_5 (Z_6 F_1) recorded the moderate increase in this respect, meanwhile the lowest significant leaf area was measured for T_6 (Z_8 F_0). It can also be detected from (Fig.2) that, the gradual increase of zeolite caused significant decrease in the chlorophyll content of leaves from T_1 to T_6 with the lowest value for T_6 i.e. a deficiency in nitrogen.

It is worth mentioning that, the strong reduction of fertilizer (~80%) from T_1 (Z_0 F_5) to T_5 (Z_6 F_1) should be reflected in high deficiency in the leaves chlorophyll levels (N content), however our samples showed only a slight decrease of 10.5% in the leaf chlorophyll content.

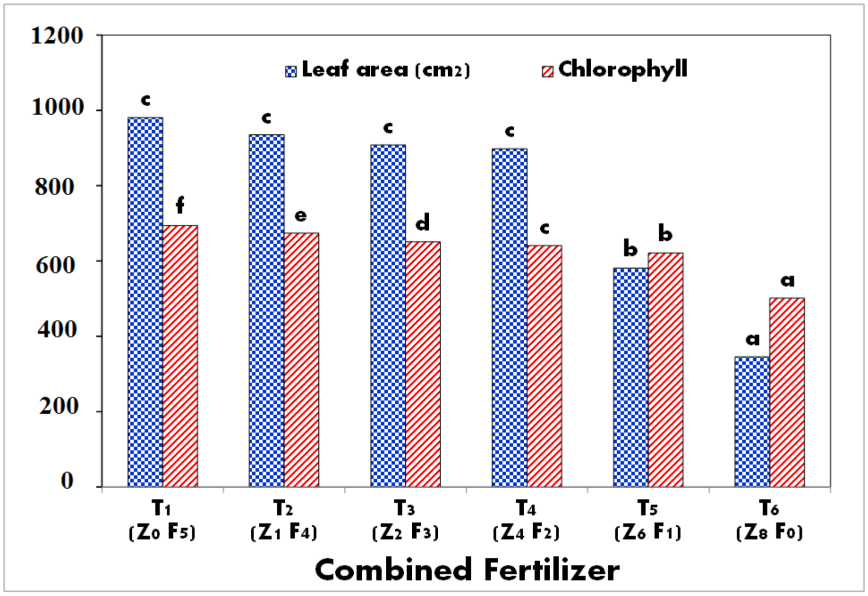

Fig. 2: Effect of applying combined **Z/ F** on leaf area (cm^2) and chlorophyll content

Taking into consideration that, the starting soil is very poor in all nutrients and the addition of NPK mineral fertilizer was the main source for nitrogen (N) in all samples. Although, there was up ward increase in zeolite amounts in samples T_1 to T_6, there was also clear decrease in the N amounts in the same trend. Since the chlorophyll content is approximately proportional to leaf nitrogen (Evans, 1983), the decrease in N content might cause chlorophyll and leaf areas reduction, especially for T6 in which no NPK was added.

4.1.3. Fresh and Dry Weights (g / Plant

Figure 3 presented the shoot and root fresh (Fig.3a) and dry weights (Fig.3b) of the papaya on using different Z/F rates. In Figure 3a, there was an obvious direct relation between the fresh weight and the zeolite addition, the best results obtained with T_4 and T_5, which recorded the highest significant values of plant fresh weight, meanwhile the lowest recorded statistical value was that of T_6 treatment. The previous results ascertained the role played by zeolite in retaining the nutrients in appropriate manner for the plant growth as seen in T_4 and T_5.

Dry weight of plant (D.W) is an important standard for evaluating vigor in all plants. Figure 3b data signed an upward increase in shoot and root dry weights (T_1-T_5) with increasing zeolite content, with the highest recorded value for T_5 and lowest for T_6.

Fertilizers are known by their enhancement action for all plant production and growth aspects, due to the activation of enzymes responsible for the formation of Adenosine Triphosphate (ATP) and regulation of photosynthesis rate. One of the direct benefits is the increase of protein, which enhances the meristematic tissues and leading to better effect on both cell division and elongation (Sönmez *et al*., 2010; Raheleh, 2011 and Hafez-Omaima *et al*., 2012).

Therefore, the increased rates of zeolite over those of the mineral fertilizer was assumed to probably cause deterioration in all growing features resulted in the papaya fresh and dry weighs reduction. In contrast, the replacement of zeolite by appreciable amounts of fertilizer (up to 80% in $\mathbf{T_5}$) promoted better growth of Solo papaya shoots, as expressed by the fresh and dry weights (Fig.3). The present results are in harmony with those of the literature (Ayan and Tillki, 2007; Al-Busaidi *et al*., 2008 and Rabia and Qureshi, 2014). The high retention and leaching prevention of nutrient, caused by zeolite porous structure, could be the suitable explanation for maximizing the fertilizer role (Ayan *et al*., 2006).

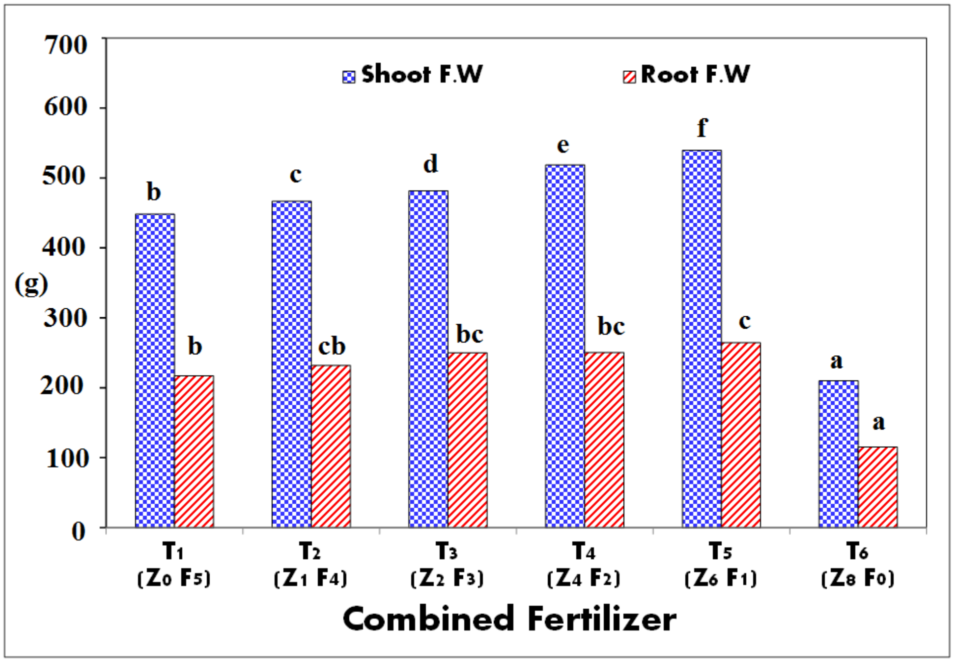

Fig. 3a: Effect of using combined Z/ F on shoot and root fresh weight

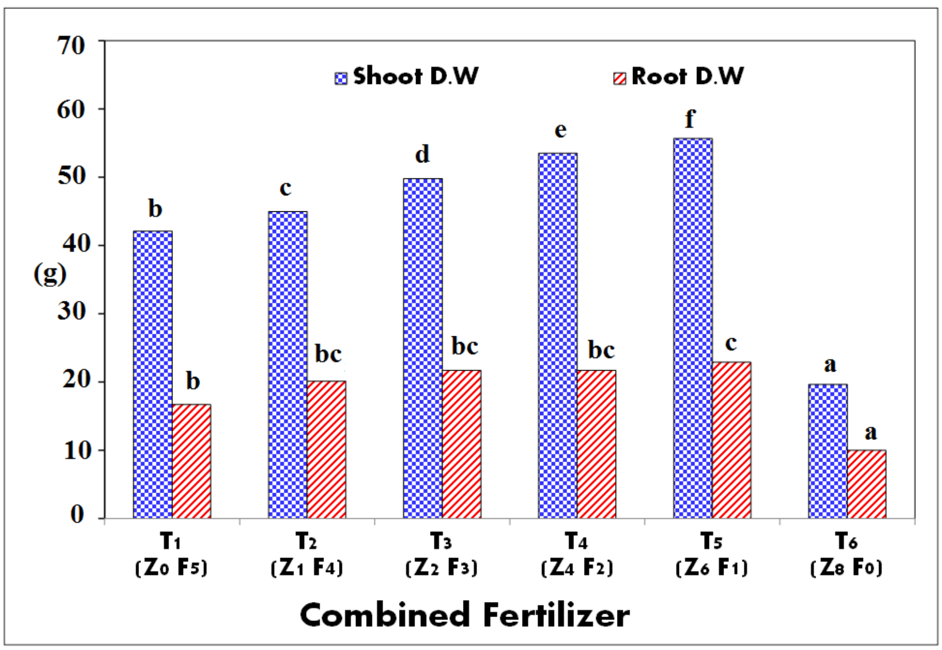

Fig. 3b: Effect of using combined Z/ F on shoot and root dry weight

4.2. Nutrition Status (Uptake)

In the first six months of papaya plantation and due to its fast growth ability, there must be a maximum availability of the applied macronutrient with plentiful amounts of nitrogen (N) and lesser amounts of P and K (Mohamed, 1995). The previous conclusion seemed compatible with the data given in Table (2 a, b &c) where the recorded whole plant-uptake values presented a common increase in the macronutrients in the direction of increasing Z over F. High significant values of (N) were measured in T_4 & T_5 (Z_6F_1); meanwhile comparable amounts of (P) and (K) were contained in T_2 (Z_1F_4).

Table 2a: Effect of applying Z/ F admixtures on macronutrient uptake in papaya shoots

Treatments	Macronutrient Uptake in Shoots (mg/ plant)			
	N	P	K	Mg
T_1 (Z_0F_5)	761	170	859	38
T_2 (Z_1F_4)	831	160	884	54
T_3 (Z_2F_3)	964	145	867	63
T_4 (Z_4F_2)	1036	137	795	70
T_5 (Z_6F_1)	1071	130	767	74
T_6 (Z_8F_0)	313	30	232	19
$LSD_{0.05}$	**27.5**	**14.1**	**90**	**2.43**

Table 2b: Effect of applying Z/ F admixtures on macronutrient uptake in papaya roots

Treatments	Macronutrient Uptake in *Roots* (mg/ plant)			
	N	P	K	Mg
T_1 (Z_0F_5)	428	118	344	20
T_2 (Z_1F_4)	508	137	398	29
T_3 (Z_2F_3)	475	100	399	33
T_4 (Z_4F_2)	472	80	365	33
T_5 (Z_6F_1)	497	71	352	35
T_6 (Z_8F_0)	175	23	112	14
$LSD_{0.05}$	**60**	**9**	**36**	**4**

Although contained the least amount of fertilizer, T_4&T_5 treatments reflected the highest levels of (N), the result that coincide with the elevation of Mg content in the same trend. Since, N and Mg are essential for chlorophyll formation (Evans, 1983), the increased zeolite fraction might cause good retention of both elements that facilitated much control on nutrient leaching and established appropriate conditions for chlorophyll building, as imprinted in the enrichment of the vegetative growth especially for those particular samples (T_4 and T_5). According to (Mohamed, 1995), papaya needs less feed of both P and K for its growth in the first six months, which agreed well with the results of P and k in Table (2).

Table 2c: Effect of applying Z/ F admixtures on macronutrient uptake in whole plant of papaya.

Treatments	Macronutrient Uptake in Whole Plant (mg/plant)			
	N	P	K	Mg
T_1 (Z_0F_5)	1072	271	1137	55
T_2 (Z_1F_4)	1339	297	1282	83
T_3 (Z_2F_3)	1439	245	1266	96
T_4 (Z_4F_2)	1508	218	1159	103
T_5 (Z_6F_1)	1568	201	1119	109
T_6 (Z_8F_0)	488	53	344	34
$LSD_{0.05}$	**66**	**27**	**128**	**3.97**

In general, the micronutrients followed the same trend of macronutrients one and showing negligible differences between treatments. From the previous data, Tables (2&3) cleared that; the addition of zeolite to fertilizer greatly improves the uptake of the whole nutrients (macro& micro), the result which supported by (Mohamed, 1995).

Commonly, different zeolites have been added to fertilizers for cultivating many types of crops (Anonymous, 2004 b) to help in preventing nutrients from leaching and thus improving the long-term soil quality by enhancing its absorption ability. Zeolite structure helped in retaining (N) & (K) in the root zone for the plants needs and offering a more efficient use of the fertilizers at minimum rates for the same yield and prolonging activity. The said effects found ambient to the sandy soil, which suffers from large fertilizer losses due to leaching that turns the soil very poor with low nutrient levels (Flanigen and Mumpton, 1981 and Mumpton, 1981). Therefore, the combined zeolite/fertilizer is probably the best choice in cultivating crops and plants in sandy soil, as the one in this research.

Table 3: Effect of applying combined Z/ F on micronutrient uptake in shoot and root.

Treatments	Micronutrient Uptake (mg/ plant)								
	Fe			Mn			Zn		
	Shoots	Roots	whole plant	Shoots	Roots	whole plant	Shoots	Roots	whole plant
T_1 (Z_0F_5)	6.44	2.39	8.38	3.24	1.38	4.38	4.20	0.90	4.78
T_2 (Z_1F_4)	6.84	2.85	9.70	3.34	1.52	4.87	3.70	1.01	4.72
T_3 (Z_2F_3)	7.21	2.97	10.18	4.00	1.60	5.60	3.95	1.01	4.96
T_4 (Z_4F_2)	7.39	2.89	10.28	4.79	1.43	6.23	3.89	0.98	4.87
T_5 (Z_6F_1)	7.24	3.03	10.27	4.12	1.20	5.31	3.08	0.99	4.07
T_6 (Z_8 F_0)	2.2	1.17	3.37	1.25	0.48	1.73	1.02	0.41	1.44
$LSD_{0.05}$	**0.63**	**0.34**	**0.67**	**0.23**	**0.12**	**0.24**	**0.22**	**0.1**	**0.22**

5. Correlation coefficient

Table 4 showed the relation between the leaves nutrient uptake, the actual nutritional indicator for the whole plant, and quality. Results indicated common positive relations with different strengths between nutrient uptake and the studied characteristics. The very strong significant positive relation was recorded between nutrients uptake and dry weight meanwhile, the strong relation was found between plant length, thickness, and chlorophyll. Some discrepancies (moderate relation) in thickness (Mg, Fe, Mn and Zn) and chlorophyll (N, Mg, Fe and Mn) relations are noted.

Table 4: Correlation coefficients of leaves nutrient uptake with papaya plant quality.

Nutrient uptake of leaves	Correlation coefficients			
	Dry weight	Chlorophyll	Thickness	Length
Nitrogen uptake	0.99122***	0.36808*	0.40083**	0.68591**
Phosphorus uptake	0.88670***	0.53695**	0.44366**	0.47720**
Potassium uptake	0.94179***	0.53819**	0.55044**	0.54002**
Magnesium uptake	0.98176***	0.47382*	0.47756*	0.64991**
Iron uptake	0.99010***	0.39690*	0.39238*	0.62956**
Manganese uptake	0.98275***	0.34002*	0.34643*	0.65733**
Zinc uptake	0.88528***	0.59980**	0.52831*	0.43077**

$r_{0.05}$=0.468 , $_{0.01}$=0.590 , $_{0.001}$=0.708 ,
* = Moderate positive relation, **= Strong positive relation, *** = Very strong positive relation

Generally, the nutrient elements are essential for the plant vitality and growth. Each particular nutrient has mutual relation between its concentration in soil and in plant. This relation serves as a guide to obtain maximum plant growing strength and quality. The obtained results especially for the N, P and K showed very strong positive relation and indicated the high efficiency of zeolite when combined with the mineral fertilizer to retain the ambient and necessary elements and sustainably releasing them to the plant when required. Similar results were published by many authors (Kumar and Chandel, 2004; Dar *et al*., 2012 and Hamouda *et al*., 2015).

6. Conclusion and Recommendation

In conclusion, application of zeolite-A/NPK fertilizer composite on growing papaya plant in sandy soil of semi-arid conditions is proved effective and greatly influenced the plant quality. As fare from the obtained results; enhanced vegetation and growth rates, fresh and dry plant weights, nutrients availability and uptake were recorded on using much less rates of NPK which saved 60 to 80% of the fertilizer costs.

Authors of this work are seriously recommending the establishment of this combined zeolite/fertilizer with the T_4 (Z_4F_2) and T_5 (Z_6F_1) compositions to the agricultural markets. It is of low-cost and simple processing from local resource, environmentally safe, along with its substitution of large part of the expensive NPK fertilizer, and finally with retail of high possibility for long-term sandy soil amendment and development of new-added reclaimed areas.
Supplementary studies are needed to decide whether comparable effects will be found under field conditions and/or for other types of plants and crops.

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