

## Improving Quality of Municipal Solid Waste Compost through Mg-Modified Zeolite

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### ABSTRACT

Developing materials to improve the efficiency of fertilizers and increase their performance is one of the main areas of research in the agricultural science. To the best of our knowledge, this is the first time that Mg-modified zeolite is used for modification of composting process of urban organic solid waste. Natural zeolite was clinoptilolite with a particle size smaller than 250  $\mu\text{m}$  modified with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  salt. Different ratios (i.e. 5, 10, and 15% , on a weight basis) of natural and/or Mg-modified zeolite were used to modify the Municipal Solid Waste (MSW) compost. Experimental results revealed that the pH of the final compost product with the Mg-modified zeolite was effectively buffered at 7.7. Furthermore, in comparison to the control treatment (without zeolite), the compost with natural and Mg-modified zeolite showed 32.13 and 41.25% reduction in electrical conductivity, respectively. Ammonium retention of the compost containing 15% natural and Mg-modified zeolite was increased by 64.51 and 110.10%, respectively. Metals mobility test of the matured composts also revealed that adding zeolite, especially the Mg-modified zeolite, could decrease the mobility of Cu, Pb, Zn, Fe, Ni, and Mn metals. The most decrease in the mobility of metals was observed in Cu, which was about 44.16 and 47.82%, in the compost with the natural and Mg-modified zeolite, respectively.

**Keywords:** Ammonium retention, Composting, Conductivity reduction, instead of Composting, Metals mobility.

### INTRODUCTION

Composting is a clean and sustainable method to manage and recycle the Municipal Solid Waste (MSW) (Diaz *et al.*, 2011; Lim *et al.*, 2016). Composting increases the capacity of waste recycling, improves the effect of waste disposal on environment, and helps its use in the agriculture land, thereby decreasing the usage of chemical fertilizers (Zhang *et al.*, 2006; Toscano *et al.*, 2013; Lim *et al.*, 2016). It seems that organic farming is growing because of the positive

effects of the compost on physical, biological, and chemical properties of soil (Maftoun and Moshiri, 2008; Watteau and Villemin, 2011). Large amounts of the MSW compost are needed to provide enough Nitrogen (N) and other nutrients for plants. However, salts and heavy metals contained in the MSW composts can be harmful to plants, causing several unfavorable effects in the soil (Hargreaves *et al.*, 2008; Gautam *et al.*, 2010).

Nowadays, agricultural science professionals are working to develop eco-

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friendly materials and methods to improve the performance and efficiency of fertilizers (Behin and Sadeghi, 2016; Gholamhoseini et al., 2013). Natural zeolites are being used due to their high adsorption and ion exchange ability, helping to improve the quality of fertilizers and decrease their environmental effects (Gholamhoseini, et al., 2013; Wang et al., 2014).

Zeolites are microporous crystalline aluminosilicate minerals that consist of three-dimensional frameworks of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra (Costa et al., 2012). Voids and pores are the main characteristics of zeolite materials. The interconnected voids and pores are engaged by water molecules and cations. The internal surface area of these channels are informed to reach as much as several hundred square meters per gram of zeolite, causing zeolites as very effective ion exchangers (Ramesh and Reddy, 2011). Zeolites are commonly used as commercial adsorbents in a wide range of environmental processes (Zorpas and Inglezakis, 2009; Kazemian et al., 2012).

Many types of research have shown that the quality of MSW composting and sewage sludge can be improved by adding zeolite (Turan and Ergun, 2007; Stylianou et al., 2008). Zeolites have also been used to adsorb heavy metals, and ammonia ( $\text{NH}_3\text{-N}$ ) from compost (Chiang et al., 2007; Turan and Ergun, 2007; Turan, 2008; Villasenor et al., 2011). Zorpas (2011) showed that 70% of Cd, 67% of Cr and Mn, 46% of Zn, 43% of Ni, 41% of Pb, 37% of Fe and 27% of Cu were taken up from clinoptilolite. Turan (2008) demonstrated that by enhancing the amount of natural zeolite from 5 to 10%, the salinity uptake efficiencies increased from 66.64 to 88.92%, respectively. The losses of  $\text{NH}_3\text{-N}$  must be controlled during composting to enhance the agronomic value of the compost and reduce atmospheric pollution (Villasenor et al., 2011). Turan and Ergun (2007) showed that the natural zeolite readily trapped excess N during the processes and reduced  $\text{NH}_3\text{-N}$  odors. The adsorbed ammonium ( $\text{NH}_4\text{-N}$ ) by zeolite and its reuse in slow release fertilizers have been reported in different studies

(Gholamhoseini et al., 2013; Wang et al., 2014; Chan et al., 2016). Using 21% zeolite during the composting of manure increased the  $\text{NH}_4\text{-N}$  from 0.08 to 0.21% (Gholamhoseini et al., 2013). During the composting process, 22 and 38% N was lost in zeolite applied row and row without zeolite, respectively (Jaghan et al., 2010).

In many applications, different modification processes have been carried out to improve the sorption capacity of the natural zeolite. The conventional modification/regeneration methods often include treatments with acid and salts of alkaline metals (Watanabe et al., 2005; Huang et al., 2014). Furthermore, a Magnesium (Mg) modified zeolite triggers two reaction mechanisms simultaneously. These include adsorption and struvite crystallization. The Mg-modified zeolite can adsorb  $\text{NH}_4\text{-N}$  and release  $\text{Mg}^{2+}$ , which is a source of struvite precipitant employed in the sorption of  $\text{NH}_4\text{-N}$  and phosphates. Adsorption of  $\text{NH}_4\text{-N}$  and phosphate from wastewater using the Mg-modified zeolite has shown higher efficiency, as compared to the natural zeolite (Huang et al., 2014). Chan et al. (2016) showed that adding Mg and P salts increased  $\text{NH}_4\text{-N}$  retention, pH, and salinity effectively. A compost modified with 10% zeolite showed the effective reduction of EC from 6.45 to 2.82  $\text{mS cm}^{-1}$ .

Retention of  $\text{NH}_4\text{-N}$  in compost is important because of the nutritional value. To the best of our knowledge, the effect of Mg-modified zeolite on improving the compost properties is not studied thoroughly. Therefore, the main objective of this study was to investigate the effects of natural and Mg-modified zeolite on the quality of the MSW compost.

## MATERIALS AND METHODS

### Materials Preparation

This study was performed at the Isfahan Compost Factory, Isfahan, Iran ( $51^{\circ}43'\text{E}$ ,

32°39'N). This plant receives 1,200 tons d<sup>-1</sup> of solid waste gathered from the Isfahan City and its surrounding areas. The organic waste constitutes about 70% of the solid waste. To prepare the feed material for composting process, the following process was followed: First, a crusher hammer was used to reduce physical size of the solid waste. As the next step, non-compostable material was separated from MSW by a vibration process. Third, during the movement of waste from conveyor, ferrous metals was separated using a strong magnet. Then, during the course of moving solid waste in rotary hull, plastic impurities were separated. Finally, the organic waste was fed into the decomposition site. In this research, the raw material in the decomposition site was used as feed for composting process. Particle size of materials was prepared to be smaller than 60 mm. The organic wastes were mixed with the zeolites at different ratios and the composting process was performed. Natural and Mg-modified zeolite were used for the modification of the compost.

### Natural and Modified Zeolite

Natural zeolite was clinoptilolite obtained from Semnan Province, Iran. Zeolite with a particle size smaller than 250 μm was chosen using ASTM standard sieves. The

natural zeolite had the following chemical compositions (mass%): SiO<sub>2</sub>= 65.90, Al<sub>2</sub>O<sub>3</sub>= 11.20, Na<sub>2</sub>O= 2.10, K<sub>2</sub>O= 2.31, CaO= 3.20, Fe<sub>2</sub>O<sub>3</sub>= 1.25, MgO= 0.52, LOI= 11.89, and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>= 5.9 (Malekian *et al.*, 2011).

Zeolite was modified by MgCl<sub>2</sub>.6H<sub>2</sub>O salt. Prior to the modification process, the natural zeolite was washed with distilled water to remove soluble impurities and dried at the ambient conditions for 36 hours. Subsequently, 15 kg dried zeolite was suspended in 150 L of a 2M (MgCl<sub>2</sub>.6H<sub>2</sub>O) solution decanted and stirred for five minutes every 30 min during 48 hours. Finally, the modified zeolite sample was dried at the ambient temperature. The X-Ray diffraction technique (XRD) was used to analyze modified zeolite. Some close resemblance was observed between the diffraction patterns of the natural and Mg-modified zeolite, suggesting that the structural integrity of zeolite remained intact after modification (Figure 1). The XRD pattern showed that the sample of natural and Mg-modified zeolite mainly consisted of clinoptilolite with an ideal formula of KNa<sub>2</sub>Ca<sub>2</sub>(Si<sub>129</sub>Al<sub>17</sub>)O<sub>72</sub>.24H<sub>2</sub>O and some quartz (Figure 1). The cation exchange capacity (CEC) of natural and Mg-modified zeolite were measured using ammonium acetate method (Page *et al.*, 1982). Concentrations of some typical alkaline and alkaline earth cations of the natural and

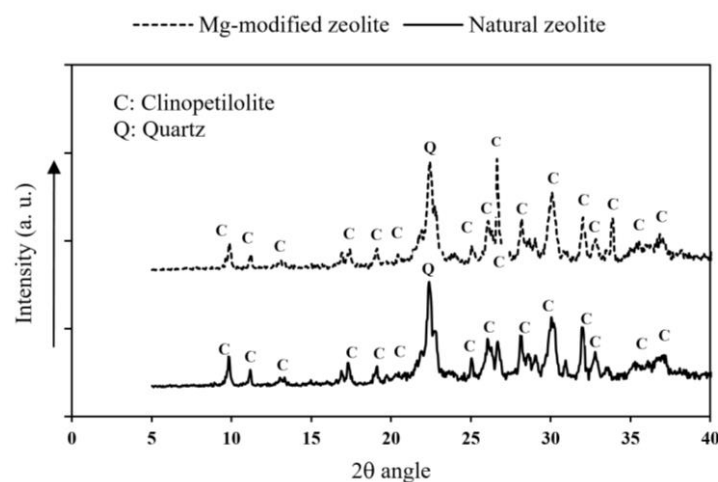


Figure 1. XRD patterns of the natural and modified zeolites.

modified zeolite were extracted by an ammonium acetate solution (Huang *et al.*, 2014) and measured by the atomic adsorption Spectrometry (AA 3030 Perkins Elmer), as reported in Table 1.

### Composting Setup and Operation

Twenty-one lysimeters made of PVC with 40 cm inner diameter and 60 cm height were used. A randomized complete block design was employed with seven treatments and three replications. Different dosages of 5, 10, and 15% of the natural and Mg-modified zeolite were added to the MSW at the beginning of the composting process. The composts were mixed manually, once every other days, throughout the composting period. Treatments were labeled as follows: F1 presents the compost without zeolite. F2, F3 and F4 are the composts treated with 5, 10, and 15% natural zeolite, respectively; F5, F6 and F7 are the composts treated with 5, 10, and 15% Mg-modified zeolite, respectively.

The composting process was carried out for two months. The temperature inside the lysimeters was recorded every 4 days by a Testothermometer. Representative 150 g compost samples were taken every other two weeks to measure the moisture content, electrical conductivity, pH, total N,  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$ . Samples were taken from three different parts of lysimeter and mixed together. Moisture content, pH and electrical conductivity were immediately measured in the wet samples. The moisture content was determined by drying at  $105^\circ\text{C}$  for 24 hours. During the composting period, the moisture

of the composting lysimeters was measured every 2 days and kept at 40 to 60% by adding distilled water whenever needed. The pH and EC were measured by a digital pH-meter and a conductometer (AZ-8301 Cond), respectively, in a 1:10 water extract (Thompson *et al.*, 2002). A 2-molar KCl solution was used to extract the N content of the samples.  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  contents were determined using the steam distillation Kjeltex (Gerhardt-Germany) apparatus and spectrophotometer (Perkin Elmer 550S-Germany), respectively. The Total Nitrogen (TN) was also measured using Kjeldahl method (Vandenabeele *et al.*, 1990). Carbon, germination index and mobility of the heavy metals were measured at the end of the period. The total C was measured by the Walkley-Black method after drying samples at  $105^\circ\text{C}$  (Nelson and Sommers, 1996). The metals mobility of the matured compost was measured by extracting with diethylene-Triamine-Pentaacetic Acid (DTPA) solution. The concentration of heavy metals was measured by the Atomic Adsorption Spectrometry (AA 3030 Perkins Elmer). The Germination Index (GI) was determined using the relative seed germination and the relative root elongation of garden cress. Seed germination and root length tests were done on water extracts by mechanically shaking the fresh samples at a solid to distilled water ratio of 1:10 (w/v dry weight basis) for one hour. Later, 0.5 mL of each extract was pipetted into a sterilized plastic petri dish lined with Whatman filter paper. Ten cress seeds were evenly distributed on the filter paper and incubated at  $25^\circ\text{C}$  in the dark for 48 hours. Treatments were assessed by measuring the length of the root radical

**Table 1.** The extractable cation concentration in the natural and modified zeolite.<sup>a</sup>

| Cations | Natural zeolite (meq L <sup>-1</sup> ) | Modified zeolite (meq L <sup>-1</sup> ) |
|---------|--|---|
| Mg      | 0.7±0.05                               | 11.7±0.72                               |
| Ca      | 2.9±0.12                               | 1.8±0.05                                |
| Na      | 12.2±0.46                              | 2.7±0.15                                |
| K       | 0.3±0.03                               | 0.1±0.01                                |

<sup>a</sup> Results are mean±SD of three determinations.

and counting the number of germinated seeds. The GI was determined by the following formula (Wong *et al.*, 2001).

$$GI (\%) = \frac{\text{Seed germination (\%)} \times \text{Root length of treatment}}{\text{Seed germination (\%)} \times \text{Root length of control}} \times 100$$

### Statistical Analyses

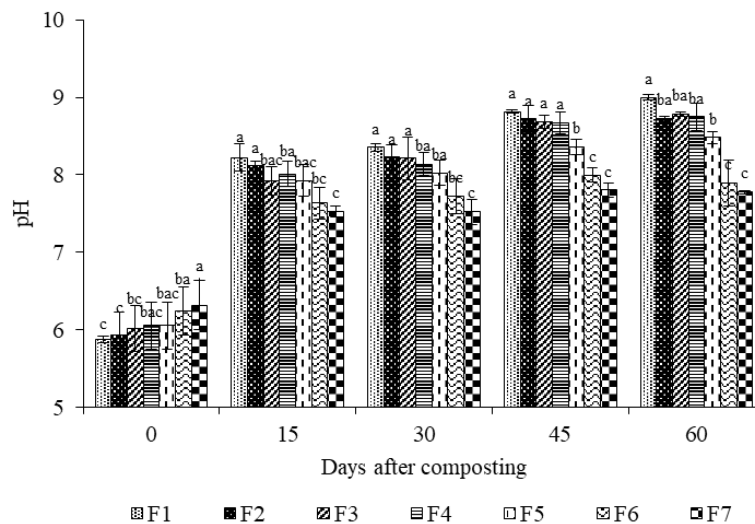
One-way Analysis Of Variance (ANOVA) was employed to test the significance at 1% level (LSD) by the SAS software (2002).

## RESULTS AND DISCUSSION

### Change in the pH Profile

Variation of pH during the composting process is illustrated in Figure 2. The pH value of MSW was 5.88 before composting. The pH value was increased, reaching a value close to 8 at the end of composting for all treatments, except F6 and F7 (Figure 2). Jumnoodo and Mohee (2012) suggested that the optimal pH during the composting process was between 7.0 and 8.0, because pH in that range facilitated higher microbial activities. According to the analysis of

variance, the type of zeolite (natural and modified) and percentage of zeolite in the applied compost were significant factors ( $P < 0.01$ ) (Table 2). Increasing the zeolite dosage and using the modified zeolite helped the normalization of pH. The results also showed that the maximum and minimum pH of the matured compost was recorded for F1 (control) and F7 (15% Mg-modified zeolite) treatments, respectively (Figure 2.). Zeolite could decrease the pH of the compost product because of retaining  $\text{NH}_3\text{-N}$  as a result of cation adsorption and ion exchange ability (Chiang *et al.*, 2007; Stylianou *et al.*, 2008; Turan, 2008). In this research, pH was reduced using Mg-modified zeolite, while Chan *et al.* (2016) did not observe any significant change in pH by using MgO,  $\text{K}_2\text{HPO}_4$  salts and zeolite. This could be attributed to the fact that the buffer capacity of the phosphate salt is higher than that of chlorides (i.e. HCl is stronger than  $\text{H}_3\text{PO}_4$ ).  $\text{NH}_3\text{-N}$  volatilization is dramatically increased once the pH is raised above 8.0, causing N losses and odor problems (Raphael and Velmouroungane, 2011). The result showed that Mg-modified zeolite was more effective than natural forms for reduction of pH. It seems that due to higher absorption of  $\text{NH}_4\text{-N}$  in compost



**Figure 2.** Changes in the pH of different treatments. Different letters in each composting time indicate significant differences between the values ( $P < 0.01$ ) by LSD test. Results are mean  $\pm$  SD (error bars) of three determinations. F symbols are defined under Table 3 and in the text.



**Table 2.** Mean comparison of the type and percent of zeolite at the end of the composting process.<sup>a</sup>

| Factors               |          | pH                | EC<br>(mS cm <sup>-1</sup> ) | NH <sub>4</sub> -N (mg<br>kg <sup>-1</sup> ) | NO <sub>3</sub> -N<br>(mg kg <sup>-1</sup> ) | Total<br>nitrogen<br>(%) |
|-----------------------|----------|-------------------|------------------------------|--|--|--------------------------|
| Type of<br>zeolite    | Natural  | 8.75 <sup>a</sup> | 3.45 <sup>a</sup>            | 507.50 <sup>b</sup>                          | 162.78 <sup>a</sup>                          | 1.59 <sup>a</sup>        |
|                       | Modified | 8.05 <sup>b</sup> | 2.99 <sup>b</sup>            | 631.94 <sup>a</sup>                          | 154.29 <sup>a</sup>                          | 1.57 <sup>a</sup>        |
| Percent of<br>zeolite | 5%       | 8.60 <sup>a</sup> | 3.70 <sup>a</sup>            | 446.25 <sup>b</sup>                          | 172.03 <sup>a</sup>                          | 1.65 <sup>a</sup>        |
|                       | 10%      | 8.33 <sup>b</sup> | 3.15 <sup>b</sup>            | 586.25 <sup>ba</sup>                         | 156.92 <sup>ba</sup>                         | 1.58 <sup>ba</sup>       |
|                       | 15%      | 8.26 <sup>b</sup> | 2.82 <sup>c</sup>            | 676.66 <sup>a</sup>                          | 146.66 <sup>b</sup>                          | 1.53 <sup>b</sup>        |

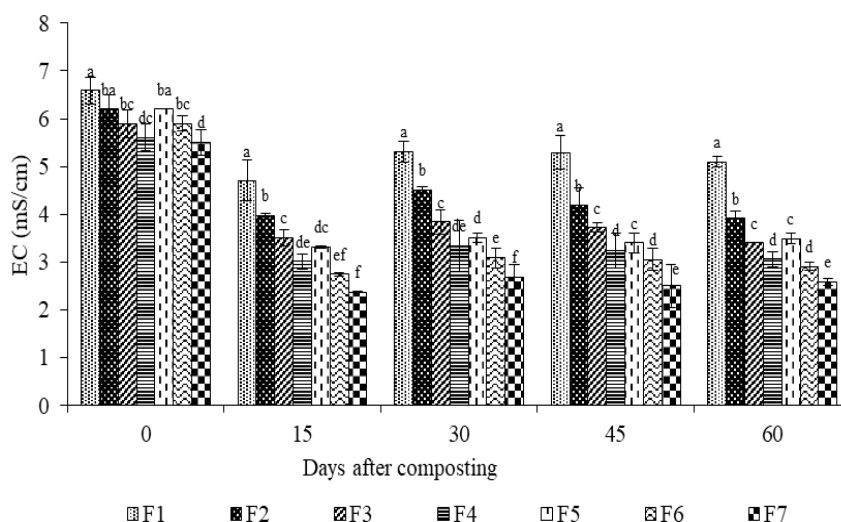
<sup>a</sup> In each column, data with the same alphabet are not significantly different ( $P < 0.01$ ).

containing Mg-modified zeolite (see section “Changes in NH<sub>4</sub>-N”), less amount of NH<sub>3</sub>-N was produced, so the pH was decreased more.

### Change in Electrical Conductivity (EC)

As shown in Figure 3, the EC value was reduced with time in the composting process for all treatments. At the beginning of the composting, the EC value of MSW was 6.59 mS cm<sup>-1</sup>. During the initial phase of composting, EC was reduced. After this stage, there was a small change in EC. The acceptable level of EC for the mature compost is 4 mS cm<sup>-1</sup> (Karak *et al.*, 2013). The final EC values in all composts, except the control

treatment (5.1 mS cm<sup>-1</sup>), were in an acceptable range for agricultural use (Figure 3). According to the experimental results, the type (natural and modified) and percentage of zeolite in the applied compost could have a significant effect on the EC of the compost ( $P < 0.01$ ) (Table 2). As shown in Table 2, the average of EC values in the composts with natural and modified zeolite, at the end of the composting process, was 3.45 and 2.99 mS cm<sup>-1</sup>, respectively. The maximum and minimum EC of the matured compost was observed for F1 (i.e. control) and F7 (i.e. 15% Mg-modified) treatments, respectively (Figure 3). Increasing the zeolite dosage and using the modified zeolite significantly reduced the EC of the compost. Other studies have reported the same results for the natural zeolite (Chiang



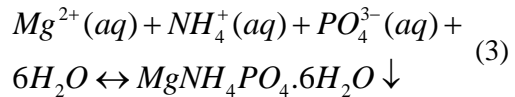
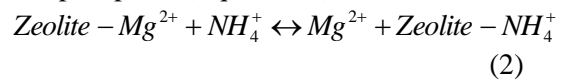
**Figure 3.** Changes of EC in different treatments during the composting process. Different letters in each composting time indicate significant differences between the values ( $P < 0.01$ ) by *LSD* test. Results are mean  $\pm$  *SD* (error bars) of three determinations.

et al., 2007; Turan and Ergun, 2007; Stylianou et al., 2008; Turan, 2008; Zhang and Sun, 2015; Chan et al., 2016). The natural zeolite can have negative charges balanced by freely moving cations with the positive charges. This provides an ideal trap for positive cations like potassium or NH<sub>4</sub>-N, which are released when required by plants. Zeolites porous structure leads to a large specific surface helping to trap and exchange valuable nutrients. The natural zeolite adsorbs Na<sup>+</sup> and Cl<sup>-</sup> that enter the cavities, consequently, reducing the salinity of composts (Turan, 2008). Zeolite not only exchanges cations, but also adsorbs ions; thus, the EC of the compost is reduced. The decomposition process may either lead to organic forms that are neutral (not charged as ions), or gaseous products which escape the mixture (Stylianou et al., 2008). Slightly higher CEC of Mg-modified zeolite (141.3 meq 100 gr<sup>-1</sup>) compared to natural zeolite (130.5 meq 100 gr<sup>-1</sup>) can be attributed to the fact that modification process will facilitate access to some of zeolites cationic sites that are otherwise inaccessible, therefore, more cations will be exchanged.

Changes in NH<sub>4</sub>-N

The results indicated that the amount and

type of zeolite (i.e. natural and modified) had significant effects on retaining NH<sub>4</sub>-N in the compost (P< 0.01) (Table 2). Both natural and modified zeolites retained more NH<sub>4</sub>-N in comparison to F1 (control treatment), while the modified zeolite was more effective (Figure 4). Many researchers have reported that the retention of NH<sub>4</sub>-N and NH<sub>3</sub>-N by clinoptilolite could be due to ion exchange and adsorption processes, respectively (Villasenor et al., 2011; Gholamhoseini et al., 2013). Huang et al. (2014) used the Mg-modified zeolite for the retention of NH<sub>4</sub>-N in a wastewater treatment process. The higher retention involves two reaction mechanisms: ion exchange and struvite crystallization (Huang et al., 2014) (see equations 2 and 3). Struvite is a phosphate mineral with the formula: NH<sub>4</sub>MgPO<sub>4</sub>·6H<sub>2</sub>O. The Mg-modified zeolite can adsorb NH<sub>4</sub>-N and release Mg<sup>2+</sup> (Equation 2). The released Mg<sup>2+</sup> is a source of struvite formation to retain more NH<sub>4</sub>-N and phosphate (Equation 3).



Chan (2016) showed that Struvite formation, through the addition of MgO and

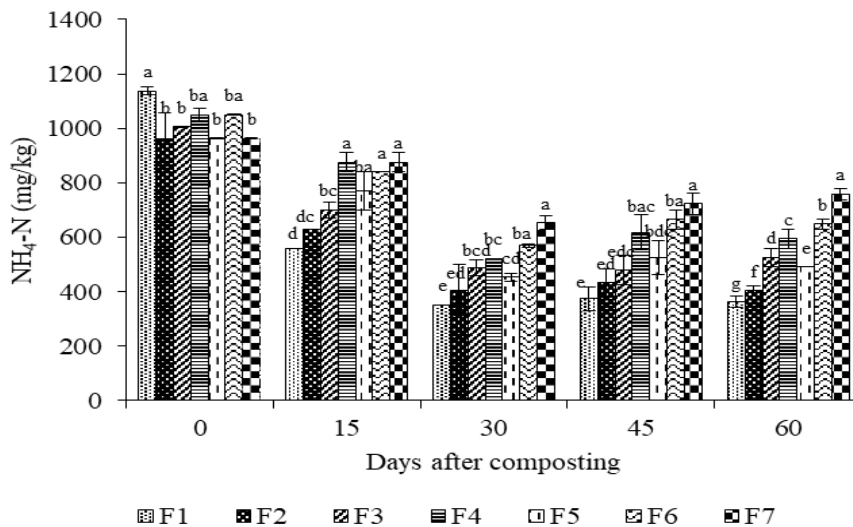


Figure 4. Changes of NH<sub>4</sub><sup>+</sup>-N in different treatments during the composting process. Different letters in each composting time indicate significant differences between the values (P< 0.01) by LSD test. Results are mean±SD (error bars) of three determinations.

$K_2HPO_4$  during composting, significantly conserved  $NH_4-N$ . In this study, it was found that changes in the compost pH increased the  $NH_4-N$  retention in the case of Mg-modified zeolite as compared to the natural and control treatments. Previous studies showed the optimum pH of 7 (Maranon *et al.*, 2006), 8 (Saltali *et al.*, 2007), and 8.5 (Huang *et al.*, 2014) for the adsorption of  $NH_4-N$  by zeolites. Huang *et al.* (2014) reported that at  $pH > 8.5$  more  $NH_4-N$  was converted into  $NH_3-N$  forms, which could not be adsorbed by zeolite, resulting in the decline of the retention ratio of the TN. The results also revealed that the  $NH_4-N$  level was stabilized at the end of the composting process. The control treatment had a lower  $NH_4-N$  content than the other treatments (Figure 4), according to the procedure reported before (Villasenor *et al.*, 2011).

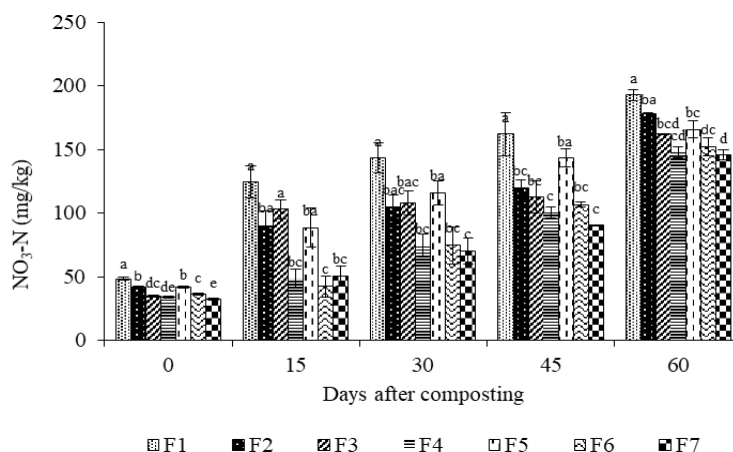
### Changes in $NO_3-N$

The amount of  $NO_3-N$  was increased during the composting process (Figure 5). Ko (2008) showed that  $NH_4-N$  concentrations decreased during the composting process, while  $NO_3-N$  concentrations increased sharply after 30 days. Our results indicated that the amount of zeolite had a significant effect on the amount of compost  $NO_3-N$  ( $P < 0.01$ ). More zeolite dosage caused more

reduction in  $NO_3-N$  production (Table 2). These results were consistent with the previous studies (Gholamhoseini *et al.*, 2013). A possible explanation could be that zeolite prevented nitrification and conversion of  $NH_4-N$  to  $NO_3-N$  (Taheri-Sodejani *et al.*, 2015). Minimum and maximum  $NO_3-N$  levels at the end of process were observed in F7 and the control, respectively (Figure 5).

### Changes in Total Nitrogen (TN), Total Weight of Compost, and C/N Ratio

TN contents during the composting process are shown in Figure 6. The results showed that the most reduction in the TN content occurred in the control treatment. Increasing the zeolite dosage caused less reduction in the TN content of the final compost. It has been reported that  $NH_3-N$  content causes reduction in the N content and some undesirable odor that could be increased during the composting process due to the anaerobic conditions at the higher pH levels (Turan and Ergun, 2007; Wang *et al.*, 2014). Turan and Ergun (2007) and Turan (2008), used 5 and 10% of zeolite, achieving the TN losses reduction of 11 and 9%, respectively. The compost quality with respect to the agricultural use depends on its inorganic N content, which should not exceed 10% of the TN (Zorpas *et al.*, 1999; Zorpas *et al.*,



**Figure 5.** Changes of  $NO_3-N$  in different treatments during the composting process. Different letters in each composting time indicate significant differences between the values ( $P < 0.01$ ) by *LSD* test. Results are mean  $\pm$  *SD* (error bars) of three determinations.



2003). In this research, the total inorganic N did not exceed the limit, showing that the zeolite-modified compost produced in this research had an appropriate quality for agricultural use.

The total weight of the produced compost and N in different treatments is summarized in Table 3. The differences between treatments were significant at the 1% level. The highest amounts of compost and N were obtained in F4 and F7 treatments. Increasing the zeolite dosage enhanced the amount of the compost and the total N retained in the compost (Table 4). Retention of N in the compost is important for plants because of its nutritional value.

The carbon (C) content in different treatments is shown in Table 3. The ideal mature compost should have a total C content of 8 to 35% (Turan and Ergun, 2007). Therefore, the total C contents of the matured

composts can be in the acceptable range. Increasing the zeolite dosage in the composting process caused the reduction in the C content due to the bulking effect (Table 4). The C/N ratio representing the compost maturity was decreased in all zeolite treatments. The C/N range of 9 to 10 could be considered suitable in the mature compost (Bernai *et al.*, 1998; Zorpas *et al.*, 1999). With increasing the rate of zeolite, C/N got close to the acceptable range.

### Germination Index (GI)

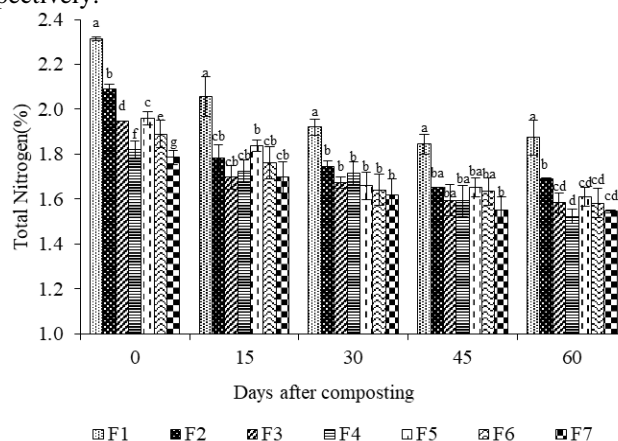
The *GI* for the zeolite treatments was higher, as compared to the control treatment. This index was 100 for the control treatment, while it was 104.32 and 104.94 for the compost with the natural and modified

**Table 3.** Properties of the compost product after 60 days of composting.<sup>a</sup>

| Treatments <sup>b</sup> | Carbon (C) (%)     | C/N                 | Amount compost product (kg) | Total N retained (gr) | Germination Index   |
|-------------------------|--------------------|---------------------|-----------------------------|-----------------------|---------------------|
| F1                      | 24.60 <sup>a</sup> | 13.14 <sup>a</sup>  | 3.41 <sup>f</sup>           | 63.88 <sup>f</sup>    | 100.00 <sup>a</sup> |
| F2                      | 21.55 <sup>b</sup> | 12.74 <sup>a</sup>  | 4.20 <sup>e</sup>           | 71.16 <sup>fe</sup>   | 105.55 <sup>a</sup> |
| F3                      | 17.81 <sup>c</sup> | 11.46 <sup>b</sup>  | 5.34 <sup>dc</sup>          | 84.48 <sup>dc</sup>   | 103.70 <sup>a</sup> |
| F4                      | 16.13 <sup>c</sup> | 10.60 <sup>cb</sup> | 6.32 <sup>b</sup>           | 96.23 <sup>b</sup>    | 103.70 <sup>a</sup> |
| F5                      | 21.05 <sup>b</sup> | 13.08 <sup>a</sup>  | 4.85 <sup>de</sup>          | 74.24 <sup>de</sup>   | 105.55 <sup>a</sup> |
| F6                      | 18.10 <sup>c</sup> | 11.46 <sup>b</sup>  | 5.97 <sup>bc</sup>          | 94.31 <sup>bc</sup>   | 103.70 <sup>a</sup> |
| F7                      | 15.54 <sup>d</sup> | 10.04 <sup>c</sup>  | 6.92 <sup>a</sup>           | 106.90 <sup>a</sup>   | 105.55 <sup>a</sup> |

<sup>a</sup> In each column, data with the same alphabet are not significantly different at  $P < 0.01$ .

<sup>b</sup> F1: Presents the compost without zeolite, and F2, F3 and F4 are composts treated with 5, 10, and 15% natural zeolite, respectively; F5, F6 and F7 are composts treated with 5, 10, and 15% Mg-modified zeolite, respectively.



**Figure 6.** Changes of the total N in different treatments during the composting process. Different letters in each composting time indicate significant differences between the values ( $P < 0.01$ ) by *LSD* test. Results are  $\text{mean} \pm \text{SD}$  (error bars) of three determinations.

zeolite, respectively (Table 3). Adding zeolite improved the *GI*; however, this effect was not statistically significant.

### Evaluation of Mobility of the Heavy Metals in the Composts

The DTPA extractable metal concentration is an index for mobility that predicts the potential plant availability of these elements (Chiang *et al.*, 2007). Metal mobility of the produced composts is shown in Figure 7. The Chromium (Cr) mobility was far below the detection limit (0.1 ppm). Chromium in the compost has a valence of three; thus, it has a stronger affinity for the adsorption sites than the other targeted divalent metals. Accordingly, Cr tends to form stable complexes being adsorbed on the clay surfaces (Chiang *et al.*, 2007). Application of natural zeolite in composting process reduced the DTPA-extractable of Cu, Pb, Mn, Ni, Zn and Fe by 44.16, 13.19, 32.38, 28.36, 22.22, and 37.05% in comparison to the compost without zeolite, while in the modified zeolite treatments the reductions were 47.82, 14.36, 42.61, 35.57, 25.00 and 42.07%, respectively (Figures 7-A, -B, -C, -D, -E and -F). With increasing the zeolite amount, the mobility decreased for all metals. Decreased mobility of heavy metals in compost modified with zeolite can be attributed to selectivity of zeolite toward heavy metals governed by a cation exchange mechanism. Natural zeolite (clinoptilolite) is used for remediating soils contaminated with heavy metals. Because of zeolite's high CEC, it will trap heavy metals resulting in reduced bioavailability of adsorbed

cations (Ansari Mahabadi *et al.*, 2007). The other research reported that clinoptilolite could take up the heavy metals associated with the mobile forms such as the carbonate and the exchangeable fractions due to the high cation exchange capacity and adsorption processes (Stylianou *et al.*, 2008; Zorpas, 2011). DTPA-extractable Pb, Cu, Zn, Mn, Ni and Fe decreased more with using Mg-modified zeolite, while the effect of kind of zeolite was just significant in Mn and Fe. *CEC* values of natural and Mg-modified zeolite were 130.5 and 141.3 meq 100 gr<sup>-1</sup>, respectively. Choi *et al.* (2016) reported that the adsorption capacity of Mg-zeolite for heavy metals was 1.5-folds higher than that of zeolite modified with Na or K due to high *CEC* and greater pore size of Mg-modified zeolite. Using zeolite decreased the mobility of heavy metals, as shown in some previous studies (Chiang *et al.*, 2007; Stylianou *et al.*, 2008, Villasenor *et al.* 2011).

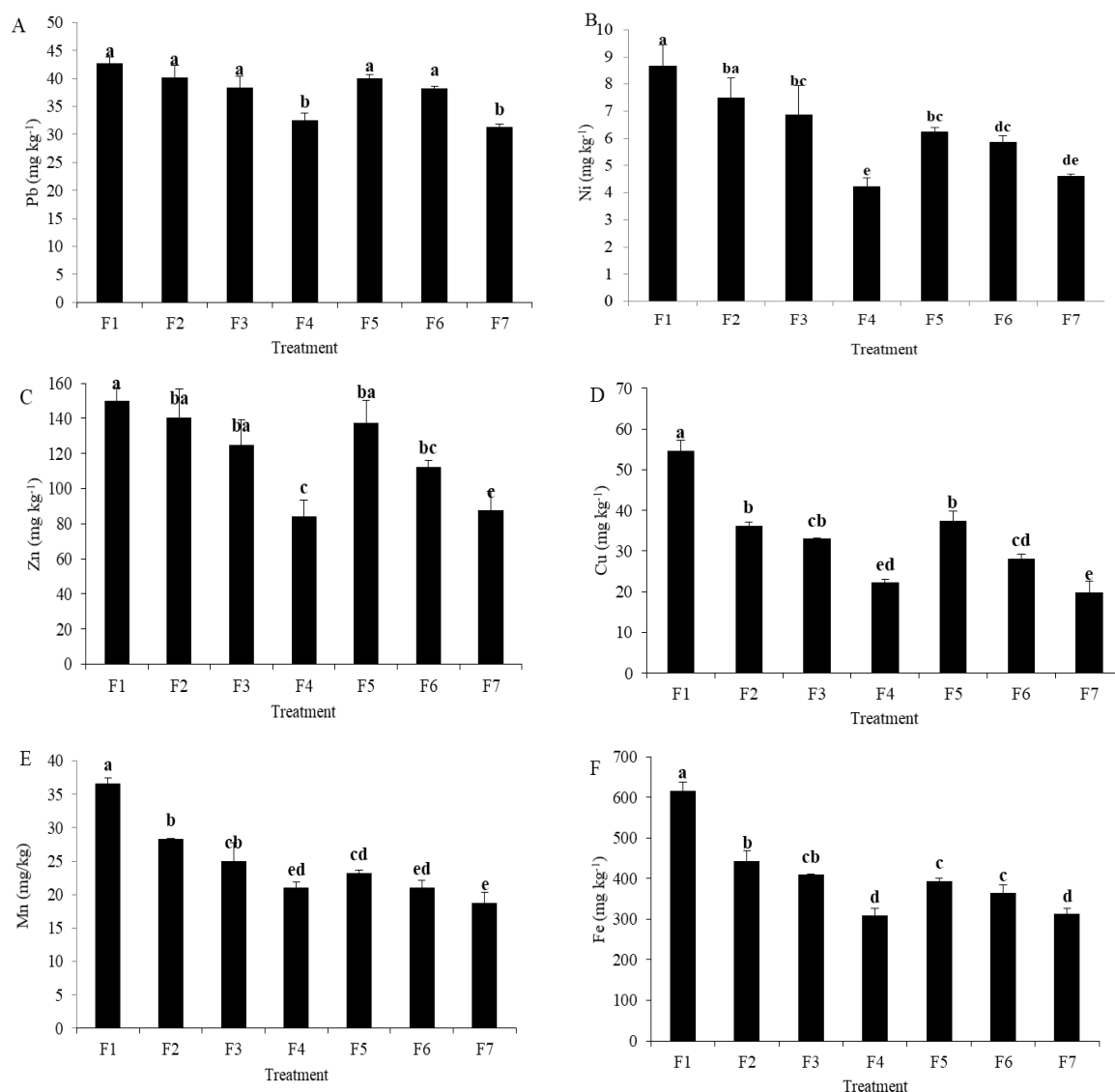
### CONCLUSIONS

This research showed that traditional composting process could be improved using natural and Mg-modified zeolite. According to the experimental results, increasing the zeolite dosage and using the Mg-modified zeolite had a positive effect on the pH normalization process. It was found that using the natural and modified zeolite could decrease the salinity level of the matured compost by 32.13 and 41.25%, respectively. Using 5, 10, and 15% of zeolite decreased the salinity level by 27.33, 38.06, and 44.66%, respectively. It was found that adding natural and Mg-modified zeolite to

**Table 4.** Results of the mean comparison test of the type and percent of the zeolite effect.<sup>a</sup>

| Factors            |                  | The amount of compost produced (Kg) | Total N retained    | Carbon (C) (%)     | C/N                |
|--------------------|------------------|-------------------------------------|---------------------|--------------------|--------------------|
| Type of zeolite    | Natural zeolite  | 5.29 <sup>b</sup>                   | 83.96 <sup>b</sup>  | 18.5 <sup>a</sup>  | 11.53 <sup>a</sup> |
|                    | Modified zeolite | 5.92 <sup>a</sup>                   | 93.15 <sup>a</sup>  | 18.2 <sup>a</sup>  | 11.53 <sup>a</sup> |
| Percent of zeolite | 5%               | 4.53 <sup>c</sup>                   | 74.70 <sup>c</sup>  | 21.30 <sup>a</sup> | 12.91 <sup>a</sup> |
|                    | 10%              | 5.65 <sup>b</sup>                   | 89.39 <sup>b</sup>  | 17.95 <sup>b</sup> | 11.36 <sup>b</sup> |
|                    | 15%              | 6.62 <sup>a</sup>                   | 101.56 <sup>a</sup> | 18.84 <sup>c</sup> | 10.33 <sup>c</sup> |

<sup>a</sup> In each column, data with the same alphabet are not significantly different at  $P < 0.01$ .



**Figure 7.** Concentration of the heavy metals of the compost at the end of the composting process (mg kg<sup>-1</sup>). *F* symbols are defined under Table 3 and in the text. [DL: Detection Limit; DL(Pb)= 0.2 ppm; DL(Ni)= 0.1 ppm; DL(Zn)= 0.1 ppm; DL(Cu)= 0.2 ppm; DL(Mn)= 0.2 ppm; DL(Fe)= 0.15 ppm].

the compost increased NH<sub>4</sub>-N retention by 64.51 and 110.10%, respectively. Adding 5, 10, and 15% of zeolite to the compost increased the retention of NH<sub>4</sub>-N by 23.38, 62.09, and 87.09%, respectively. Experimental results revealed that adding 5 to 10% of zeolite to compost reduced NO<sub>3</sub>-N production by 14.74%, therefore, zeolite could prevent the nitrification process. Furthermore, it was revealed that using zeolite decreased the mobility of Cu, Pb, Mn, Ni, Zn, and Fe in the matured compost.

The most decrease in the mobility of metals was observed in Cu, which was 44.16 and 47.82%, in the compost with natural and modified zeolite, respectively. Considering the experimental data of this study, we suggest to use natural clinoptilolite zeolite and its Mg-modified form to improve composting of MSW. Zeolite-modified compost should be considered as a value-added soil amender with higher content of nutrient that is produced via an environmental friendly process. Further

research considering organic farming practices is needed to investigate the effects of these zeolite modified composts on plants and the environment.

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### بهبود خصوصیات کمپوست زباله شهری با کاربرد زئولیت اصلاح شده با منیزیم

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#### افیونی

#### چکیده

توسعه مواد جدید برای بهبود راندمان استفاده از کودها و افزایش عملکرد آن ها یکی از اهداف اصلی محققان در بخش کشاورزی است. مطالعات انجام شده نشان می دهد که این تحقیق برای اولین بار اثر زئولیت اصلاح شده با منیزیم را بر بهبود خصوصیات کمپوست زباله شهری بررسی می کند. زئولیت طبیعی از نوع کلینوپتیلولیت و با اندازه ذرات کمتر از ۲۵۰ میکرون بود که با استفاده از نمک منیزیم کلرید اصلاح شد. مقادیر مختلفی از زئولیت طبیعی و اصلاح شده (۵، ۱۰ و ۱۵ درصد وزنی) به منظور اصلاح کمپوست مورد استفاده قرار گرفت. نتایج مطالعه نشان داد با کاربرد کمپوست حاوی زئولیت اصلاح شده، pH کمپوست در انتهای دوره به طور موثری تا حدود ۷/۷ کاهش یافت. علاوه بر این، با کاربرد کمپوست حاوی زئولیت طبیعی و اصلاح شده، هدایت الکتریکی به ترتیب ۳۲/۱۳ و ۴۱/۲۵ درصد نسبت به تیمار شاهد (کمپوست بدون زئولیت) کاهش نشان داد. میزان نگهداشت آمونیم با کاربرد کمپوست حاوی ۱۵ درصد وزنی از زئولیت طبیعی و اصلاح شده ۶۴/۵۱ و ۱۱۰/۱۰ درصد افزایش یافت. با کاربرد زئولیت به ویژه زئولیت اصلاح شده تحریک فلزات Cu، Pb، Zn، Fe، Ni و Mn کاهش یافت. بیشترین میزان کاهش تحریک فلزات سنگین در فلز مس مشاهده شد. به گونه ای که با کاربرد کمپوست حاوی زئولیت طبیعی و اصلاح تحریک فلز مس به ترتیب ۴۴/۱۶ و ۴۷/۸۲ درصد نسبت به تیمار شاهد کاهش یافت.