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ZEOLITE AS SLOW RELEASE FERTILIZER ON SPINACH YIELDS AND QUALITY IN A GREENHOUSE TEST

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ZEOLITE AS SLOW RELEASE FERTILIZER ON SPINACH YIELDS AND QUALITY IN A GREENHOUSE TEST

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There has been a great need to reduce the non-point source pollution due to pesticide and fertilizer applications. With a high surface area and large cation exchange capacity, zeolite was proposed to use as carriers to control ammonium and potassium release. A greenhouse test was conducted to evaluate spinach growth and spinach quality after application of zeolite pre-load with ammonium (NH\textsubscript{4}\textsuperscript{+}) and potassium (Eco-zeolite). An increase in spinach yield with comparable vitamin C content was achieved using the Eco-zeolite. However, elevated oxalate content was unexpected, possible due to the presence of NH\textsubscript{4}\textsuperscript{+} as the exchangeable cations after modification.

Keywords: fertilizer, oxalate, spinach, yield, zeolite

INTRODUCTION

Improved nutrient use efficiency in production agriculture is a research priority for both agronomic and environmental reasons. To minimize groundwater contamination caused by nitrate and phosphate during irrigation after application of fertilizers and maximize the efficiency of input fertilizers, slow release fertilizers (SRFs) have drawn great attention recently. Current additives to SRFs include natural occurring minerals that have high cation exchange capacity as well as synthetic cation and anion exchange resins.

Zeolites are a family of crystalline aluminosilicates, while clinoptilolite is a naturally occurring zeolite, formed by devitrification of volcanic ash in...
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Lake and marine waters. Many tests were conducted to evaluate clinoptilolite as additives to SRFs to control the release of ammonium (NH$_4^+$) and potassium (K$^+$). In a greenhouse study, less than 5% of the added nitrogen (N) leached out from the sandy soil when ammonium-loaded clinoptilolite was used in contrast to 10 to 73% of N leaching when ammonium sulfate was applied depending on the N leaching rate (Perrin et al., 1998). More N was assimilated when ammonium-loaded clinoptilolite was used compared to ammonium sulfate. Both cation exchange and occlusion methods were commonly used for preparation of zeolite-based SRFs. A two-fold increase in N loading capacity was achieved using an occlusion method, while the slow release of N was not affected (Park and Komarneni, 1998). Separately, a series of studies were undertaken using zeolite mixed with phosphate rocks to control phosphate release (Barbarick et al., 1990; Allen et al., 1995). In such a system the slightly soluble phosphate rock served as the source for the slow release of P while the ammonium cation-exchanged zeolite as the source for the slow release of N (Allen et al., 1995).

Zeolite could also be modified by surfactant as SRF carriers to control nitrate (Li, 2003), phosphate (Bansiwal et al., 2006) and sulfate (Li and Zhang, 2010) release. A 20-fold reduction in nitrate concentration in the effluent was achieved when nitrate-loaded surfactant-modified zeolite was used in comparison to water soluble nitrate of the same loading (Li, 2003). Phosphorus supplies from phosphate-loaded surfactant-modified zeolite were available even after 1080 h of continuous percolation in contrast to 264 h from monopotassium phosphate (KH$_2$PO$_4$) (Bansiwal et al., 2006).

The above-mentioned studies were focused on SFR preparation and its improvement on water quality and reduction in fertilizer usage. Tests on the influence of using zeolite on plant quality and yield were also conducted. Direct addition of zeolites to soils as soil conditioners resulted in increased germinability of spinach seed relative to controls (Burriesci et al., 1984). Use of zeolite led to increased plant growth, higher N and K contents in plant tissues and reduced K leaching in trials for the growth of Lactuca sativa var. capitata, and the cultivars Bombola and Brogan in autumn and spring seasons (Gül et al., 2005). For tomato growth, the addition of zeolite resulted in an average increase in tomato yield by more than 50% in comparison with the control (Valente et al., 1982). SRFs resulted in a greater root mass development for the growth of Chrysanthemums in comparison to liquid fertilizer with more efficient uptake of fertilizer and 64 to 68% of applied N recovery in plant tissues compared to 41 to 46% from liquid fertilizer treatment (Catanzaro et al., 1998). For the growth of Lolium multifloru, yield increased considerably and nitrogen uptake efficiency was enhanced when clinoptilolite-NH$_4^+$ was used, possibly due to its ability to retain and slowly liberate NH$_4^+$ ions (Millán et al., 2008).
The focus of this study was to evaluate the use of zeolite as SFRs for spinach growth as well as its influence on spinach quality.

**MATERIALS AND METHODS**

**Preparation of Eco-Zeolite**

Zeolite used was from Weifang district, Shandong, China, with a cation exchange capacity (CEC) of 0.35 mol c kg$^{-1}$. The N fertilizers used for zeolite modification were ammonium chloride and monoammonium orthophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) while the K fertilizer was potassium sulfate. The concentrations of N fertilizer solution and K fertilizer solution were both 1 mol L$^{-1}$. Zeolite was added to the N and K fertilizer solution with a liquid to zeolite ratio of 2:1, respectively. The mixture was stirred 5 min for every 1 to 2 hours for a total of 5–6 times. Then the mixture was allowed to settle overnight. After the supernatant removed, the nutrient-laden zeolite was dried naturally and used as Eco-zeolite. The N and K contents in the supernatant were measured and the difference between the initial and equilibrium concentrations was used to calculate the N and K loading on the zeolite. The amounts of Eco-zeolite used were based on the loading of N or K.

**Growth Conditions**

The experiments were conducted in the greenhouse of the Institute of Soil and Fertilizer, Shandong Academy of Agricultural Sciences. The soil used was a brown soil obtained from Weihai, Shandong, China. Its physical and chemical properties are listed in Table 1. Spinach (locally cultivated Duo-neng) was used in the experiments. To each 2-gallon lysimeter 10 spinaches were planted. There were a total of 7 trials: (a) no nutrients (CK); (b) without N and Ca nutrient (N1Ca1); (c) optimum treatment (N2Ca2); (d) conventional fertilizer (N3Ca2); (e) conventional fertilizer + zeolite (N3Ca2+Z); (f) Eco-zeolite loaded with NH$_4^+$ and K$^+$ to 100% CEC and the amount of N and K applied was the same as treatment (d) (Z+N+K); (g) Eco-zeolite loaded with proper NH$_4^+$/K$^+$ for spinach, i.e., half of the amounts of N and K used for treatment (d) (Z+1/2N+1/2K). In the above notations, N1, N2, and N3 refer 0.0, 0.2 and 0.4 g kg$^{-1}$ (N), respectively. N nutrient was urea in conventional fertilizer and ammonium chloride in SRFs. Ca1 and Ca2 refer

<table>
<thead>
<tr>
<th>pH</th>
<th>OM (g kg$^{-1}$)</th>
<th>Total N (g kg$^{-1}$)</th>
<th>Total P (g kg$^{-1}$)</th>
<th>Total K (g kg$^{-1}$)</th>
<th>Alkali-hydro N (mg kg$^{-1}$)</th>
<th>Olsen P (mg kg$^{-1}$)</th>
<th>Avail. K (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.27</td>
<td>12.72</td>
<td>0.96</td>
<td>0.46</td>
<td>30.66</td>
<td>84.64</td>
<td>39.2</td>
<td>81.0</td>
</tr>
</tbody>
</table>
to 0.0 and 0.3 g kg$^{-1}$ of calcium carbonate (CaCO$_3$). P and K nutrients were supplied with 0.15 and 0.2 g kg$^{-1}$. P was used as KH$_2$PO$_4$ and K was supplied with KH$_2$PO$_4$ and potassium sulfate (K$_2$SO$_4$). See Table 2 for detail about the nutrient application rate.

Nitrogen, P, and K fertilizers of treatments b, c, and d were mixed in topsoil of pot soils as the base fertilizer. N, P, K fertilizers and zeolite of treatment e were mixed in topsoil of pot soils as base fertilizer. P fertilizer, Eco-zeolite with N and K of treatments f and g were mixed in topsoil of pot soils as base fertilizer. The spinaches were harvested after two and half months and yield measured. The nitrate, soluble oxalate and total oxalate, and vitamin C contents were determined as the spinach quality parameters. Each trial was tested in three replicates, i.e., 30 spinach plants per treatment. Due to low water evaporation rate, the leachate was not collected.

### Measurements

The total oxalate was determined using a method from Baker (1952) with some modifications (Zhang et al., 2005). Two g of plant sample were grounded in a mortar with 2 mL 6 M hydrochloric acid (HCl). The homogenate was then transferred to a 50 mL centrifugal tube with 30 mL distilled water. Two drops of capryl alcohol were added and the mixture boiled for 15 minutes in water-bath, before being cooled down overnight. The mixture was centrifuged for 10 minutes at 5000 rpm and 20 mL of the supernatant transferred to a new centrifugal tube. Five mL of phosphoric-tungstate reagent was added. The mixture was allowed to set aside for more than 5 hours before it was centrifuged again for 10 minutes at 5000 rpm. The supernatant was transferred to a new centrifugal tube, and ammonium hydroxide was added dropwise from a burette until pH was between 4.5 and 5.0 monitored by a pH meter. A 5 mL of acetic acid buffer solution of pH4.5 (including calcium chloride reagent) was then added. After being stirred with a fine glass rod, the tube was left overnight in a refrigerator at 4–7°C. The mixture was centrifuged for 10 minutes at 5000 rpm, and the supernatant was
removed carefully. The precipitate was washed with 20 mL of washing solution, stirred vigorously with a fine rod until the precipitate was broken up and the impurities were dissolved. The mixture was centrifuged for 10 minutes, the supernatant carefully removed, and the precipitate dissolved with 10 mL of 10% sulfuric acid and transferred to an Erlenmeyer flask. The Erlenmeyer flask was placed in a water-bath at 100°C for two minutes and the oxalic acid was titrated with 0.02 mM potassium permanganate till the pink color stayed for more than 30 seconds. The oxalic acid concentration of spinach was calculated according to the volume of potassium permanganate consumption. The above procedure was followed for the extraction of water soluble oxalate except that 2 mL of distilled water was used instead of 2 mL 6 M HCl.

Nitrate content was measured by a salicylic acid colorimetric method, while vitamin C content was determined by a titration method using 2, 6-Dichlorophenolindophenol sodium salt hydrate (Li, 2000).

The data obtained from this study were statistically analyzed using DPS 2000 (Data processing system) (version 6.05) (Tang and Feng, 2007).

RESULTS AND DISCUSSION

Effects of Different Types of Fertilizers on Spinach Biomass

Different fertilizers had obvious effects on spinach yields (Figure 1). The control had the lowest yield, only 1.24 g plant\(^{-1}\), due to absence of fertilizer application, followed by N1Ca1, in which only K and P fertilizers were applied. Among the other five treatments, the N2Ca2 treatment produced

![Figure 1](image_url)

**FIGURE 1** Effects of different fertilizers on spinach biomass. Different letters above each bar indicate significant difference at P = 0.05 level.
the highest yield, followed by Z+1/2N+1/2K, Z+N+K, and N3Ca2+Z. The conventional fertilizer N3Ca2 had a lower yield compared to those treatments applied with Eco-zeolite. Compared to the conventional fertilizer with the same amount of nutrients applied higher yields could be achieved when Eco-zeolite was used even though, the difference was statistically not significant. In addition, the treatment with Z+1/2N+1/2K had a higher yield than N3Ca2 treatment even though only half of N and K amounts were used. It could be speculated due to improved nutrient utilization efficiency of spinach and reduced fertilizer loss in the presence of zeolite.

Tests on growth of tomatoes showed no improvement of fruit size or marketable yields when SRFs was used in comparison to water soluble ammonium nitrate (NH4NO3)- potassium nitrate (KNO3) control (Csizinszky, 1994). This study showed that use of zeolite as SRFs to increase spinach yield was feasible.

### Effects of Different Treatments on Nutritive Quality of Spinach

Vitamin C (VC) is thought as one of the important nutritive qualities of vegetables. In the test, different treatments had markedly influence on VC content in spinach (Figure 2). The highest VC content was achieved when N2Ca2 was applied, followed by N3Ca2. Statistically the lowest vitamin C levels occurred with the N1Ca1, N3Ca2+Z, and the Z+N+K treatments. Meanwhile, Z+1/2N+1/2K had relative higher VC content.

![FIGURE 2](image-url) Effects of different treatments on vitamin C content of spinach leaves. Different letters above each bar indicate significant difference at \( P = 0.05 \) level.
Effects of Different Treatments on Safe Quality of Spinach

Nitrate and oxalate were two important factors, which can limit safe quality of vegetables and hinder human health (Zhang et al., 2008). The results from this study showed that different treatments had no obvious effects on nitrate content in spinach except for the treatments of CK and N1Ca1, in which N supply was not provided (Figure 3). This could be attributed to the improved nitrogen quantity, which could increase the absorption of nitrate, resulting in less nitrate accumulation in spinach. Calcium can also affect the nitrate content in plants. Ca\(^{2+}\) can inhibit the activity of nitrate reductase to certain degree (Lillo, 1993), which would result in more nitrate absorption than reduction and less nitrate accumulation in spinach. The latter could be the major cause for the lower nitrate content in spinach with CK and N1Ca1 application.

Oxalate was thought as a toxin and anti-nutrient. Oxalate can not only reduce the bio-availability of calcium (Ca), magnesium (Mg), and iron (Fe), but also increase the amount of oxalic acid excreted, thus increasing the probability of stones in kidney and bladder (Franceschi and Nakata, 2005; Lewandowski and Rodgers, 2004). Concentrations of different oxalate in the edible parts of spinach have been of a concern because of their different human health effects.

In the study, different treatments had obvious effects on total oxalate content in spinach (Figure 4). The treatments with Eco-zeolite had higher total oxalate contents than those without zeolite. Soluble oxalate increased as N supply increased from 0 to 0.4 g kg\(^{-1}\) soil (Figure 5). When nitrogen

![FIGURE 3](image-url) Effects of different treatments on nitrate content in spinach. Different letters above each bar indicate significant difference at P = 0.05 level.
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FIGURE 4 Effects of different treatments on total oxalate content of spinach. Different letters above each bar indicate significant difference at \( P = 0.05 \) level.

was supplied at a rate of 0.4 g kg\(^{-1}\), \( Z+K+N \) treatment resulted in the highest soluble oxalate content, followed by \( N3Ca2+Z \) treatment.

The N and Ca content could affect the oxalate contents in spinach. Previous studies showed that higher N content in the culture solution would result in an accumulation of nitrate and oxalate contents (Elia et al., 1998; Ahmed and Johnson, 2000; Zhang et al., 2009). Fertilizers containing N under forms not readily available to the crop, i.e., urea \([\text{CO(NH}_2\text{)}_2]\) and ammonium sulfate \([\text{(NH}_4\text{)}_2\text{SO}_4]\), increased nitrate and oxalate accumulations

FIGURE 5 Effects of different treatments on soluble oxalate content of spinach. Different letters above each bar indicate significant difference at \( P = 0.05 \) level.
less fast than N-release fertilizers (Stagnari et al., 2007). Therefore, increasing the ratio of N in ammonium form to N in nitrate form can effectively decrease the nitrate and oxalate contents in vegetables (Ahmed and Johnson, 2000; Palaniswamy et al., 2004). However, the N in Eco-zeolite was in ammonium form. Thus, these results are unexpected.

An increase in oxalate content was found when N supply increased and Ca supply decreased. The release of ammonium during irrigation is through cation exchange processes. The substitution of Ca for ammonium will reduce the availability of Ca for the plant, which may result in higher oxalate content. On the other hand, it was suggested that the exchange properties of the aluminosilicates did not play an important role in tomato-growing and the beneficial effect was due to other factors such as the presence of iron (Fe) and K (Valente et al., 1982). Although this is not a desired result, irrigation with harder water with high Ca content may overcome this drawback.

CONCLUSIONS

In this study, zeolite used as SRFs can increase spinach yields compared to conventional fertilizer with the same fertilizer amounts used, although the same yield was achieved when both optimum and Eco-zeolite were used. Zeolite with 1/2N+1/2K can reduce the cost of fertilizer and achieve the same vitamin C content of spinach, so zeolite used as SRFs has a good market prospect. Although the results using Eco-zeolite showed no decrease on nitrate and oxalate content in spinach compared to the conventional fertilizers, the process of producing SRFs using zeolite could be modified and the nutrients releasing mechanism would be further studied.

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