



EFFECT OF ZEOLITE, POTASSIUM HUMATE, BIOCHER AND BIOFERTILIZER ON AMMONIA LOSS FROM CALCAREOUS SOIL

[36]

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Keywords: Ammonia loss, Zeolite, Biofertilizer, Urea, Calcareous Soil, Air pollution.

ABSTRACT

Application of urea to agricultural soil may pollute the air environment due to ammonia (NH_3) volatilization. Zeolite, Humate, biocher and biofertilizer may be used to control N losses resulting from urea transformation to NH_3 . A laboratory soil incubation experiment was conducted to determine the effects of zeolite, K-humate, biocher and biofertilizer on controlling NH_3 losses out of applied urea. Calcareous soil sample from El-Nobaria area, Beheira Governorate was treated with different amendments and incubated under laboratory condition for 13 weeks. Results obtained showed that soil treated with urea in the presence of different amendments significantly reduced NH_3 release from urea as compared to the control. During the first 80 days of the incubation ammonia losses were highest in control compared to soil treated with the different amendments. Biocher treatment showed the highest effect in reducing ammonia volatilization from calcareous soil. Therefore, treating calcareous soil with biocher and biofertilizer can decrease urea losses as ammonia and increase nitrogen availability in soil, and hence reduces air pollution by ammonia.

INTRODUCTION

Because of its high N content and low price urea is considered the most widely used Nitrogen fertilizer in agriculture. Depending on soil pH, moisture content, soil temperature and application

method, urea undergoes chemical transformation to produce either NH_4^+ or NO_3^- (He, et al 2002). Miles, et al (2011) reported that maximum NH_3 emission was up to 7 times greater at 40.6°C vs. at 18.3°C. In addition, NH_3 loss is known to be low at pH below 7. Because NH_4^+ is positively charged, it can be held by the negative sites of soils (e.g., clay and humus); therefore, NH_4^+ leaching was less in mineral soils which are particularly high in clay (Brady and Weil, 2010). In contrast, NH_4^+ leaching is significant in coarse-textured sands and some muck soils (Vitosh, et al 1995). Thus, agricultural research can lead to management practices that improve N utilization efficiency and decrease N losses (Powlson et al 2008). Reducing loss of mineral N from agricultural systems is difficult to achieve through reduction of N fertilizers use (Wolf and Snyder, 2003).

Clinoptilolite zeolite is a mineral with a unique structure which allows entrapping or releasing various cations due to its high cation exchange capacity (Kamarudin, et al 2003). Therefore, zeolite can be used to control N loss from urea because of the small molecular size of the open-ringed structure of clinoptilolite zeolite which physically protect NH_4^+ ions against microbial nitrification (Ferguson and Pepper, 1987). Studies have shown that the use of clinoptilolite zeolite and N fertilizers improves N use efficiency (Bouzo, et al 1994 and Ahmed, et al 2009). The increased efficiency of N utilization when urea is used together with clinoptilolite zeolite has been demonstrated by a number of researchers (Rabai, et al 2013). In contrast, unbalanced use of N fertilizers could cause environmental pollution (McGilloway, et al 2003).

(Received 20 June, 2016)

(Revised 29 June, 2016)

(Accepted 3 July, 2016)

To manage the risk of NH_3 loss, several studies have been done to alleviate the problem. Research has shown that one of the ways to enhance plant N use efficiency of urea is to mix with humic acids (Rivera-Cruz, et al 2008). Humic acids are known to have chemical properties such as high total CEC useful in retaining NH_4^+ (Sharma and Kumar, 2008). Humic substances are the most chemically active compounds in soils with cation and anion exchange capacities far exceeding those of clays and having various capabilities beneficial to agricultural soils (Aulakh and Malhi 2005). The major sources of humic substances, in general, can be found in coal as it contains the largest amount of humified substances particularly, humic acid (HA), fulvic acid (FA) and humin. Paramasivam, et al (2001) reported that commercial grade lignite from North Dakota compose substantial amount of HA (99.0%) in contrast to that of FA (1%). Lignite or Leonardite samples were also noted, to compose 99.5% HA and 0.5% of FA (Wolf and Snyder 2003).

Biochar is persistent in soils and its beneficial effects are longer lasting when compared to other forms of organic matter such as manure. Biochar application can increase soil organic carbon levels (McHenry, 2011) and can improve soil structure (Glaser, et al 2002). Its application can improve the soil's ability to retain moisture (Steiner, et al 2010), can prevent nutrient leaching (Spokas, et al 2012) and also increases cation exchange capacity (Clough and Condon, 2010). In addition to biochar improves the biological conditions of soils, increase soil microbial biomass and support beneficial organisms like earthworms (Lehmann, et al 2011).

Biological fertilization is based on the use of natural inputs including fertilizers, decaying of the remains of organic matter, excess crops, domestic sewage, animal manure and microorganisms such as fungi and bacteria (Chirinos, et al 2006). Biofertilization application very important in providing the plants with their nutritional requirements without having an undesirable impact on the environment (Abou El-Yazied and Sellim, 2007). Moreover, biofertilizers are known to improve fixation of nutrients in the rhizosphere, produce growth stimulants for plants, improve soil stability and provide biological control (Rivera-Cruz, et al 2008). In addition, biofertilizers containing azotobacter can

produce many growth regulators such as IAA and GA2 which are positively influence plant growth (Sharma and Kumar, 2008). Hence, this study aimed to investigate the effect of zeolite, K-Humic, biochar and biofertilizer in reducing ammonia volatilization from urea fertilizer applied to calcareous soil. Moreover, to evaluate the effectiveness of biochar as a soil conditioner and fertility enhancer and ascertain its nutrient-supplying capability when applied singly or in combination with biofertilizer. Comparison between the effect of different rates of biochar application on soil health and crop productivity in the sandy soil was also examined.

MATERIALS AND METHODS

In this study, calcareous soil samples were collected from El-Nobar area, Beheira Governorate, Egypt, (30 28 15.85 N latitude and 30 47 7.23" E longitude). Some physical and chemical characteristics of the studied soil samples were determined according to Jackson (1958) and are shown in Table (1).

Zeolite was taken from the El-Ahram Mining Company. There after dried in an oven at $100 \pm 5^\circ\text{C}$ for 24h. The chemical analyses and some characteristics of zeolite are presented in Tables (2 and 3). Potassium humate powder made in China, as well as biochar from bring wood were used in this experiment. Some properties of the biochar and potassium humate are shown in Tables (3 and 4).

Biofertilizer solution was prepared by mixing a combination of natural substances present in the environment such as straw, plant leaves, rice haske beside soil from rhizosphere, and was prepared as follows:

One Kg soil was collected from rhizosphere at a depth of 5cm and mixed with 2 Kg of the rice haske and 1Kg of green leaves. All were mixed in a dish, with a hole in the middle, then the dish was covered, and placed place in a dark for 30 days. After that the mixture was placed in a bag and potted in tank containing 75 liters of water and 15 liters of molass, with stirring for 30 days. Then, the clear solution was analyzed and used as biofertilizer. The chemical composition of the obtained biofertilizer is presented in Table (4). The biological analysis of biofertilizer is shown in Table 5.

Table 1. Some physical and chemical characteristics of the calcareous soil sample

Characteristics	
Particle size distribution (%)	
Sand	96.2
Silt	2.70
Clay	1.10
Texture Class	Sandy
Sp(%)	22.5
CEC (Cmolc.kg ⁻¹)	8.40
EC _e (dS.m ⁻¹)	0.71
pH (1:2.5)	8.26
OM (%)	0.47
CaCO ₃ (%)	18.5
SAR	0.655
Soluble ions (Cmol.kg⁻¹)	
Ca ²⁺	3.53
Mg ²⁺	2.11
Na ⁺	1.10
K ⁺	0.36
Cl ⁻	3.19
HCO ₃ ⁻	2.35
CO ₃ ⁻²	-
SO ₄ ⁻²	1.56
Chemically available nutrients (mg.kg⁻¹)	
N	14.0
P	2.54
K	94.0
Total content of nutrients (%)	
N	0.388
P	0.003
K	0.014

Table 2. Chemical composition of zeolite

	%
SiO ₂	71.0
Al ₂ O ₃	11.8
Fe ₂ O ₃	0.64
CaO	1.35
MgO	1.40
SO ₃	1.74
K ₂ O	0.69
Na ₂ O	0.27
CaCO ₃	1.74
P ₂ O ₅	0.02

Table 3. Some characteristics of zeolite and biocher

Characteristics	Zeolite	Biocher
pH (1:2.5)	7.58	9
EC _e (dS.m ⁻¹ (1:2.5))	0.88	4.75
CEC (Cmolc. kg ⁻¹)	77.85	18.9
Total elements content (%)		
Ca	4.00	-
Mg	-	-
N	0.31	1.25
P	0.29	0.55
K	0.86	1.13
Na	0.34	-
Chemically available nutrients (mg.kg⁻¹)		
N	66.15	84
P	2.33	6.54
K	302	-
Soluble cations and anions (meq. l⁻¹)		
Ca ²⁺	5.00	2.8
Mg ²⁺	0.00	1.8
Na ⁺	2.00	13.5
K ⁺	2.16	22.8
Cl ⁻	1.60	46
HCO ₃ ⁻	2.00	1.6
CO ₃ ⁻²	-	-
SO ₄ ⁻²	5.56	-

Table 4. Some characteristics of potassium humate and biofertilizer

Characteristics	Potassium humate	Biofertilizer
pH	9.17	5.83
ECe (dS.m ⁻¹ (1:10))	5.32	4.51
bulk density (g.cm ⁻³)	ND*	ND
Chemically available nutrients (mg.l⁻¹)		
N	130.6	896.0
P	13.13	2.848
K	1947	4988
Chemical constituent		
Total free amino acids (FAA).	ND*	2.123
VEL	ND	0.790
LYS	ND	1.142
Proline	ND	0.089
Total Phenol.	ND	0.345
Total S. Sugar	ND	0.495
Antioxidant Capacity, (1:5000)	ND	45.00
Total Protein	ND	25.00
Total elements content (%)		
N	1.615	19.00
P	1.082	3.530
K	0.526	2.594
Humic and Fulvic Compounds (%)		
Humic acid	61.70	9.00
Fulvic acid	38.33	91.0

ND* = Not Detected

Table 5. Biological analyses of biofertilizer

Parameters		
Total count Bacteria	CFU/ml 10 ⁶ ×176	<i>Bacillus</i> sp. <i>Micrococcus</i> sp. <i>Streptomyces</i> sp. Short rods
Total count mold & yeast	36 × 10 ⁴ CFU/ml	Yeast <i>Aspergillus</i> sp. <i>Rhizopus</i> sp. <i>Penicillium</i> sp.
Total Coliform group	CFU/ ml 0.0	
Total Fecal <i>E. Coli</i>	0.0 CFU/ ml	
Detection of <i>Salmonella</i> sp.	-	
Detection of <i>Shigella</i> sp.	-	
Detection of <i>B. cerus</i>	-	
Detection of <i>Listeria</i> sp.	-	
Protein analysis	+	
Cellulose analysis	+	
Starch analysis	+	
Fat analysis	+	
Antibiotics	+	

The following treatments were conducted in order to study the effect of different sources of amendments (zeolite, potassium humate, biochar and biofertilizer) mixed with calcareous soil at different incubation periods on the loss of ammonia, the management of the total treatments with three replicates were as follow:

- 1- Control (Soil without any amendments).
- 2- Zeolite (1%).
- 3- Potassium humate (1%)
- 4- Biochar (1%)
- 5- Biofertilizer (1%).
- 6- Treatment 2 + treatment 5
- 7- Treatment 3 + treatment 5
- 8- Treatment 4 + treatment 5

The closed-dynamic air flow system method (Elbordiny, 2004) was used to determine the daily ammonia loss for 104 days of incubation. The system was consisted of an exchange chamber (pot), 24 cm height and 26 cm diameter containing 14 kg air dried calcareous soil and moistened to 70% of water holding capacity. Dose of 10 g/ Kg of urea fertilizer was added on the surface of amended soil samples and thoroughly mixed. Erlenmeyer flask containing 75 ml of boric acid, bromocresol green and methyl red indicator as ammonia trap were used. Both pots and Erlenmeyer flask were stoppered and fitted with an inlet/ outlet. The inlet of the pot was connected to an air pump and the outlet was connected by polyethylene tubing to the ammonia trap. Air was passed through the chambers at a rate of 2.50 L/ min/ pot. This incubation was conducted at room temperature (18[±].5°C) for 104 days. The boric acid indicator traps were replaced every 7 days. The released ammonia was captured in the trapping solution and back-titrated with 0.01 M HCl, until the colour changed from green to purple to measure the ammonia released. The experiment was a completely randomized design with three replicates for each treatment.

RESULTS AND DISCUSSION

Data illustrated in **Table (6)** show the amounts of NH₃ released under different treatments as calculated per Fadden. In general, ammonia volatilization rates were generally increased by increasing incubation time with the different amendments. The total amount of NH₃ lost at the end of the study is shown in **Table (6)**. Soil samples treated with different amendments markedly decreased NH₃ loss compared to the untreated soil. The culmination of zeolite, biochar or biochar with bioferti-

lizer pronounced reduced NH₃ loss as compared to other treatment. Moreover the total NH₃ losses out of soil were effectively reduced by treatments of biochar, biochar with biofertilizer or zeolite compared to the total loss from the control. **Table (5)**, indicates that the biofertilizer containing living microorganisms, which have an ability to make important elements available via biological processes. Therefore, biofertilizer may increase the urea use efficiency and hence decrease nitrogen loss. The present result is in agreement with **Ippolito, et al (2011)** who reported that the microbial inoculants could be used as an economic input to increase crop productivity with chemical fertilizers. Also, the reduction of ammonia loss for treatment of potassium humate compared with urea alone could be due to the temporary acidic condition at the urea micro site. These results agreed with the work of **Ahmed, et al (2009)** who found a reduction in ammonia loss when urea was mixed with humic acid. This may have effectively increased the volume of soil treated with humic acid and also increased the time required for complete hydrolysis of urea (**Fan and Mackenzie 1993**).

The NH₃ loss release at the second week of incubation for control treatment, while NH₃ loss was at the fifth weeks with application of potassium humate. The high loss of NH₃ for untreated soil was most likely due to the high pH value of the soil that accelerated the hydrolysis of urea. Since potassium humate was more acidic, the formation of more ammonium over ammonia was possible. A part from having low pH, the total acidity of potassium humate was also high, as urea hydrolysis. A large amounts of ammonium ions may be released into the soil solution due to urea hydrolysis. This positively charged ammonium ions are in turn adsorbed to the negatively charged sites of phenolic and carboxylic groups of potassium humate. As a result, the concentration of ammonia gas in the soil solution which is subject to volatilization was reduced.

On the other hand, application of zeolite, biochar and biofertilizer prolongs the period of NH₃ presence to 7 and 8 weeks from incubation. Combination between biofertilizer and potassium humate or zeolite decreased NH₃ loss from soil, while biofertilizer mixed with biochar resulted in un formation of NH₃. Due to high pH of the calcareous soil, more microorganisms were able to thrive in the soil and actively breakdown soil organic materials, therefore increasing the total organic carbon in the soil. Increasing ammonia volatilization from untreated calcareous soil may be due to hydro-

lyzed urea to ammonium carbonate by urease enzyme. Afterwards, ammonium carbonate can decomposes into NH_3 , CO_2 and H_2O (Francis, et al 2008). Also, McGarry, et al (1987) found that the ammonia loss is higher under warm - dry and cool - wet conditions which can be overcome by using zeolite. Thus, addition of zeolite to urea fertilizer can improve nitrogen use efficiency as noticed by (McGilloway, et al (2003), Rehakova, et al (2004) and Alberto, et al (2010). Also, Fergunson and peppeer (1987) reported that the main action of zeolite in ammonium conservation is to decrease nitrogen concentration in soil solution through cat ion exchange capacity, high water holding capacity in the free channels, high adsorption capacity and retaining large quantities of ammonium ion in these minerals.

However, the maximum NH_3 loss from the control treatment occurred after four weeks of incubation while with potassium humate and zeolite plus biofertilizer occurred at 6 weeks after incubation. In this concern, Hronec, et al (1989) demonstrated that the sorption of ammonium nitrogen on zeolite is extraordinary fast, While in the first minute the sorption of more than 90% of the maximum potential ammonia concentration on zeolite happened. They added that, during the next period from 2 minutes up to several hours the concentration rate of adsorbed ammonium did not change significantly and it remained almost constant. Therefore, it

can be assumed that this process depends on side of the zeolite particles, so increasing the stabilization of sorption equilibrium in time.

Date in Table (7) showed that the maximum lost value from urea is 3.6% resulted from control treatment, while the lowest value was found by biochar + biofertilizer treatment. The residual values of urea in the studied soil showed an increase by the tested treatments compared to the control with the highest value by biochar + biofertilizer, followed by zeolite, biochar and biofertilizer by rate of 100, 99.99, 99.99 and 99.99%, respectively. These means that the applied treatments increased the available amount of urea to grown plants. On the other hand, application of zeolite, biocher and biofertilizer reduced the amount of urea losses from soil. These results due to zeolite can be used to control N loss from urea because of the small molecular size of the open-ringed structure of clinoptilolite zeolite which physically protects NH_4^+ ions against microbial nitrification (Ferguson and Pepper, 1987). It was started by biochar improved the biological conditions of soils, increased soil microbial biomass and supported beneficial organisms like earthworms Lehmann et al (2011). That biofertilizers are known to improve fixation of nutrients in the rhizosphere, produce growth stimulants for plants, improve soil stability and provide biological control as mentioned by (Rivera-Cruz, et al (2008).

Table 6. Effect of different treatments on ammonia loss (g\fed) from the used Calcareous Soil

Incubation period (weeks)	Control	Soil Treatments					zeolite 1%+ biofertilizer + 1%	biocher 1%+ biofertilizer +1%
		Potassium humate 1%	zeolite + 1%	Biocher +1%	biofertilizer + 1%	Potassium humate 1% + biofertilizer + 1%		
1	ND*	ND	ND	ND	ND	ND	ND	ND
2	265.0	ND	ND	ND	ND	ND	ND	ND
3	587.2	ND	ND	ND	ND	226.4	8.7	ND
4	761.4	ND	ND	ND	ND	482.5	119.4	ND
5	744.6	342.0	ND	ND	ND	460.7	218.0	ND
6	544.8	399.1	0.7	0.7	ND	247.9	269.1	ND
7	347.4	293.7	ND	ND	1.4	44.4	241.1	ND
8	153.9	225.6	ND	ND	ND	ND	20.3	ND
9	57.8	175.8	ND	ND	ND	ND	ND	ND
10	4.3	150.8	ND	ND	ND	ND	218.7	ND
11	ND	192.0	ND	ND	ND	ND	269.1	ND
12	ND	274.4	ND	ND	ND	ND	281.7	ND
13	ND	271.5	ND	0.7	ND	ND	230.1	ND
SUM	3466.6	2325	0.7	1.4	1.4	1461.9	1876.2	ND

Table 7. Effect of different treatments on ammonia loss and available urea after 13 weeks from calcareous soil

Treatment	% of urea loss	% of avail. Urea
Control	3.60	96.40
Potassium humate	2.40	97.60
Zeolite	0.0007	99.99
Biochar	0.001	99.99
Biofertilizer	0.001	99.99
Potassium humate + biofertilizer	1.50	98.50
Zeolite + biofertilizer	1.94	98.01
Biochar + biofertilizer	0.00	100

CONCLUSIONS

The nitrogen loss due to ammonia volatilization is one of the main factors for low efficiency of urea applied on the surface soil. The reduction of losses by volatilization can be achieved by amending soil using urea mixed with biofertilizer. Moreover, application of biochar and biofertilizer may increase the formation NH_4 over NH_3 which is retaining more to the soil particles. Reducing ammonia volatilization from urea may also contribute to the reduction of environmental pollution from excessive utilization of nitrogen fertilizers.

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