

## Ammonia Volatilization Reduction Induced by Bentonite Application to Sandy and Calcareous Soils

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### Abstract

A laboratory incubation experiment was carried out to study the effect of bentonite application on ammonia volatilization from applied urea fertilizer to sandy and calcareous soils using a closed dynamic air flow system. Four bentonite levels of 0, 1.25, 2.5 and 5% and two urea levels of 250 and 500 kg urea fed<sup>-1</sup> wt/wt. All treatments were arranged in a completely randomized design with three replications. The soils treated with these treatments were moistened to field capacity and incubated for 29 days. The volatilized NH<sub>3</sub> was collected from the soil chambers every 24 hours. The results revealed that amending the soil with bentonite reduced the average percentage of ammonia loss from 26.07 and 67.09% in control to 8.27 and 24.61% for the high level of bentonite application to the sandy and calcareous soils, respectively. Bentonite may be recommended as an amendment in sandy and calcareous soils.

**Keywords:** Nitrogen, Ammonia volatilization, Bentonite, Sandy soil, Calcareous soil.

### Introduction

Nitrogen is one of the important yield-limiting nutrients for plants. Nitrogen fertilization plays a significant role in increasing the crop yield (Ekbic *et al.*, 2010; Xia *et al.*, 2011). Nitrogen derived from a fertilizer that is not taken up by plants may be immobilized by micro-organisms or lost to the environment through the volatilization and leaching (Chien *et al.*, 2009). Urea is the cheapest form of granular nitrogen is widely used for crop nutrition (Dong *et al.*, 2009) and accounts for more than 50% of the world's nitrogenous fertilizers (Schwab and Murdock, 2005 ; Claus-Peter, 2011). Ammonia (NH<sub>3</sub>) volatilization is one of the main factors that is responsible for the low efficiency of urea and it may reach extreme values, close to 80% of the applied N (Alberto, 2014). Loss of NH<sub>3</sub>

from urea fertilized soils varies with the type and temperature and ranges from 8.2 to 31.9% of the applied N. After the surface application, urea is quickly hydrolyzed by urease enzyme within one or two days to ammonium carbonate [NH<sub>2</sub>CONH<sub>2</sub> + 2H<sub>2</sub>O → (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>] which decomposes into NH<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>O. This process sharply increases the soil pH and NH<sub>4</sub><sup>+</sup> ions around the urea granules. Under the alkaline conditions, the equilibrium of NH<sub>3</sub> + H<sub>2</sub>O ↔ NH<sub>4</sub><sup>+</sup> + OH<sup>-</sup> shifts more to NH<sub>3</sub> resulting in an increase in volatilization losses (Brady and Weil, 2002; Fan and Mackenzie, 2003 ; Howard and Tyler, 2009).

Bentonite clay ore consists mostly of montmorillonite, which is a 2:1 layer clay mineral with one octahedral sheet and two silica tetrahedral sheets. It has permanent negative

charges on its surfaces due to the isomorphous substitution. Mineral clay layers are held together by Vander Waals forces. Because of these weak forces, low layer charges in the structure and the high surface area, bentonite has an ability to expand and absorb large amounts of water and shows a high cation exchange capacity (CEC) (Sheta *et al.*, 2003). Bentonite was reported to decrease volatilization losses of  $\text{NH}_3$  due to its high adsorption capacity for ammonium ( $\text{NH}_4^+$ ) cations (Redding, 2013). Bell *et al.* (2015) suggested that adding clay amendments such as bentonite has increased the soil CEC and could decrease nitrate leaching. Moreover, from the findings of Sitthaphanit *et al.* (2010), the application of bentonite could reduce ammonia volatilization losses, slow the  $\text{NH}_4^+$  nitrification and hence increase the plant N uptake in sandy soils. In sands amended with clay-rich soil, bentonite reduced the N loss and increased both the soil N retention and plant N utilization (DO *et al.*, 2016). The main action of aluminosilicates such as bentonite in the reduction of  $\text{NH}_3$  loss was due its ability to retain  $\text{NH}_4^+$  ions produced from urea hydrolysis on the soil exchange complex, avoiding the volatilization (Alberto and Washington, 2015). This study aims to investigate bentonite application effects on the  $\text{NH}_3$  volatilization loss from sandy and calcareous soils fertilized with urea.

## Materials and Methods

### Soil sampling

The sandy soil sample used in the experiment was collected from Sohag University campus from uncultivated area near El-Kawamel

farm located at  $26^\circ 27' 38.1''$  N and  $31^\circ 39' 50.6''$  E, Sohag University at El-Kawamel city which is located in about 15 km south west of Sohag Governorate the western part of the Nile Valley (Table 1). On the other side, the calcareous soil sample was collected from cultivated area at  $26^\circ 35' 27.6''$  N and  $31^\circ 48' 11''$  E in El-Kawsar farm, Sohag University, El-Kawsar area which lies in the south-eastern direction of Sohag Governorate (Table 1). The soil samples were air-dried, sieved by a 2 mm sieve and mixed thoroughly. The naturally occurring bentonite ore used in this study (Table 1) was obtained in powder form by International Company for Mining and Investments (ICMI).

### Soil and bentonite analysis:

The Particle size distribution of soil was carried out using the pipette method (Piper, 1950). The pH of the soil samples and bentonite was determined using pH meter in 1:2.5 suspensions. The electrical conductivity of the soil samples was estimated in soil paste extract, and in 1:5 extract for bentonite. The CEC of soil and bentonite was determined using ammonium acetate buffered at pH 7.0 (Chapman and Pratt, 1961). The total  $\text{CaCO}_3$  content was volumetrically measured using the calibrated Collin's calcimeter method (Jackson, 1973). The total N content of the soil samples was determined using the modified Kjeldahl procedure according to Jackson (1973). The specific surface area of bentonite ( $S_{\text{Bet}}$ ) was measured using the  $\text{N}_2$  adsorption/desorption analysis using micromeritics (ASAB 2000, USA), at the Department of Chemistry, Faculty of Science, Sohag

University (Table 1). The XRD analysis of bentonite was carried out using a Philips X-ray diffraction equipment model PW/1710, X-ray Lab., Department of Physics, Faculty of Science, Assiut University (Table 2).

**Laboratory experiment:**

A laboratory incubation experiment was conducted to monitor the effect of adding four levels of bentonite as a soil conditioner on NH<sub>3</sub> volatilization from urea amended sandy and calcareous soils under room temperature. The system used as described by Gameh (1987) consists of an air source, an air compressor from which the air was pumped through a distilled water tank, for filtration and humidification and then distributed through a manifold into soil chambers connected to the system. The soil chambers were glass bottles of 400 cm<sup>3</sup> in volume with a diameter of 6.5 cm and a height of 14cm. The outgoing air was bubbled through 25 ml of 2% boric acid mixed with bromo-cresol green and methyl red indicators which were placed in Bochner flasks to trap the volatilized NH<sub>3</sub>. The flasks were periodically replaced every 24 hours and titrated using 0.01 N H<sub>2</sub>SO<sub>4</sub> for 29 days on incubation. The amounts

of volatilized NH<sub>3</sub>-N were calculated and daily presented and the cumulative loss was estimated as a percentage of the applied urea-N. A 400 g of air dried sandy (S) or calcareous (C) soil samples were placed in each glass bottle. Bentonite was added at four levels namely: 0, 1.25, 2.5 and 5 %. These levels were equivalent 0, 5, 10 and 20 g bentonite (0, B1, B2 and B3) per bottle, respectively and mixed thoroughly with the soil. The soil sample in each bottle was moistened to field capacity, and then urea (46.5 % N) was added to soil surface at two levels of 0.1 g (U1) and 0.2 g (U2) per bottle. These levels are equivalent to 250 and 500 Kg urea fed<sup>-1</sup> (wt/wt). Then, the bottles were closed immediately, and connected to the system. All treatments were arranged in a completely randomized design with three replications (Table 3). The nitrogen (N) recovery was plotted as a function of the time and fitted the following exponential kinetic equation according to Cohen *et al.* (2010):

$$[N]_t = [N]_0 e^{-kt}$$

Where:

[N]<sub>t</sub> , [N]<sub>0</sub> = N concentration (mg) at time (t) and t<sub>zero</sub> respectively.

t = time in days, K = constant, i.e. depletion rate of [N].

**Table 1. Selected properties of the studied soils and bentonite.**

Property	Sandy soil	Calcareous soil	Bentonite
pH (1:2.5) suspension	7.34	8.33	7.88
EC (dS/m)	1.18 (soil paste extract)	4.10 (soil paste extract)	4.07 (1:5 extract)
CaCO <sub>3</sub> (%)	2.17	18.57	0.41
Sand (%), Clay (%), Silt (%)	92.16 , 5.11 , 2.73	87.13 , 6.11 , 6.76	-
Texture grade	Sandy	Loamy sand	-
CEC (cmol(+)/kg)	5.04	8.01	85.23
Total N (%)	0.003	0.023	Nil
S <sub>Bet</sub> (m <sup>2</sup> /g)	-	-	698

**Table 2. X-ray diffraction clay analysis of bentonite ore.**

Mineral (%)		
Montmorillonite	Kaolinite	Quartz
80.60	16.90	2.50

**Table 3. The used treatments in both sandy and calcareous soils.**

Treatment No	Sandy soil	Treatment No	Calcareous soil
T1	U1B0 (control)	T9	U1B0 (control)
T2	U1B1	T10	U1B1
T3	U1B2	T11	U1B2
T4	U1B3	T12	U1B3
T5	U2B0 (control)	T13	U2B0 (control)
T6	U2B1	T14	U2B1
T7	U2B2	T15	U2B2
T8	U2B3	T16	U2B3

U1 = 250 kg fed<sup>-1</sup> urea, U2 = 500 kg fed<sup>-1</sup> urea

B0, B1, B2 and B3 = 0, 1.25, 2.5 and 5% bentonite, respectively.

## Results and Discussion

### 1- Bentonite effect on ammonia loss in the sandy soil

The daily and cumulative losses of NH<sub>3</sub> as a percentage of the applied urea-N to the sandy soil that was recorded during the incubation experiment are shown in Figs. 1 and 2 as well as 3 and 4, respectively.

#### a. Daily volatilized ammonia

The daily percentage of NH<sub>3</sub> loss in the sandy soil differed among the investigated treatments. Ammonia loss (%) daily decreased with increasing the bentonite applied level, particularly up to 20 days of incubation beginning, it was found that the maximum daily NH<sub>3</sub> loss (%) for the tested treatments occurred between the 9<sup>th</sup> to 12<sup>th</sup> day of incubation period beginning. It was 1.29, 0.73 and 0.53% for T2, T3 and T4, respectively, compared to 2.59% for the control (T1) (Fig. 1). On the other hand, for the high urea applied level (U2), the maximum daily NH<sub>3</sub>-N loss (%) for the investigated treatments took place between the 8<sup>th</sup> and 11<sup>th</sup>

day of incubation beginning (Fig. 2). It showed 1.90, 1.17 and 0.77% for T6, T7 and T8, respectively, compared to 2.74% for the control (T5) (Fig.2). After this maximum loss, the daily NH<sub>3</sub> loss decreased gradually with increasing the incubation time for bentonite treatments. Percentages of NH<sub>3</sub> loss were greater in the soil amended with the high urea level (U2) than that of the low one (U1).

#### b. Cumulative volatilized ammonia

The cumulative volatilized NH<sub>3</sub> from the sandy soil received two levels of urea (250 (U1) and 500kg/fed (U2)) and amended four levels of bentonite are illustrated in Figs. 3 and 4, respectively. For the 250 kg urea (U1) level, the application of bentonite significantly reduced the total NH<sub>3</sub> loss at the end of the experiment from 24.79% in the control treatment (T1) to 15.81, 9.02 and 6.59% of the total applied urea-N in the T2, T3 and T4 respectively (Table 4 and Fig. 3). Moreover, for 500 kg urea (U2) level, the sandy soil amended with ben-

tonite exhibited a reduction in the total  $\text{NH}_3$  loss from 27.35% for the control treatment (T5) to 18.55, 12.89

and 9.95% of the total applied urea-N for T6, T7 and T8, respectively (Table 4 and Fig. 4).

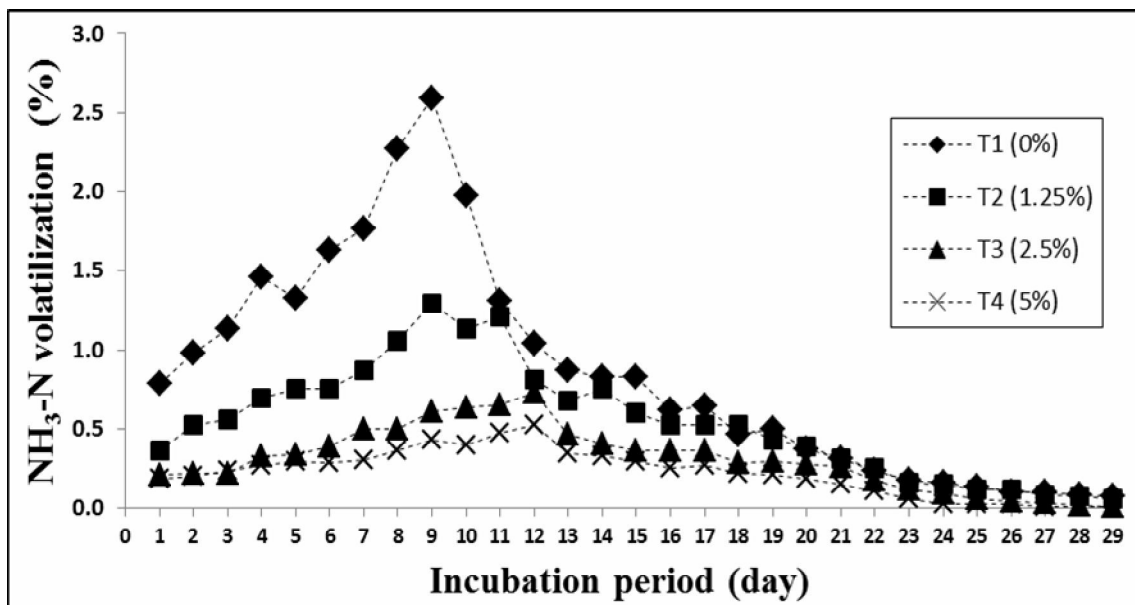


Fig. 1: Daily  $\text{NH}_3$  volatilization (%) from the sandy soil fertilized with  $250\text{kg fed}^{-1}$  urea (U1) level and amended with bentonite levels.

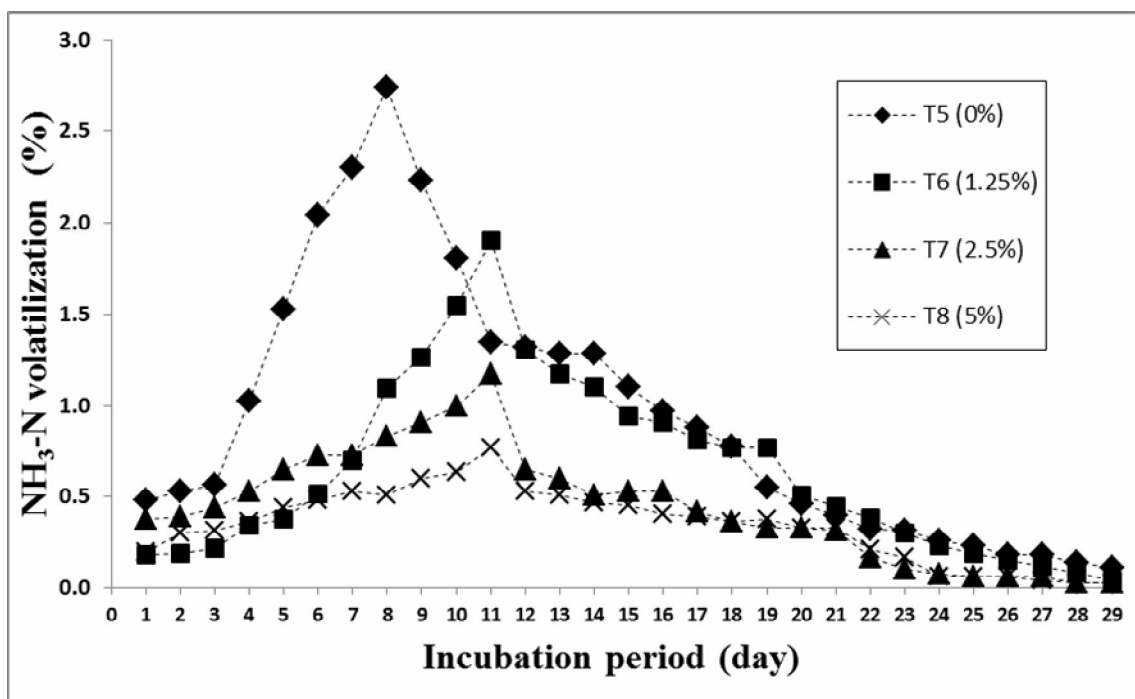


Fig. 2: Daily  $\text{NH}_3$  volatilization (%) from the sandy soil fertilized with  $500\text{kg fed}^{-1}$  urea (U2) and amended with bentonite levels.

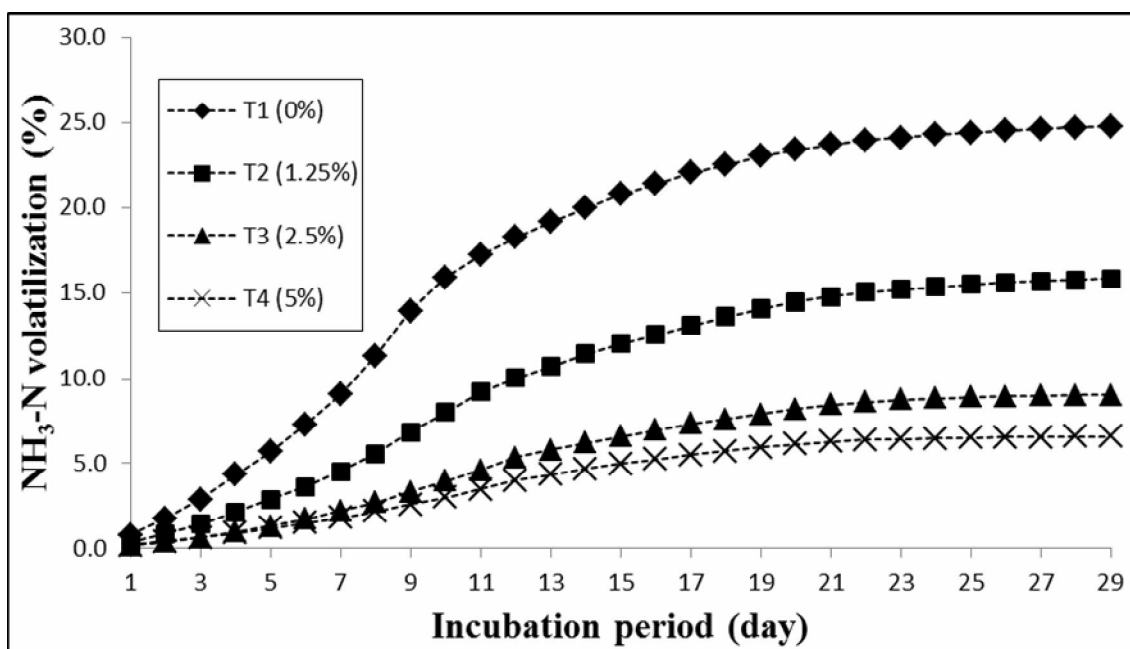


Fig. 3: Cumulative NH<sub>3</sub> volatilization (%) from the sandy soil fertilized with 250 kg fed<sup>-1</sup> urea (U1) and amended with bentonite levels.

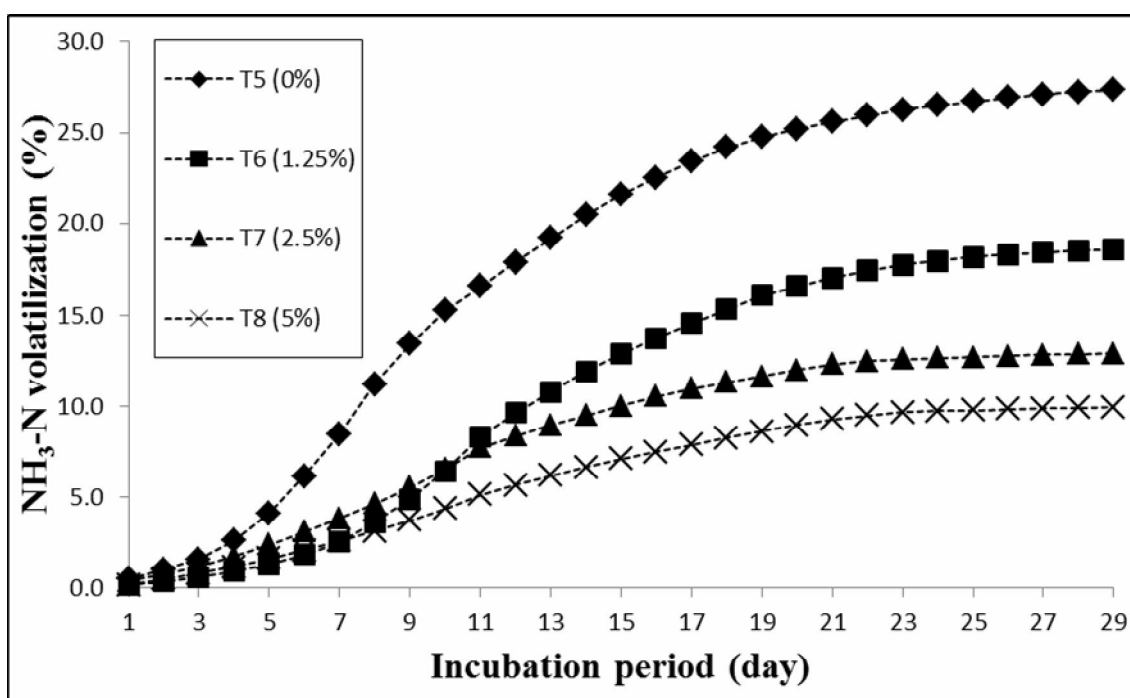


Fig. 4: Cumulative NH<sub>3</sub> volatilization (%) from the sandy soil fertilized with 500 kg fed<sup>-1</sup> urea (U2) and amended with bentonite levels.

**Table 4. Effect of bentonite levels on total volatilized NH<sub>3</sub> (%) from sandy and calcareous soils fertilized with 250 kg fed<sup>-1</sup> urea (U1) and 500 kg fed<sup>-1</sup> (U2).**

Sandy Soil					
Urea level	B0	B1	B2	B3	Mean
U1	24.79 <sup>b</sup>	15.81 <sup>d</sup>	9.02 <sup>t</sup>	6.59 <sup>g</sup>	14.05 <sup>a</sup>
U2	27.34 <sup>a</sup>	18.55 <sup>c</sup>	12.89 <sup>e</sup>	9.95 <sup>t</sup>	17.18 <sup>a</sup>
Mean	26.07 <sup>a</sup>	17.18 <sup>b</sup>	10.95 <sup>c</sup>	8.27 <sup>d</sup>	
L.S.D <sub>5%</sub>	U= 3.20	B= 1.68	UB= 2.32		
Calcareous Soil					
U	B0	B1	B2	B3	Mean
U1	61.74 <sup>b</sup>	46.24 <sup>d</sup>	32.10 <sup>t</sup>	21.05 <sup>g</sup>	40.28 <sup>b</sup>
U2	72.45 <sup>a</sup>	55.08 <sup>c</sup>	38.85 <sup>e</sup>	28.17 <sup>t</sup>	48.64 <sup>a</sup>
Mean	67.09 <sup>a</sup>	50.66 <sup>b</sup>	35.47 <sup>c</sup>	24.61 <sup>d</sup>	
L.S.D <sub>5%</sub>	U= 7.87	B= 3.46	UB= 5.09		

Different letters indicate statistically significant differences between variables according to SAS program. B0, B1, B2, B3 = 0, 1.25, 2.5 and 5.0 % bentonite.

## 2-Bentonite effect on ammonia loss in the calcareous soil

Daily and cumulative losses of NH<sub>3</sub>-N as a percentage of the applied urea-N to the calcareous soil incubated for 29 days are illustrated in Figs. 5 and 6 as well as 7 and 8, respectively.

### a. Daily ammonia loss

As in the sandy soil, the daily percentage of NH<sub>3</sub> loss increased to reach a maximum value and then decreased with time of incubation for all investigated treatments (Figs. 5 and 6). The daily maximum for the investigated treatments occurred between the 3<sup>th</sup> and 5<sup>th</sup> day of incubation beginning with difference among treatments (Figs. 5 and 6). Then, it gradually decreased until the end of incubation period (Fig. 5 and 6). The daily NH<sub>3</sub> loss exhibited maximum values of 5.31, 3.09 and 1.58 % for T10, T11 and T12, respectively, compared to 10.27 % for the control (T9) for U1 level. However, for the high urea applied level (U2), the daily

NH<sub>3</sub> loss exhibited maximum values of 5.70, 3.07 and 2.19% for T14, T15 and T16, respectively, compared to 11.30% for the control (T13).

### b. Cumulative volatilized ammonia loss

Cumulative ammonia losses (%) from the calcareous soil fertilized with urea and amended with bentonite is present in Figs. 7 and 8. For the U1 level, the addition of bentonite significantly decreased the total NH<sub>3</sub> loss (%) in the calcareous soil at the end of experiment from 61.73% in for the control (T9) to 46.24, 32.10 and 21.05% of the total applied urea-N for T10, T11 and T12, respectively (Table 4 and Fig. 7). However, For the U2 level, amending this soil with bentonite significantly reduced the total NH<sub>3</sub> loss from 72.45% for the control (T13) to 55.08, 38.85 and 28.17% of the total applied urea-N for T14, T15 and T16, respectively (Table 4 and Fig. 8).

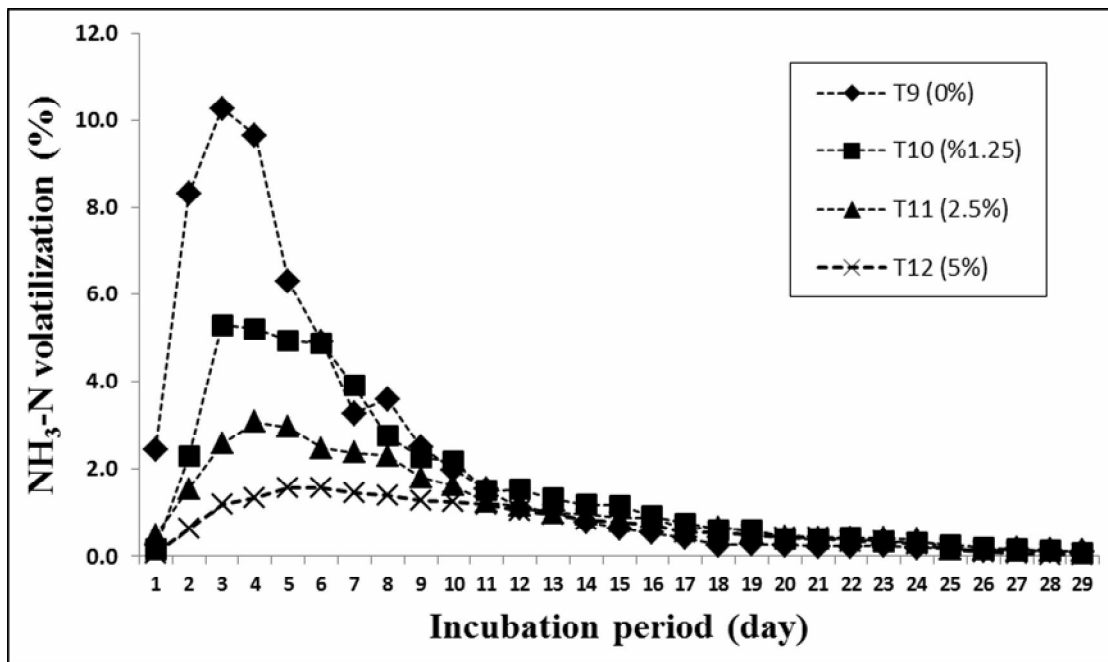


Fig. 5: Daily NH<sub>3</sub> volatilization (%) in the calcareous soil fertilized with 250 kg fed<sup>-1</sup> urea (U1) and amended with bentonite levels.

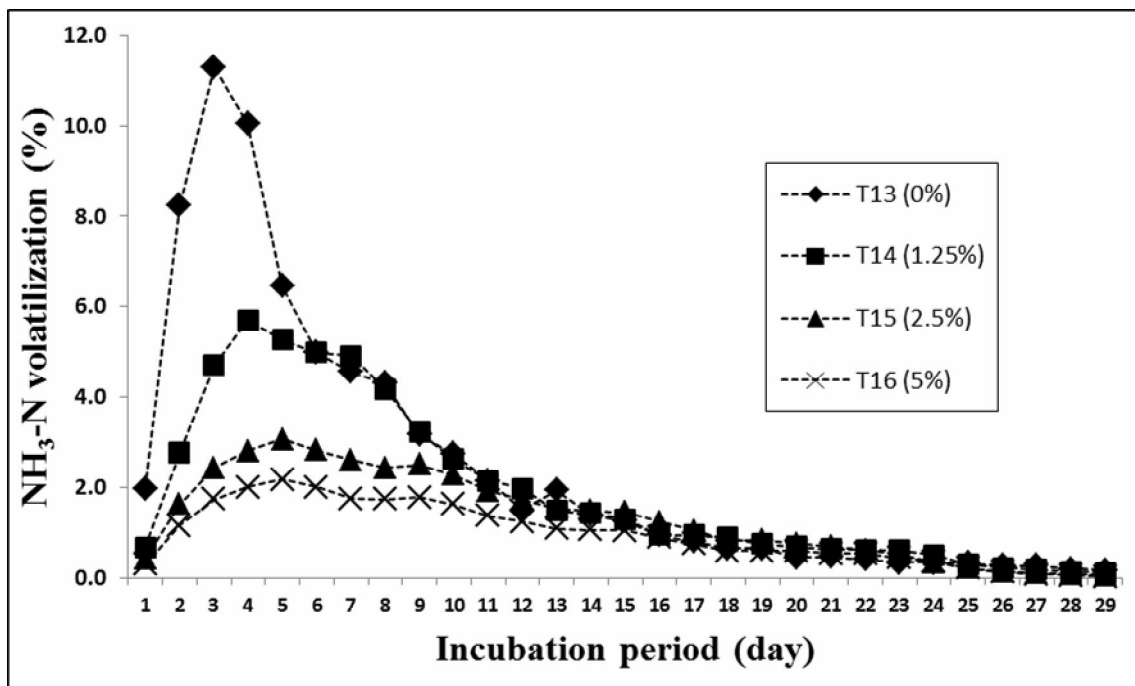


Fig. 6: Daily NH<sub>3</sub> volatilization (%) in the calcareous soil 500 kg fed<sup>-1</sup> urea (U2) and amended with bentonite levels.



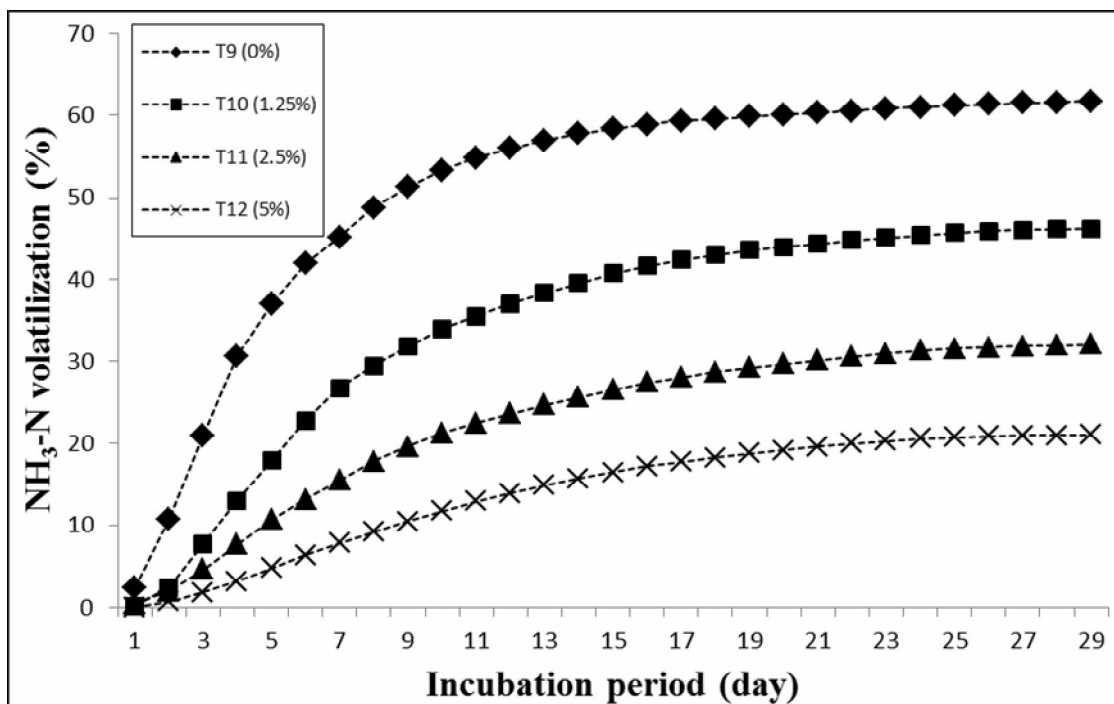


Fig. 7: Cumulative  $\text{NH}_3$  volatilization (%) in the calcareous soil  $250 \text{ kg fed}^{-1}$  urea (U1) and amended with bentonite levels.

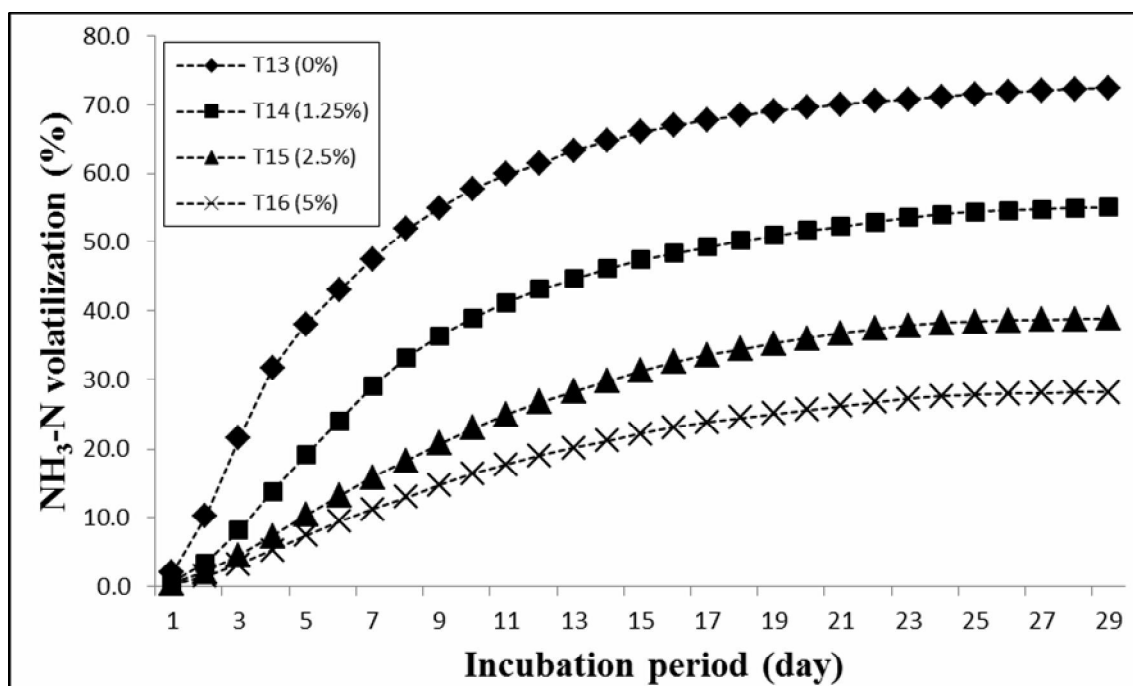


Fig. 8: Cumulative  $\text{NH}_3$  volatilization (%) in the calcareous soil fertilized with  $500 \text{ kg fed}^{-1}$  urea (U2) and amended with bentonite levels.

In general, the data showed that ammonia loss (%) from calcareous soil is higher than that from the sandy

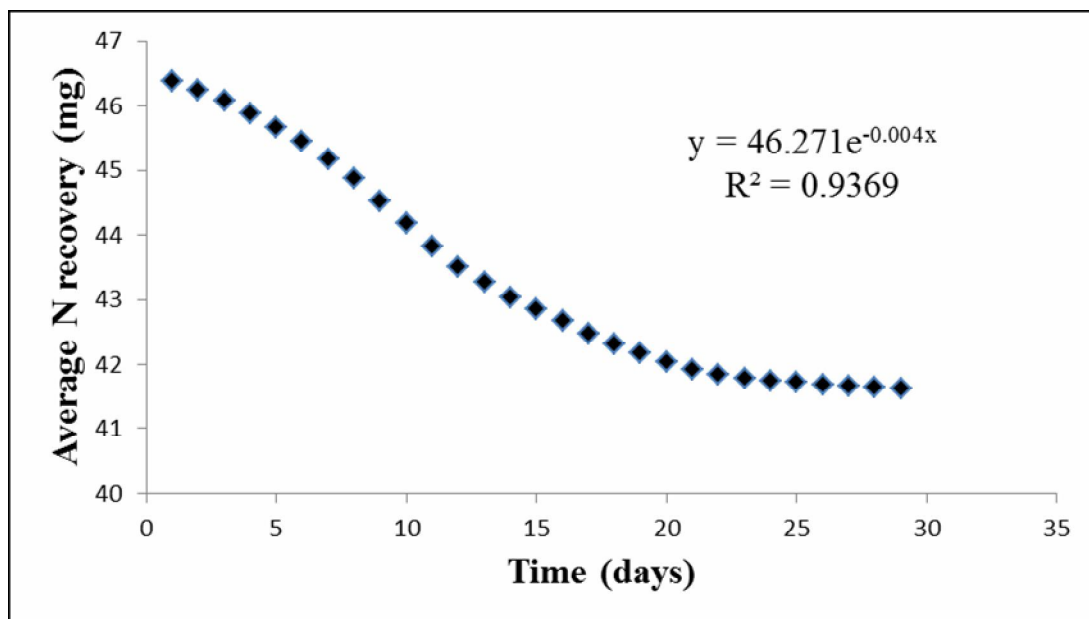
soil which may be attributed to the higher pH value and the higher  $\text{CaCO}_3$  content of the calcareous soil.

Where  $\text{CaCO}_3$  increases  $(\text{NH}_4)_2\text{CO}_3$  production that separated into  $\text{NH}_3\uparrow$  and  $\text{CO}_2\uparrow$ , which was confirmed by Gameh (1991) and Jones *et al.* (2013). It is noticeable that the total  $\text{NH}_3$  loss percentage from the high urea applied level (U2) was higher than that from the low one (U1) in both soils due to the fact that the nitrogen use efficiency decreases as the amount of applied nitrogen fertilizer increases. These results are in an agreement with those of Gameh (1991), Ibrahim (1999), El-Mamlouk (2006) and Rochette *et al.* (2013).

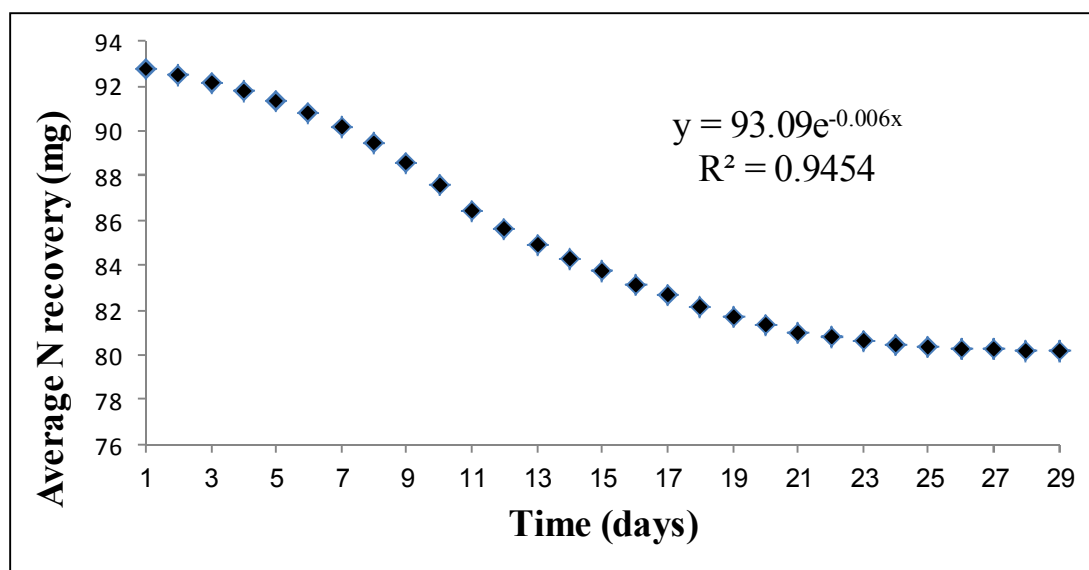
It is clear that the reduction percentage of  $\text{NH}_3$  loss from the soil increased as the applied level of bentonite increased. The effective role of bentonite in reducing the volatilization loss of  $\text{NH}_3$  may be due to montmorillonite which is the most dominant clay mineral in the studied bentonite ore. Montmorillonite contains several permanent charge sites on its surface as well a high surface area that give it the ability to exchange and adsorb  $\text{NH}_4^+$  cation and hence to reduce the  $\text{NH}_3$  volatilization loss (Redding, 2013 ; Angar, 2016).

### **3-Kinetics of urea-N loss in the sandy and calcareous soils**

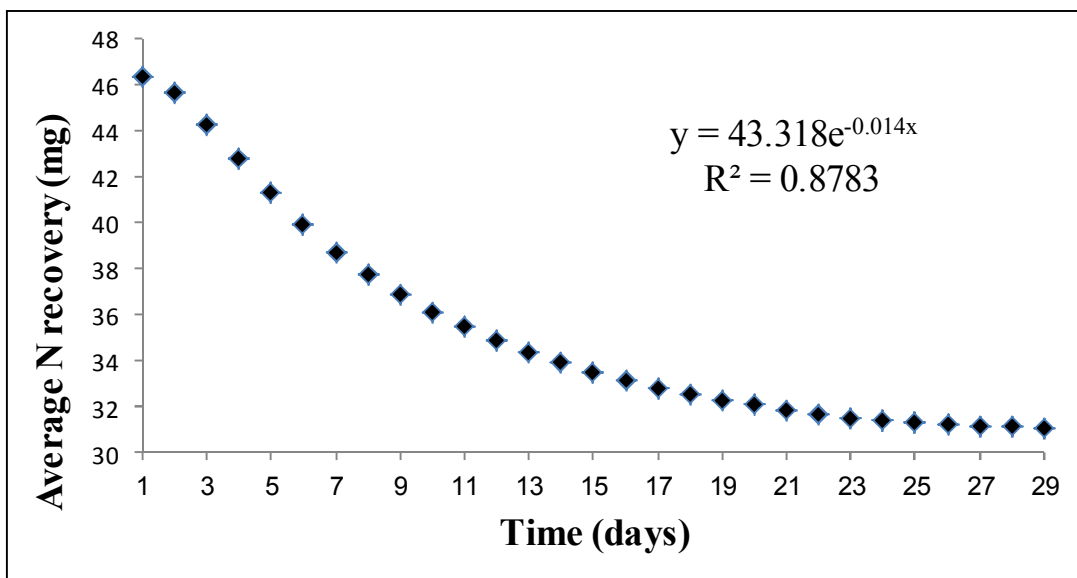
The average values of N recovery (mg) from the applied levels of urea as a function of the incubation time are present in Figs. 9 and 10, respectively for the sandy soil, and Figs. 11 and 12, respectively, for the calcareous soil. The nitrogen depletion rate (K) as a result of the ammonia volatilization loss was higher in the calcareous soil than that in the sandy soil. Bentonite amended sandy soil showed a reduction in the K value from - 0.010 in the control (T1) to -0.007, -0.004 and - 0.003 in T2, T3 and T4, respectively for U1 treatment, and from -0.012 in the control (T5) to -0.009, -0.005 and -0.004 in T6, T7 and T8, respectively, for U2 treatment (Table 5). However, the nitrogen depletion rate of the bentonite amended calcareous soil decreased at the U1 level from - 0.027 in the control (T9) to - 0.021, -0.013 and -0.009 in T10, T11 and T12, respectively, and for that fertilized at the U2 level from -0.041 in the control (T13) to - 0.028, - 0.018 and -0.012 in T14, T15 and T16, respectively (Table 5). Similar results were obtained by Ibrahim (1999) who indicated that the depletion rate of ammonium increased as the fertilization level increased and decreased as the bentonite level increased.



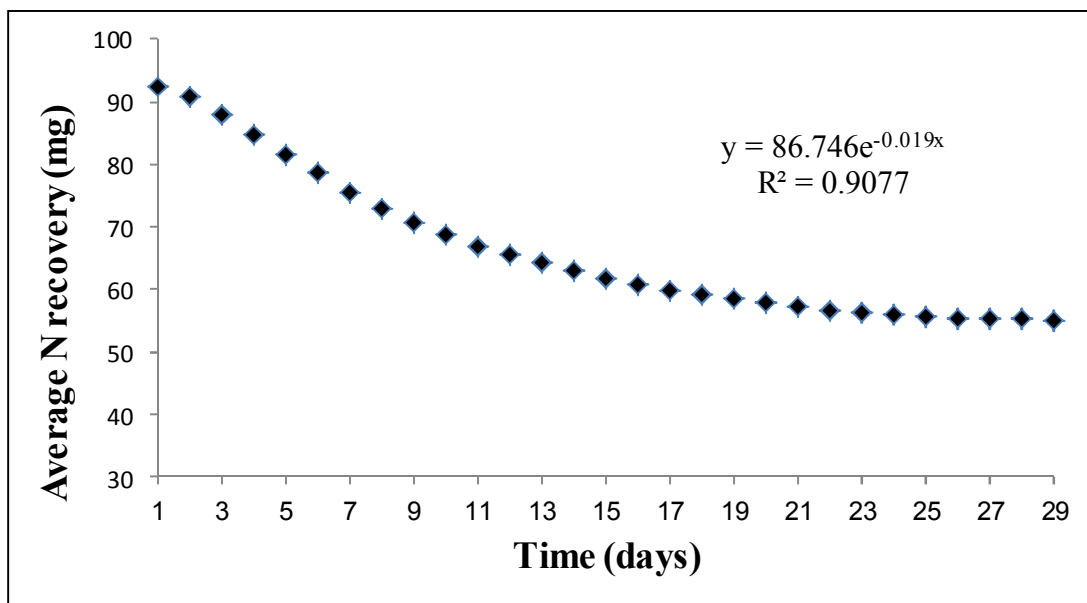
**Fig. 9:** Nitrogen recovery (an average value) from 250 kg fed<sup>-1</sup> urea (U1) after bentonite additions as a function of the time in the sandy soil.



**Fig. 10:** Nitrogen recovery (an average value) from 500 kg fed<sup>-1</sup> urea (U2) after bentonite additions as a function of the time in the sandy soil.



**Fig. 11:** Nitrogen recovery (an average value) from 250 kg fed<sup>-1</sup> urea (U1) after bentonite additions as a function of the time in the calcareous soil.



**Fig. 12:** Nitrogen recovery (an average value) from 500 kg fed<sup>-1</sup> urea (U2) after bentonite additions as a function of the time in the calcareous soil.

**Table 5. Nitrogen decrease rate (k) and coefficient of determination (R<sup>2</sup>) of the sandy and calcareous soils fertilized with 250 urea kg fed<sup>-1</sup> (U1) and 500 kg urea fed<sup>-1</sup> (U2) and amended with bentonite.**

Sandy Soil					
Treatment	k	R <sup>2</sup>	Treatment	k	R <sup>2</sup>
T1	-0.010	0.8855	T5	-0.012	0.9184
T2	-0.007	0.9335	T6	-0.009	0.9493
T3	-0.004	0.9441	T7	-0.005	0.9234
T4	-0.003	0.9351	T8	-0.004	0.9531
Calcareous Soil					
T9	-0.027	0.8423	T13	-0.041	0.8550
T10	-0.021	0.8470	T14	-0.028	0.8863
T11	-0.013	0.8901	T15	-0.018	0.9267
T12	-0.009	0.9243	T16	-0.012	0.9278

### Conclusion

The results from this study suggest that amending the sandy or calcareous soils with bentonite has a significant role in the reduction of volatilization loss of ammonia from the applied urea-N over the soil surface without additives and consequently, increasing the plant growth as a result of remaining the N element in form of NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup> in the soil and raise the ability of the plants to take up N.

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تأثير اضافة البنتونيت على خفض تطاير الأمونيا من الأراضي الرملية والجيرية  
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**الملخص:**

أجريت تجربة تحضين معملية لدراسة تأثير اضافة البنتونيت على فقد الأمونيا بالتطاير من سماد اليوريا المضاف الى التربة الرملية والتربة الجيرية وذلك بأستخدام نظام تدفق الهواء المغلق. حيث تم استخدام (٤) مستويات من البنتونيت وهى (صفر - ١,٢٥ - ٢,٥ - ٥ %) ومستويين من سماد اليوريا وهما ٢٥٠ - ٥٠٠ كجم يوريا /فدان على أساس الوزن فى تصميم كامل العشوائية من ثلاثة مكررات لكل معاملة. تمت اضافة البنتونيت وسماد اليوريا الى التربة وريها وتحضينها لمدة ٢٩ يوما وتم قياس نسبة الأمونيا المتطايرة من التربة كل ٢٤ ساعة. وقد اوضحت النتائج ما يلى:

- ١- أن اضافة البنتونيت الى التربة الرملية أدت الى خفض متوسط نسبة تطاير الأمونيا الكلية خلال فترة التحضين من ٢٦,٠٧ % فى معاملة الكنترول الى ٨,٢٧ % عند اضافة المستوى الأعلى من البنتونيت الى هذه التربة.
  - ٢- أن اضافة البنتونيت الى التربة الجيرية أدت الى خفض متوسط نسبة تطاير الأمونيا الكلية خلال فترة التحضين من ٦٧,٠٩ % فى معاملة الكنترول الى ٢٤,٦١ % عند اضافة المستوى الأعلى من البنتونيت الى هذه التربة.
  - ٣- ازدياد نسبة الأمونيا المتطايرة بزيادة مستوى سماد اليوريا المضاف فى كلا الترتين.
  - ٤- انخفاض نسبة الأمونيا المتطايرة بزيادة مستوى البنتونيت المضاف الى كلا الترتين.
- لذلك نوصى باستخدام البنتونيت كمحسن للأراضي الرملية والجيرية لخفض نسبة الأمونيا المتطايرة وزيادة كفاءة السماد النيتروجينى الأمونيومى.