Jurnal
Teknologi

Full Paper

CONSEQUENCES OF Cu and Zn COATED UREA TO MINIMIZE AMMONIA VOLATILIZATION

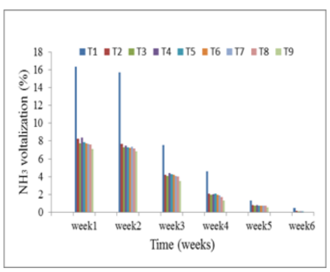
Saima Kalsoom Babar[a,b*], Mohd Khanif Yusop[a], Shakeel Ahmed Babar[b], Aijaz Ali Khooharo[c]

[a]Department of Land Management, Faculty of Agriculture, Universiti Putra Malaysia, 43400 Serdang Selangor, Darul Ehsan, Malaysia
[b]Agriculture Chemistry (Soils), Agriculture Research Institute, Tanda Jam 70060, Sindh, Pakistan
[c]Faculty of Social Sciences, Sindh Agriculture University Tando Jam 70060, Sindh, Pakistan

Article history
Received
23 May 2015
Received in revised form
12 November 2015
Accepted
22 December 2015

*Corresponding author
saima_babar2006@yhoo.com

Graphical abstract



Abstract

Nitrogen (N) losses from agricultural fields are commonly observed particularly from urea. The rate of urea hydrolysis is accelerated as it remains in conventional form and about 70% of applied urea losses in different forms to atmosphere. Ammonia volatilization is persuasive loss among all the losses from urea. Therefore to minimize ammonia (NH_3) volatilization the micronutrient coated urea is applied to enhance N-efficiency and its uptake. This study is an application of micronutrient coated urea with zinc (Zn) and copper (Cu) for two soil series of Malaysia. A laboratory experiment was designed according to the force draft technique for trapping the NH_3 loss. The results have manifested that the rate of ammonia volatilization was 16% from uncoated urea and 8% from coated urea with micronutrients during the first two weeks of observations. After the six weeks of observations it was perceived that the ammonia losses for both soil series were gradually decreased with time. The mean comparison by using Tukey's range test has shown the positive effect of micronutrient coated urea in comparison with the conventional urea. However the urea coated with the combination of both micronutrients Cu and Zn has shown significant difference in contrast to the coating urea with single micronutrient. The overall results revealed the efficacy of micronutrient coated urea on both of the soil series to maximize N-uptake and reduce NH_3 volatilization.

Keywords: Micronutrients coated urea, ammonia loss, N-uptake, soil

1.0 INTRODUCTION

Nitrogen (N) is the primary and essential nutrient for the normal plant growth and its survival. Nitrogen is responsible for metabolic process release to synthesis and transfer of energy. The common fertilizer and the main source of Nitrogen (N) in an agricultural system is urea [1]. It is estimated that the urea production will enhance from the current 70 to predicted 200 million metric tons by the year 2020 [2]. This estimation increment in production forecast is evidence that Nitrogen efficiency is still beyond the range.

Urea is relatively cheap and affordable fertilizer with more N percentage (46%) as compared to other solid N fertilizers. Therefore it is commonly used by the farmers without any loss concerns in the form of surface application. The hydrolysis rate of urea accelerated as it remains in surface application [3]. Upon the application in the soils the urea is rapidly hydrolyzed to $(NH_4)_2CO_3$ and later to NH_4OH and CO_2

[4]. Therefore the surface application of urea frequently effects on NH_3 volatilization, denitrification, immobilization and leaching, which eventually reduces the N-use efficiency (NUE) [5]. Conventional urea is a cause of detrimental emission of ammonia and nitrous oxide gases (NH_3, N_2O) to the environment [6]. The dire need is to develop such a system that can overcome the N-losses, alleviate environmental pollution and increase N-efficiency [7]. Controlled release urea may be one of its solutions, as it assumed to improve crop yield by minimizing the hazardous emission of ammonia and nitrous oxide gases (NH_3, N_2O) from the fertilizers [8]. The purpose to design the controlled release fertilizer (CRF) was to provide the specifically active fertilizing nutrients to plants in a precise and delayed manner, according to the needs of the plant for essential elements, thus reformed the nutrients use efficiency which consequently improved the crop yield [6].

These expected losses of N can be controlled and N efficiency can be increased by reducing the hydrolysis rate of urea in the soil [9]. Thus the substitute for the conventional urea is coated urea. However, the coating urea has proved its efficiency against conventional urea; but the scenario is still there in the form of the selection of coating material. An eventual selection for coating material must be a natural or semi-natural product, as it serves as inoffensive to the environment [10].

Globally the imbalance fertilization practices results in micronutrient deficiencies in soil and plants [11]. Reports have proven the inadequacy of zinc, copper and iron (Zn, Cu and Fe) as compared to the rest of the other micronutrients in current era [12]. Malaysian soils due to their acidic nature never been supplied with micronutrient fertilizers as there is a concept that acidic soils are free of micronutrient deficiencies. In spite of the chemical changes of rice fields are somehow divergent against normal acidic soils.

Mainly there are two ecosystems for rice production low land rice or anaerobic conditions and; is upland rice or aerobic condition. Under normal condition low land rice field flooded with water for 3-4weeks and maintained the water level up to 10-15cm [13]. Sub-merged soil conditions eradicate oxygen from rhizosphere, and eventually changes occur in soil chemical properties. The most substantial change appeared in paddy field is conversion of aerobic environment into anaerobic one, where oxygen is almost absent.

The most fundamental chemical changes are; soil pH, redox potential and ionic strength due to oxygen depletion in flooded rice soils. Due to the reducing conditions in rice soils, the concentration and form of applied and native nutrients inhibited. The availability of micronutrients influentially affected in flooded rice soils due to fluctuation in soil pH. Therefore the coated fertilizer has to design in such a manner that, it can provide the nutrients according to the soil conditions by reducing the hydrolysis rate. Rice is sensitive to micronutrients, and deficiency of the nutrients can cause drastic decline in production. Micronutrients have become major constraints to productivity, durability and unremitting life of soils [12]. T Therefore the present study was aimed to evaluate the N efficiency by applying the coated urea with Cu and Zn on two different types of soils. The objective of the study was to determine the effect of Cu and Zn coated urea on NH_3 volatilization loss and Cu and Zn availability.

2.0 METHODOLOGY

Two different types of Malaysian soils: (a) Riverine alluvium (Kelantan) and (b) Marine alluvium (Kedah) were used in this study. The location on the GPS coordinates were N-05-97370, E-102-29944 and N-06-13422, E-100.29527 for Cempaka (Kelantan) and Kuala kedah (Kedah) soil series respectively. These samples were taken from the surface depth (0-15cm). Soil samples were air dried, and passed through a 2mm sieve, then stored for the further soil analysis. The physical and the chemical characteristics of both soils are given as shown in Table 1. The required physical and chemical analysis was done: soil pH was measured by 1:1 soil water ratio (w/v) using pH meter [14]. Soil texture characteristics were determined by employing pipette method [15]. Plant available fraction of Cu and Zn in soils was extracted by Mehlich-I [16]. Total nitrogen was performed by using salicylic acid digestion- K-jeldhal method [15].

The fertilizer urea is applied as a main source in the form of conventional urea and coated with micronutrients copper sulfate ($CuSO_4$) and zinc sulphate ($ZnSO_4$). The detail of the treatments is listed in Table 2.

Table 1 Basic physical and chemical characteristic of sampled soils before treatment effect

Soil series	Soil type	Soil texture	Nitrogen %	Soil pH	Cu mg kg^{-1}	Zn mg kg^{-1}
Cempaka	Riverine alluvium	Clay loam	0.18	5.12	0.11	0.9
Kuala Kedah	Marine alluvium	Silty clay	0.15	5.29	0.15	1.1

Table 2 Treatments detail showing the variable rates of micronutrients

Treatments	Urea (g/flask)	Zn (g/flask)	Cu (g/flask)
T-1	0.2608 UC*	--	--
T-2	0.2608 C*	0.0461	--
T-3	0.2608 C*	0.0650	--
T-4	0.2608 C*	--	0.00175
T-5	0.2608 C*	--	0.00292
T-6	0.2608 C*	0.0461	0.00175
T-7	0.2608 C*	0.0461	0.00292
T-8	0.2608 C*	0.0650	0.00175
T-9	0.2608 C*	0.0650	0.00292

UC=Uncoated Urea; C=Coated Urea

The Fertilizer coating was performed manually in the Laboratory of Department of Land Management, Faculty of Agriculture, Universiti Putra Malaysia [17]. The Force draft technique was used to estimate the NH_3 loss [18] and in this regard 300g of air dried soil (natural condition with small clods) was transferred into ground-glass Erlenmeyer flask of 500mL, that tighten with a rubber cork and the outlet was connected to trapping flask of ground-glass Erlenmeyer flask of 250mL. Both flasks had an outlet and inlet facility. The trapping flask was filled with 75mL of 2% boric acid to capture the ammonia release. The inlet of flask was connected to heavy duty air pump whose flow rate was set at 2.5-3.5 v/m. Soil samples were flooded approximately 5cm for one week before fertilizer application and level maintains during the entire experiment as the soils belongs to paddy fields. Fertilizers used as a urea (400 µg N g^{-1}) conventional and coated with variable rates of micronutrient fertilizers: copper sulfate and zinc sulfate. Chamber analysis was set on every 2nd day of observation, as the color has started to change; extracts have titrated with 0.1N hydrochloric acid solution (HCl) to determine NH_3-N volatilization. This observation was set for six weeks in the laboratory to capture the NH_3 loss from nine treatments with three replications at two different types of soils.

Statistical analysis was carried out; in this regard the data was arranged in Microsoft Excel to run in software Statistix 8.1 version. The data had three replicates; the mean and standard error were estimated for each set. Analysis Of Variance (ANOVA) followed by the mean comparison of Tukey's HSD (Honest Significant Difference) test has been executed to assess the treatment effect. Different letters representing the significant effect in mean comparison at 5% level.

3.0 RESULTS AND DISCUSSION

Findings on the basic physical and chemical characteristics of both soils (Cempaka and Kuala Kedah) before treatment application are presented in Table 1. It is shown from the data that both soils were found to be acidic in nature and had low available Cu and Zn contents. The sampled soils were taken from the main paddy areas of Malaysia. The low availability of micronutrients in the particular regions may due to the continuous cultivation of rice without micronutrient fertilizer application. Cereals have required an appropriate amount of micronutrients for better crop yield. The reports from Malaysia in the last few years have already notified the deficiencies of boron and zinc in paddy fields. After the deficiency evidences, the application of these particular micronutrients in the form of fertilizer to paddy fields had enhance the rice yield progressively [19-20].

The findings from the six weeks of an experiment revealed the positive effect of coated urea with Cu and Zn in both soils. Overall, during the observations, it was perceived that the rate of ammonia volatilization was at its maximum percentage in the first two weeks of the experiment. When compared the N-loss from the two forms of applied urea i.e. coated and un-coated; the larger portion of ammonia volatilization was recorded from the uncoated urea. It was verified that the rate of ammonia volatilization was 50% more from the common urea as compared to Cu and Zn coated urea.

Evidences of nitrogen loss in the form of ammonia from the conventional urea were started to detect from the second day of the experiment in both soils. Results were consistent with the previous work done at China [8]. They have detected about half the rates of ammonia loss when fertilized with micronutrient coated urea.

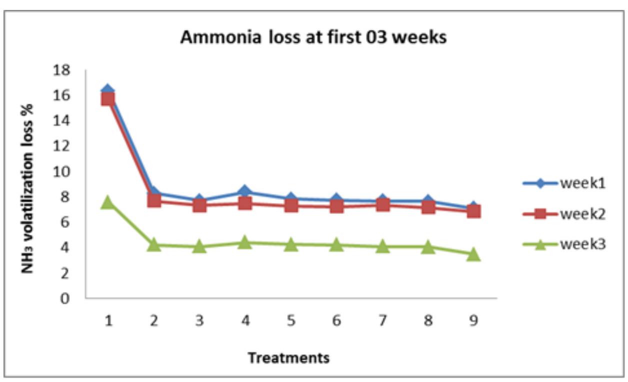
The mean comparison by using Tukey's HSD as shown in Table 3, the significant effect of the treatment where both Cu and Zn has applied in coating (Treatment 9). It was observed that the rate of NH_3 volatilization during the first two weeks was 16% in both soils where the conventional urea has been applied. Comparatively the coated urea has shown the 8% ammonia loss in both soils which was exactly the half of that of NH_3 loss recorded from uncoated urea. Further, it was observed that as the urea coated with combination of copper sulfate and zinc sulfate positively pretentious to maximize N-efficiency.

Table 3 Rate of ammonia volatilization (%) from first to six week of observation

Treatments	Detail of treatments	Rate of NH_3 Volatilization %					
		week1	week2	week3	week4	week5	week6
T1	UCU 140 kg ha^{-1}	16.33 a	15.67 a	7.561 a	4.581 a	1.321 a	0.468 a
T2	CU + Zn 7kg ha^{-1}	8.267 b	7.677 b	4.221 bc	2.063 b	0.791 b	0.158 b
T3	CU + Zn 10 kg ha^{-1}	7.711 c	7.308 cd	4.073 c	1.948 b	0.751 b	0.086 cd
T4	CU + Cu 3kg ha^{-1}	8.372 b	7.473 bc	4.408 b	2.021 b	0.801 b	0.101 c
T5	CU + Cu 5kg ha^{-1}	7.832 c	7.275 cd	4.241 bc	2.056 bc	0.763 bc	0.066 cd
T6	CU + Zn 7 + Cu 3 kg ha^{-1}	7.737 c	7.225 cd	4.215 bc	1.956 bc	0.751 bc	0.051 cde
T7	CU + Zn 7 + Cu 5 kg ha^{-1}	7.681 c	7.358 cd	4.101 c	1.925 bc	0.748 bc	0.044 de
T8	CU + Zn 10 + Cu 3 kg ha^{-1}	7.628 c	7.158 d	4.041 c	1.721 c	0.715 c	0.033 de
T9	CU + Zn 10 + Cu 5 kg ha^{-1}	7.083 d	6.851 e	3.486 d	1.298 d	0.555 d	0.003 e

UCU=Uncoated Urea
CU=Coated Urea
Means with the different letters are significantly different at p=0.05 using Tukey's HSD

Earlier the Cu and the Hydroquinone were known as famous urease inhibitors [21]. Later on the hydroquinone was eliminated due to its controversial nature and its limited use. It enhanced the N-efficiency but at the same time it promotes the methane emission [22]. Whereas the Micronutrient copper serves as urease inhibitor is also an essential element for proper plant growth; hence coating with metal elements like copper minimizes ammonia loss [17]. Therefore the minimum ammonia loss was noticed from the coating urea as its coat contains the metals such as copper and zinc. Further it was manifested from the data that the ammonia loss (%) gradually reduced with time as can be seen in Figure 1 and at the end of sixth week the ammonia volatilization (%) reached to zero.



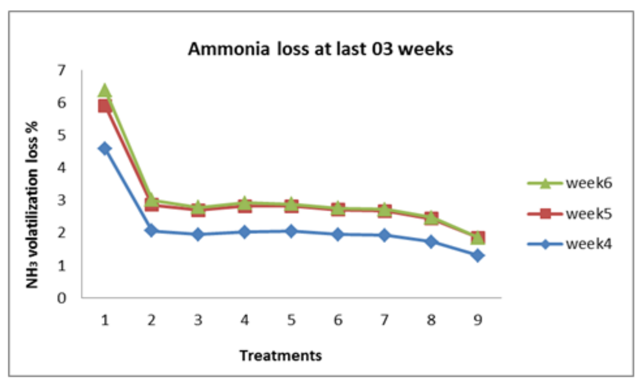


Figure 1 Effect of Cu and Zn coated urea on NH_3 volatilization throughout the six weeks

Ammonia volatilization losses (%) became negligible from Cu and Zn coated urea throughout the experiment. The concept to reduce the release rate of urea has designed to improve its efficiency and diminish the environmental pollution. Ammonia emission from the agricultural fields may cause damage to plant life [23] as some of its part converted into nitric acid (HNO_3), consequently cause acidic rains. Hence to prevent the environment degradation and improve nitrogen uptake of the plants by using coated urea. Therefore a slow release urea has introduced to provide the required amount of nutrients at particular time and demand [24-26]. Slow release urea contains a layer of coating which may extracted from the natural products; so can minimize hydrolysis rate in urea. The time and the amount of ammonia volatilization were almost same for both of the soils, and response of coated urea was significantly different to enhance N-uptake. As presented in the Figure 2, the effect of the applied coated urea on soil available Cu and Zn content was found significant.

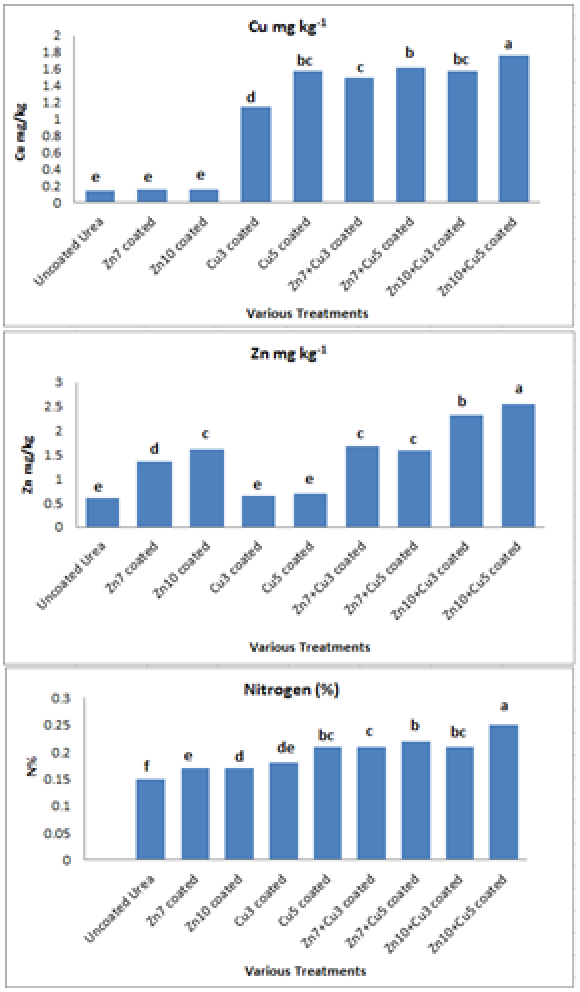


Figure 2 Effect of micronutrient coated urea on the concentration of (a) Cu, (b) Zn and (c) N after six weeks.

An average mean of both soils for the Cu and Zn content was markedly different from the un-coated urea. The soils before micronutrient coated application were found at critical level [14]; that improved after the application and slow release of micronutrient coated fertilizer. After the completion of the studies the soils were analyzed to evaluate the nutrient contents to assess the effect of micronutrient coated fertilizer on the availability of particular micronutrients. The results have exhibited that the critical values of Cu and Zn before micronutrient fertilizer application have converted into the significant quantity. The same trend was observed in nitrogen contents, the percent N showed the positive response towards coated urea and increased significantly in contrast to un-coated urea.

4.0 CONCLUSION

Studies concluded that combined Cu and Zn coated urea showed the positive response in reducing ammonia volatilization in both soils. The average ammonia volatilization loss in first two weeks was higher in both soils under uncoated urea applied treatment, which was gradually decreased with time and at last week; the ammonia volatilization was almost negligible. The loss from coated urea treatments were about half of that perceived from uncoated urea. Copper and Zn coated urea has preferably more available Cu, Zn and N contents in the soil at completion of the experiment.

Acknowledgement

The authors would like to express their gratitude towards the financial support of the Long Term Research Grant Scheme (LRGS) from Universiti Putra Malaysia (No. UPM700-1/3/LRGS).

References

[1] Patrick, H. and Michel. 2011. Conference Fertilizer outlook. Paper presented at the 79th IFA Annual Conference Montreal Canada.

[2] Gilbert, P. M. Harrison, J. Heil, C. and Seitzinger, S. 2006. Escalating Worldwide Use Of Urea–A Global Change Contributing To Coastal Eutrophication. *Biogeochemistry*. 77(3): 441-463.

[3] Khanif, Y. 1992. Ammonia Volatilization From Malaysian Soils Following Application Of Urea. *Pertanika*. 15, 115-115.

[4] Bremner, J., and Mulvaney, R. 1978. Urease Activity In Soils. *Soil Enzymes*. 501: 149-196.

[5] Kiran, J. K., Khanif, Y., Amminuddin, H., and Anuar, A. 2010. Effects Of Controlled Release Urea On The Yield And Nitrogen Nutrition Of Flooded Rice. *Communications In Soil Science And Plant Analysis*. 41, 811-819.

[6] Shaviv, A. 2005. Conference Controlled release fertilizers. Paper presented at the IFA International Workshop on Enhanced-Efficiency Fertilizers). 28-30.

[7] Chien, S. H. Prochnow, L. I. and Cantarella, H. 2009. Recent Developments Of Fertilizer Production And Use To Improve Nutrient Efficiency And Minimize Environmental Impacts. *Advances in Agronomy*. 102: 267-322.

[8] Jiang, Z. Zeng, Q. Tie, B. Liao, B. Pi, H. Feng, X. and Sun, Y. 2012. Ammonia Volatilization And Availability Of Cu, Zn Induced By Applications Of Urea With And Without Coating In Soils. *Journal of Environmental Sciences*. 24(1): 177-181.

[9] Azeem, B., KuShaari, K., Man, Z. B., Basit, A., and Thanh, T. H. 2014. Review On Materials &Amp; Methods To Produce Controlled Release Coated Urea Fertilizer. *Journal of Controlled Release*. 181: 11-21.

[10] Junejo, N., Khanif, M., Hanfi, M., Dharejo, K., and Wan, Z. 2013. Reduced Loss Of NH 3 By Coating Urea With Biodegradable Polymers, Palm Stearin And Selected Micronutrients. *African Journal of Biotechnology*. 10: 10618-10625.

[11] Cakmak, I. 2002. Conference Plant Nutrition Research: Priorities To Meet Human Needs For Food In Sustainable Ways. Paper presented at the Progress in Plant Nutrition: Plenary Lectures of the XIV International Plant Nutrition Colloquium). 3-24.

[12] Bell, R.W. and Dell, B. 2008. Micronutrients For Sustainable Food, Feed, Fibre And Bioenergy Production. (International Fertilizer Industry Association (IFA)).

[13] Fageria, N. K. Carvalho, G. D. Santos, A. B. Ferreira, E. P. B. and Knupp, A. M. 2011. Chemistry Of Lowland Rice Soils And Nutrient Availability. *Communications In Soil Science And Plant Analysis*. 42(16): 1913-1933.

[14] Jones, Jr, J. B. 2001. *Laboratory Guide For Conducting Soil Tests And Plant Analysis*. CRC press.

[15] Klute, A. and Page, A. L. 1996. Methods of Soil Analysis: Chemical methods. *American Society of Agronomy*.

[16] Perkins, H. F. 1970. A Rapid Method Of Evaluating The Zinc Status Of Coastal Plain Soils 1. *Communications in Soil Science & Plant Analysis*. 1(1): 35-42.gar, R. K. Crissey. 1982. J. Am. Chem. Soc. 104: 482.

[17] Junejo, N. Khanif, M. Y. Dharejo, K. A. and Abdu, A. 2013. Effect Of Hydroquinone And Copper Coated Urea On Ammonia Volatilization Loss And N Mineralization From Tropical Soil: Laboratory Study. *African Journal of Agricultural.* 8(18): 1983-1985.

[18] Fenn, L. and Kissel, D. 1973. Ammonia Volatilization From Surface Applications Of Ammonium Compounds On Calcareous Soils: I. General Theory. *Soil Science Society of America Journal*. 37(6): 855-859.

[19] Hafeezullah, B. 2010. Evaluation of Malaysian Rice Genotypes for Adaptability in Zinc Deficient Soil. Universiti Putra Malaysia.rino, J. B. Peri, R. J. Willey, G. Busca. 1996. *J. Catal.* 157: 482.

[20] Saleem, M. Khanif, Y. Fauziah, I. C. Samsuri, A. W. and Hafeez, B. 2010. Boron Status Of Paddy Soils In The States Of Kedah And Kelantan, Malasia. *Malasian Journal Of Soil Sciences*. 1: 83.94.

[21] Bremner, J. and Douglas, L. 1971. Inhibition Of Urease Activity In Soils. *Soil Biology and Biochemistry.* 3(4): 297-307.

[22] Malla, G. Arti Bhatia, H. Pathak, S. Prasad, Niveta Jain, and Singh, J. 2005. Mitigating Nitrous Oxide And Methane Emissions From Soil In Rice–Wheat System Of The Indo-Gangetic Plain With Nitrification And Urease Inhibitors. *Chemosphere*. 58(2): 141-147.

[23] Li, D. Watson, C. J. Yan, M. J. Lalor, S. Rafique, R. Hyde, B. Lanigan, G. Richards, K. G. Holden, N. M. and Humphreys, J. 2013. A Review Of Nitrous Oxide Mitigation By Farm Nitrogen Management In Temperate Grassland-Based Agriculture. *Journal Of Environmental Management*. 128: 893-903.

[24] Xiaoyu, N. Yuejin, W. Zhengyan, W. Lin, W. Guannan, Q. and Lixiang, Y. 2013. A Novel Slow-Release Urea Fertiliser: Physical And Chemical Analysis Of Its Structure And Study Of Its Release Mechanism. *Biosystems Engineering*. 115(3): 274-282.

[25] Liu, L. Kost, J. Fishman, M. L. and Hicks, K. B. 2008. A Review: Controlled Release Systems For Agricultural And Food Applications. Paper presented at the ACS symposium series. 992: 265-281.

[26] Ni, B. Liu, M. and Lü, S. 2009. Multifunctional Slow-Release Urea Fertilizer From Ethylcellulose And Superabsorbent Coated Formulations. *Chemical Engineering Journal*. 155(3): 892-898.