

Full Length Research Paper

Evaluation of coated urea for the effects of coating on the physical and chemical properties of urea fertilizer

Nasima Junejo^{1*}, M. Y. Khanif², M. M. Hanafi³, MD. Z. W. Y Wan⁴, K. A. Dharejo² and Arifin Abdu²

Institute of Tropical Forestry and Forest Product, University Putra Malaysia, Serdang, Selangor, Malaysia.
Department of Land Management, Faculty of Agriculture, Universiti Putra Malaysia, Serdang, Selangor, Malaysia.
Institute of Tropical Agriculture, Universiti Putra Malaysia, Serdang, Selangor, Malaysia.
Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, Serdang, Selangor, Malaysia.

Accepted 4 January, 2012

The experiment was conducted to evaluate the effects of biodegradable material and micronutrient coatings on the physical and chemical character of urea fertilizer. Six treatments were prepared by coating urea with agar, gelatine, palm stearin, CuSO₄ and Zn SO₄. Both micronutrients were used as urease inhibitor and all other materials were used as adhesive agents to keep micronutrient and nitrogen together on microsite. The treatments were labelled as, U (urea), UPSCu, UAGCu, UGCu, UCu and UCuZn. Each coated urea treatment was evaluated for coating thickness, thermal behaviour and chemical structure by using scanning electron microscopy, thermo-gravimeter and Fourier transform infrared (FTIR) techniques, respectively. The results of this study did not show significant differences among physical and chemical properties of urea treatments and accepted palm stearin and Cu coated urea which had been a modification in structural group. The study proved that addition of Cu and Zn with biodegradable material did not have adverse or severe effects on urea fertilizer properties.

Key words: Fourier transform infrared (FTIR), micronutrient, urea.

INTRODUCTION

Most of the modified urea has limited use due to their high cost and lack of availability (Ahmed et al., 2008). In addition, some of the urease inhibitors are phyto-toxic and are banned in most parts of the world (Watson, 2009). The use of micronutrients, such as Cu and Zn, as inhibitors was found effective to reduce ammonia loss from urea (Bremner and Douglas, 1971). Previous studies have shown that Cu and Zn in relatively small amounts are efficient in minimizing urea volatilization loss through urease inhibition. Furthermore, the Cu is an essential micronutrient that has the potential to increase crop yields, especially in Cu deficient soils (Purakayastha and Katyal, 1998; Reddy and Sharma, 2000).

Holding urea and a micronutrient together on a fertilizer microsite through the use of biodegradable materials and

natural by-products, such as coating or adhesive agents, proves to be a good replacement for synthetic materials, and polymers may be used to reduce environmental hazards. The concept of releasing more than one nutrient through one source is useful for improving the efficiency of chemical fertilizers (Mikkelsen and Behel, 1988). When such alternatives are applied, the modified urea is economically and environmentally useful in large agricultural fields.

Coated fertilizers are made to release their nutrient contents gradually and if possible, to coincide with the nutrient requirement of a plant. These fertilizers are made by coating the active soluble component with a membrane that serves as a diffusion barrier. Evaluation of the properties and its mechanism is essential for the selection of proper fertilizers for a given set of conditions or for the development of proper controlled release fertilizers (CRF) formulations. The efficiency of coating is affected by a number of factors, such as thickness,

*Corresponding author. E-mail: nasimajunejo85@gmail.com.

Table 1. Fertilizer treatments.

Urea treatment	Amount of Cu applied on coated urea (100 µg/g)
Urea (U)	0
Palm stearin + Cu coated urea (UPSCu)	5
Agar + Cu coated urea (UAGCu)	5
Gelatine + Cu coated urea (UGCu)	5
Cu coated urea (UCu)	5
Cu + Zn coated urea (UCuZn) (Cu:Zn)	Cu:Zn (5:5)

thermal behaviours and chemical structures of coating materials.

A number of compounds have been tested for their inhibitory effects to improve the efficiency of urea but the micronutrients have limited information. Most of these researches were conducted in the era of 1960's (Volk, 1961; Hyson, 1963; Waid and Pugh, 1967; Bremner and Douglas, 1971) on alkaline soils with high pH, and documented results are not suitable for the tropical acidic soils.

The purposes of this study were (1) to coat urea with biodegradable natural material (agar, gelatine and palm stearin) and (2) to characterize the coatings, for thickness, thermal stability, chemical structure and total N content. This evaluation will be helpful for further research and will give an understanding about the stability and reasons behind mechanism change, such as release pattern and inhibitions of urea fertilizer.

MATERIALS AND METHODS

Coating of urea with palm stearin

In three beakers, 7, 10 and 12 g of palm stearin were melted separately at the temperature of 60°C in a water bath. The entire palm stearin was melted completely and then left to cool for 5 min. Then, 100 g of urea was added in each beaker of palm stearin and were mixed with spatula. The palm stearin coated urea fertilizer was dried in the air vacuum desiccators for 48 h.

Coating of urea with agar and gelatine

One and two grams of agar and gelatine were weighed separately and each of them was dissolved in 100 ml of distilled water to prepare 1 and 2% solutions of agar and gelatine, respectively. 10 ml of each prepared solutions were applied on 100 g of urea fertilizer, using fluidized bed coating machine (Model, G70) at a set working pressure of 5 bar fixed by a locknut. Later on, the agar and gelatine coated urea fertilizer was dried by drying function of the machine.

Recoating of selected coated urea treatments with CuSO₄ and ZnSO₄

As mentioned in Table 1, six treatments were developed and named as control (only urea U), palm stearin and Cu coated urea (UPSCu), agar and Cu coated urea (UAGCu), gelatine and Cu

coated urea (UGCu), Cu coated urea (UCu) and micronutrient coated urea (UCuZn).

The three natural biodegradable-coated urea treatments were selected and recoated with CuSO₄ and ZnSO₄ at the rate of 5 µg for 100 g of coated urea. The treatments UPSCu, UAGCu, UGCu and UCu were recoated by the solution of CuSO₄. For this purpose, 0.013 mg of CuSO₄ was dissolved separately in 10 ml of water and applied as coating using fluidized bed coating machine on each treatment. The sixth treatment (UCuZn) was prepared by applying solution of CuSO₄ and ZnSO₄. The solution of CuSO₄ and ZnSO₄ were made by mixing 0.013 mg of both chemicals, dissolved in 10 ml of distilled water. The quantities of chemicals were selected on the bases of previous research (Bremner and Douglas, 1971).

Fourier transforms infrared spectral analysis (FT-IR)

The Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Perkins Elmer 1725X FT-IR spectrophotometer. Pellets were prepared using potassium bromide. Scanning was carried out from 400 to 4000 cm⁻¹ wavelength.

Thermo gravimetric and differential thermo gravimetric analysis

Thermo gravimetric (TGA) and differential thermo gravimetric analysis (DTG) of the samples were analyzed using Due Pont instruments (Model 990 thermal analyzer and Model 951 thermo gravimetric analyzer). About 10 mg of the sample was weighed and its weight loss was determined when it was heated from 30 to 900°C.

Scanning electron microscopy

Samples of coated and uncoated urea were examined for the thickness of the coating material. Initially, the coated fertilizers granule was cut into half using a blade. The cross section of the coated urea was placed on the slide. The samples were treated with ammonia oxalate and sputtered with a very thin layer of gold for about 3 min, using a coating machine called a sputter coater as described by Echlin (2009). The samples were then viewed using scanning electro-microscopy (SEM). The magnification ranged from 25 to 500x.

Elemental analysis of coated and uncoated urea

The elemental analysis was carried out for the determination of carbon, hydrogen and nitrogen and sulphur content in coated and uncoated urea to observe the effect of coating procedure on elements ratio present in urea. The analysis was conducted using elemental analyzer Perkin Elmer CE440.

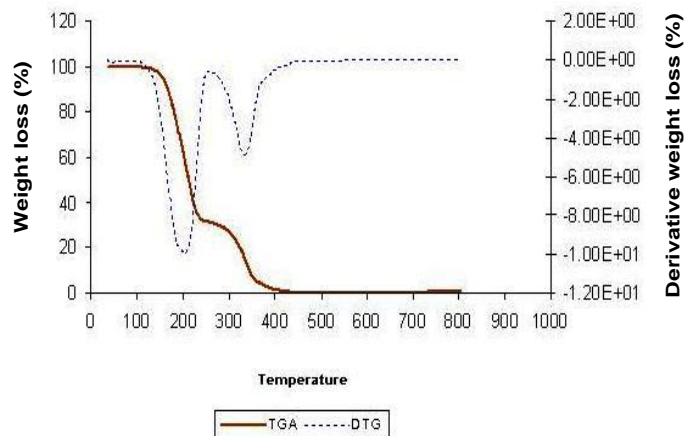


Figure 1. TGA thermogram urea.

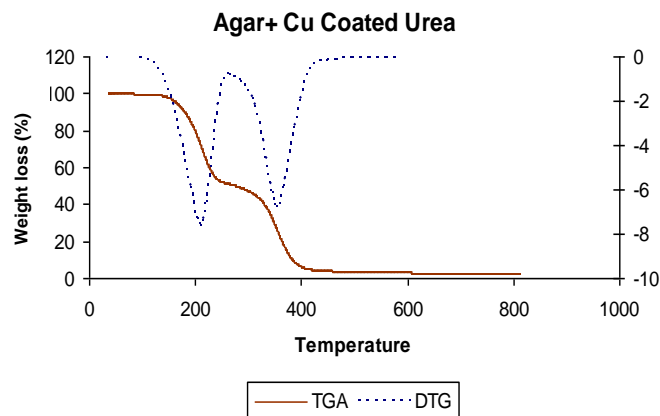


Figure 4. TGA and DTG thermogram of agar and Cu coated urea.

Gelatin coated urea

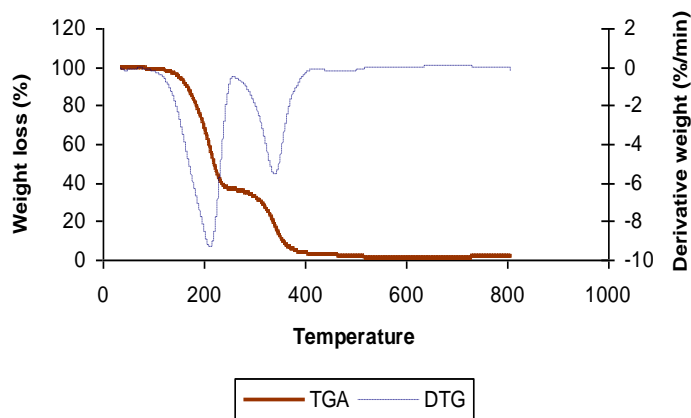


Figure 2. TGA and DTG thermogram of gelatine and Cu coated urea.

Palm stearin coated urea

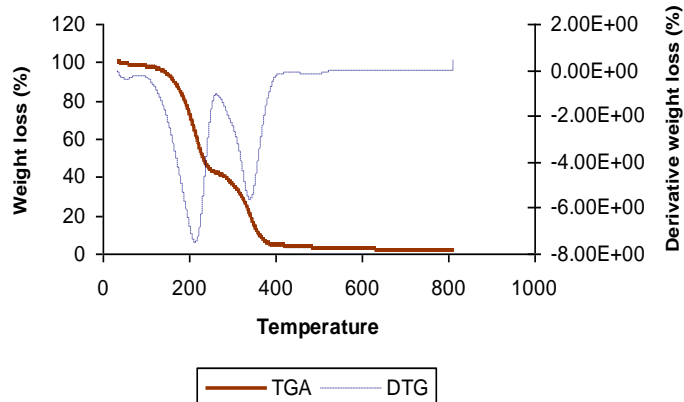


Figure 3. TGA and DTG thermogram of palm stearin and Cu coated urea.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA)

In case of urea, two-stage decomposition was observed with the first stage starts at 120 to 250°C, undergoing its main reaction which ends at 225°C with a weight loss of 60.8%. At the second stage, 39% of the remaining urea decomposed at the temperature of 390°C (Khattab, et al 1984). The thermogram is similar for the coated urea. Its' TGA analysis did not show significant variation after coating in thermal stability of urea. It is due to the minimum amount or due to same degradation temperature of coating which is not detectable (Figures 1 to 6).

Scanning electro-microscopy and element analysis

The coating layer of the material used is indicated by the outer layer of the fertilizer granule on SEM photograph (Figure 7). The thickness of the coating material, covering urea granule, was estimated using SEM micrograph and dividing with the scale of the instrument. The thickness of the coated urea varied and invisible except gelatin and agar coated urea (Table 2). It was reported that the thickness of coating fertilizers affects the release pattern of nitrogen from fertilizers (Junejo et al., 2009).

In elemental analysis, 2% reduction in total N was observed for all treatments of coated urea as compared to uncoated urea (Table 2). It is due to the coating process, while coating the urea, granule undergoes; spraying, wetting and drying process which may cause some loss of nitrogen (Hanafi et al., 2000).

Fourier transforms infrared spectral analysis

The spectra of urea, micronutrient coated urea, Agar + Cu coated urea gelatin + Cu coated urea fertilizer and Cu

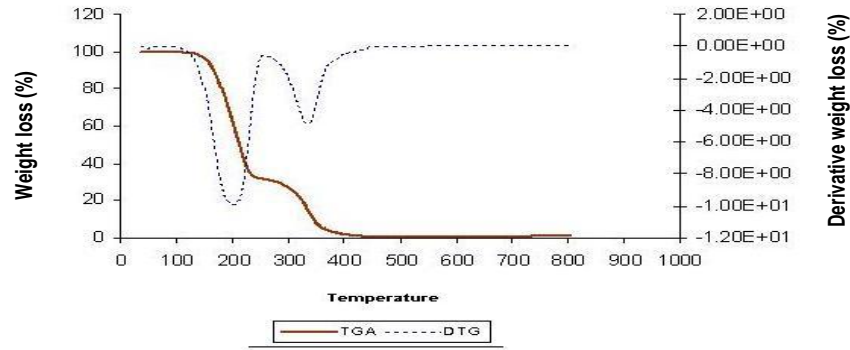


Figure 5. TGA and DTG thermogram of Cu coated urea.

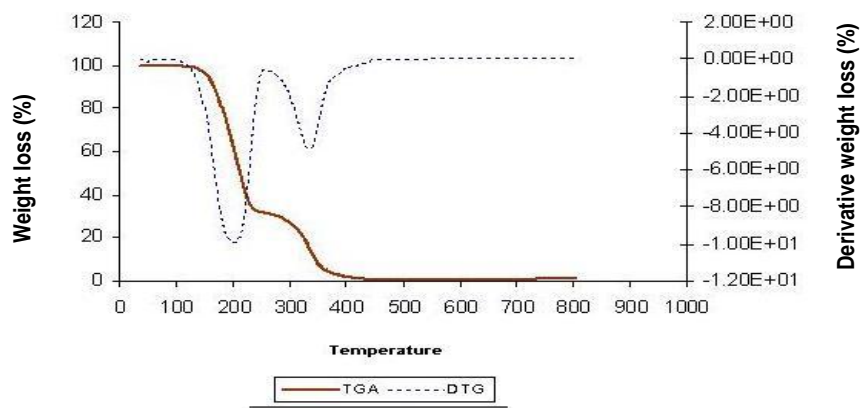


Figure 6. TGA and DTG thermogram of Cu and Zn coated urea.

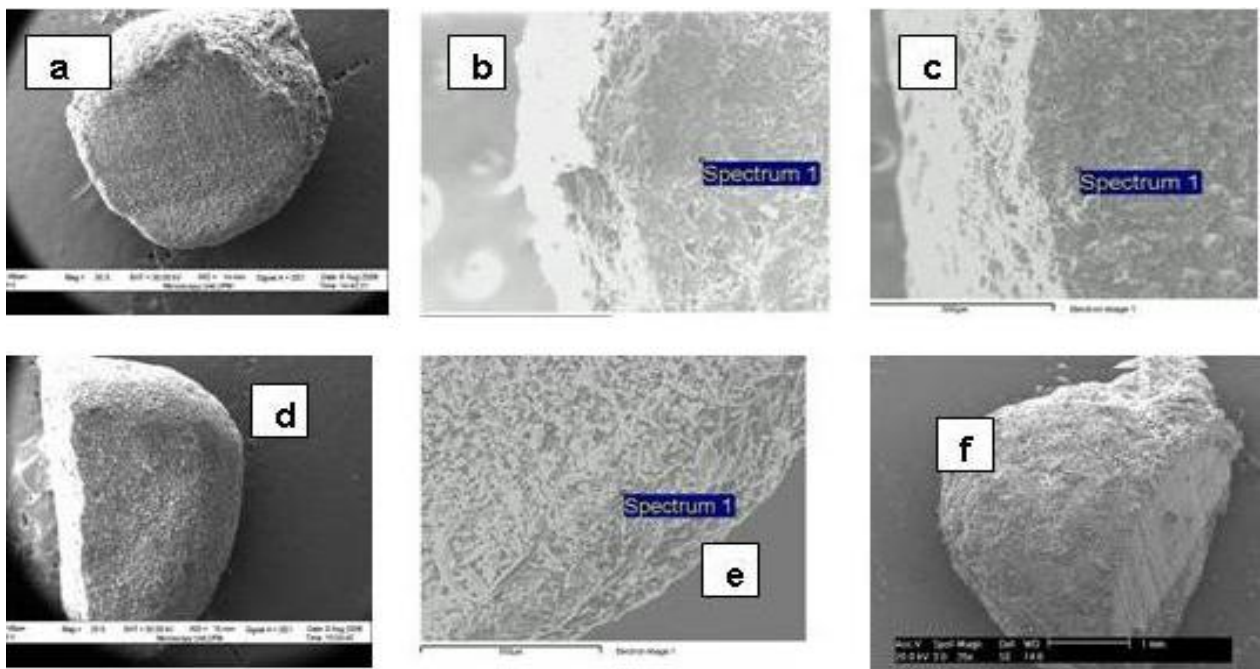


Figure 7. SEM micrograms; (a) palm stearin Cu coated urea, (b) Urea, (c) Cu coated urea, (d) agar Cu coated urea, (e) micronutrient coated urea, and (f) gelatin Cu coated urea.

Table 2. Physical and chemical properties of coated fertilizer.

Treatment	N (%)	Thickness coating (μm)	Colour
Urea	46 ^a	0.0 ^d	White
UPSCu	44 ^b	0.3 ^b	Light blue
UAGCu	44 ^b	0.4 ^a	Brown
UGCu	44 ^b	0.2 ^c	Light blue
UCu	44 ^b	0.01 ^d	Light blue
UCuZn	44 ^b	0.02 ^c	Light blue

Means with different letters are significantly different at $P < 0.05$.

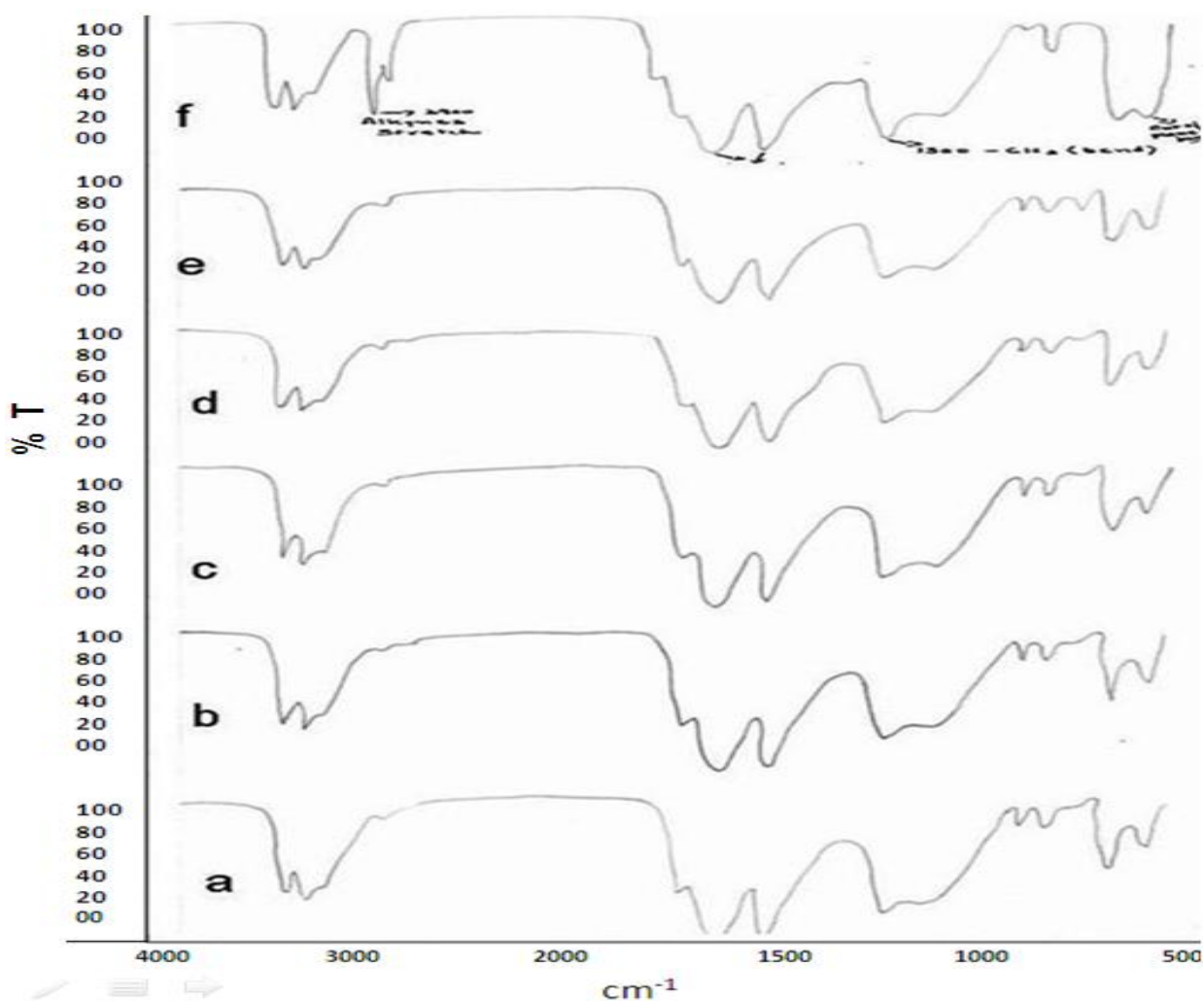


Figure 8. FT-IR spectrum of (a) urea, (b) micronutrient coated urea, (c) Agar+ Cu coated urea, (d) Gelatin + Cu coated urea, (e) Cu coated urea, and (f) Palm stearin +Cu coated urea.

coated urea showed similar strong peaks of amide group, N—H group at 3500 cm^{-1} , indicating the presence of urea molecule which belong to urea compound. The double peaks of C=O bonds at 1600 and 1700 cm^{-1} , followed this peak. The peak at 1350 cm^{-1} (Figure 8) shows the

sulphate in the fertilizer. There were no significant variation at $P < 0.05$ in peaks observed in the uncoated urea spectrum, indicating there is no chemical interaction between the urea and the coating materials. The spectrum (Figure 8f) of palm stearin and Cu coated urea,

indicating strong peak was at 2920 cm^{-1} , that is, related to C-H bond of alkenes. The strong peaks were found at 1600 and at 1150 cm^{-1} indicating the presence of the C=O and ester group, respectively. The same type of results, for other polymer coatings was observed by Tomaszewska et al (2002).

Conclusion

The elemental analysis showed 2% reduction in N percentage of urea for coated urea treatments (44%) as compared to control (uncoated urea 46%) which was attributed to coating procedure, consisting on coating urea with selected coating materials. The agar and gelatine coated urea contained 0.4 and $0.2\text{ }\mu\text{m}$ coating layer which was thicker than other coated urea treatments.

The FT-IR results showed that the uncoated and coated urea fertilizer contains various functional groups, such as alkenes, ester group, amine group and hydroxyl groups. The obtained results did not show any significant differences at $P > 0.05$ among the coated and uncoated urea treatments functional groups, due to minimum amount of coating material. All type of coated and uncoated urea has the same spectrum except palm stearin and CuSO_4 coated urea. The same results were found in analysis of TGA due to similar degradable temperature of urea and coating materials, which was not detectable to make any difference between coating thermal behaviour and stability.

REFERENCES

- Ahmed OH, Hussain AH, Ahmad MH (2008). Ammonia volatilization and ammonium accumulation from urea mixed with zeolite and triple super phosphate. *ACTA Agr. Scand*, B-S 58: 182-186.
- Bremner JM, Douglas LA (1971). Inhibition of urease activity in soil. *Soil Biol. Biochem.*, 3: 299-307.
- Echlin P (2009). Handbook of sample preparation for scanning electron microscopy and X-ray micro analysis: Choice of coating material. Spring link publisher, pp. 265-267.
- Hanafi MM, Eltaib SM, Ahmad MB (2000). Physical and chemical characteristics of controlled release compound fertilizer. *Eur. Polym. J.*, 36: 2081–2088.
- Hyson AM (1963). Urea and dithiocarbamates in fertilizers. U.S. Patent Office 3,073,694 *Chem. Abstr.*, 58: 959011.
- Junejo N, Hanafi MM, Khanif YM, Wan Yunus WMZ (2009). Effect of Cu and palm stearin coatings on the thermal behaviour and ammonia volatilization loss of urea. *Res. J. Agric. Biol. Sci.*, 5(5): 608-612.
- Khattab IF, Nariman A, Al-Rajhi, Abdel Kader SA (1984). Thermal analysis of urea, fatty acids, and their Adducts. *Thermoch. Acta*, 73: 47-66.
- Mikkelsen RL, Behel AD (1988). Gelled fertilizers as slow/delayed nutrient sources. In: *Agronomy Abstract*, pp. 303. Am. Soc. Agron. Madison, WI., p. 303.
- Purakayastha TJ, Katyal JC (1998). Evaluation of compacted urea fertilizers prepared with acid and non-acid producing chemical additives in three soils varying in pH and cation exchange capacity. NH_3 volatilization, *Nutr. Cycl. Agroecosyst.*, 51: 117-121.
- Reddy D, Sharma KL (2000). Effect of amending urea fertilizer with chemical additives on ammonia volatilization loss and nitrogen-use efficiency. *Biol. Fert. Soils*, 32: 24–27.
- Tomaszewska M, Jarosiewicz A, Karakulski K (2002) Physical and chemical characteristics of polymer coatings in CRF formulation. *Desalination*, 146: 319–323
- Volk GM (1961). Gaseous loss of ammonia from surface applied nitrogenous fertilizers. *J. Agr. Food Chem.*, 9: 280-283.
- Waid JS, Pugh KB (1967). Acetohydroxamate inhibition of the urease activity of an acid, soil. *Chem. Ind.*, pp. 71-73.
- Watson CJ (2009). Urease activity and inhibition - Principles and practice. *Int. Fert. Soc. Proc.*, p. 454.