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New Preparation, Characterization and Application for Coated Urea using Aswan Red Clay

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ABSTRACT

To enhance the effectiveness of urea fertilizers, a new coated slow-release fertilizer was developed using Aswan Red Clay (ARC) and a binder material called chitosan a biodegradable polymer was used to improve the property of urea. Characterizations of slow release of the urea granules were made using Scanning Electron Microscopy technique and energy dispersive X-ray analysis. Refractive Index method used for determine the rate of releasing. Ammonia volatilization was estimated by using the forced-draft technique. The static release experiment showed that the urea coated by Aswan Red Clay (ARCCU) gave a release of 9.78% at the first day and 95.36 at 24 day, in the same condition. The results of ammonia that volatized during 6 weeks showed that the total losses of ammonia gas for uncoated urea(UCU) and coated urea was 59.54% and 43.33%, respectively which main that the coating of urea is most costly in application.

INTRODUCTION

The fertilizer industry faced growing challenges regarding the development of improved products that result in greater nutrient use efficiencies, especially regarding nitrogen sources (Cancellier *et al*., 2016). Moreover, the industry should aim to minimize environmental impacts, avoid mineral leaching into water table or volatilization, and minimize the emissions of N oxides (a greenhouse gas) (Novoa and Tejeda, 2006; Stehfest and Bouwman, 2006; Vilain *et al*., 2014). Urea is considered one of the main source of N in agriculture because of it contains high 46.4% nitrogen added to its low cost in production (Ariayathilaka *et al*., 2008). Because of it is highly soluble in water Lundt (1971) said that, nearly 70-75% of the nitrogen of urea not be absorbed by plants and lost in high rainfalls areas . It often causes dangerous environmental pollution as well as economical cost (Kent and Riegel's, 2007) through volatilization of ammonia and leached quickly before the plants uptake to assimilate it. So, it had been suggested many technology that developing and economizing of urea using . Slow-release fertilizers (SRF) were designed to slow the speed of its release and to coincide with the requirements of nutrient-elements for the plant. This process include coating water insoluble inorganic materials and organic polymers as a binder to the granule (Wang *et al*., 2014). According to (Du *et al*., 2007) (SRF) could decrease the ammonia volatilization and N leaching to produce a green environment. Also Zhang *et al*., (2014) studied the effect of urea coated by graphene film on many crops and showed that this coating technology gave a great promise for producing of a clean environment and increase the crop yield . (Zou *et al*., (2009) studied the effect of coating by different concentrations of inorganic compounds on the releaseof urea. Their results showed that 5% of of coating gave a better characteristics of slow release. Vashishtha *et al*. (2010) found that on coating urea with gypsum decreased the losses of nitrogen through the leaching process. Also it helped to increase both the crushing strength and bulk density and lowering of caking tendency. This leaded to improve the handling properties of the urea fertilizer. Many research studied the coating of urea by silica with polyurethane (Li *et al*., 2016), or by diatomite with biodegradable polymers Xanthan Gum (Mukerabigwi *et al* 2015) to improve its utilization and efficiency for the plants. Another inorganic materials such as phosphate rock , ziolite, clay and bentonite were used as coating materials in many researches and obtained good results (Pan *et al*., 2006 and Zou *et al*., 2006). Chitosan material is a natural polysaccharide and extracted from the exoskeleton of the sea crustaceans (crabs, prawns, lobsters, shrimps etc.) (Chopra and Ruhi, 2016). chitosan is attractive due to its non-toxicity and high adhesion to the surface so it was used as a biodegradable binder for the granules and in the same time it is a non-toxic material for environment (Wu and Liu, 2008, Chassary *et al*., 2004 and Wu *et al*., 2008).

This study aims to synthesize an ecofriendly and low cost urea fertilizer coated with chitosan material as a binder and Aswan Red Clay (ARC) powder. The different properties of the product were examined and was compared with uncoated urea

Experimental:-

Materials:-

Urea granules were supplied from Abu Ker Company for Fertilizers and Chemical Industries, Alex. The N content was 46.45% and sizes ranging from 1.2 to 3.50 mm. Aswan Red Clay was collected from Aswan area. Chitosan powder was supplied by the Sigma-Aldrich Inc.

Methods:-

Producing of (ARCCU) Granules:-

(ARCCU) granules was prepared using the rotary drum machine by the following method. A certain weight of urea granules(5 kg) was placed inside the rotary drum. The diameter of the drum was of 27.5 cm where the depth was 45 cm . It was positioned at an angle range from 25^{o} to 35^{o} to the horizontal according to Blouin *et al*.(1971). Then, Chitosan after treated by acetic acid was sprayed over the granules . Then a certain weight of (ARC) powder (720 gm)was sprayed over the granules. When we made sure that the granules became homogeneous and a coating film formed around the granules the product was collected for analysis. The parameters of the operation are listed in Table 1.

Table 1. Parameters of oeration

Speed in minut	30- rpm
Total Time for one Batch	25-32 min
Drying Temp.	٦5 – ٧5 ˚C

Determination of Coating %.

Coating % was determined by weight 50 g of coated granules and crushed them . Then mixed with 100 ml of water. The solution was filtered and the remaining insoluble was dried and weight (Salman, 1988). The total coating % is determined as following.

Percentage of total coating = (weigh of insoluble (g) /50) *x* 100

Determination of Nitrogen % .

The N percentage of the urea before and after coating can be estimated by Kjeldahl method (Kjeldahl, 1883). In this method sulfuric acid was added to the sample to produce ammonium sulfate. The N content is estimated by the hydrolysis of ammonium sulphate .The nitrogen % of coating urea can be estimated as the following : N %= 46.45(100 - % coating) / 100

The results are listed in table (2)

Table 2. Nitrogen % and coating % of urea

Urea sample	Coating, %	Urea, %	Nitrogen, %
Before coating	0.00	99.6	46.45
After coating	14.91	85.89	39.89

Morphology of the surface and elemental analysis:-

The scanning electron microscopy (SEM) of model Quanta 250 FEG with JEOL microscope was used to study the morphology of the outer surface of the granules

Determination of Urea Release:-

Weight 50 g the coated sample and put with 250 ml of distilled water in an erlenmeyer flask and then is sealed. The refractive index (RI) was measured by using the Baush& Lomb Abbe- 3L Refractometer. The equipment was calibrated every day by water and at 37°C. The measurement process was continued through 24 days

Ammonia Volatilization from Uncoated and Coated Urea:-

Ammonia volatilization was measured for uncoated urea (UCU) and Aswan red clay coated urea(ARCCU) fertilizers using the forced-draft technique for 6 weeks. A closed-dynamic air flow (aerobic) system (Fan *et al*. 2011). The closed dynamic air flow (aerobic) system contained both an air-exchange chamber (500 ml Erlenmeyer flask) and a trapping flask (250 ml Erlenmeyer flask); the stopper on each flask was fitted with an inlet and outlet facility. The inlet was linked to an air pump, while the outlet was connected by polyethylene tubing to the trapping flask. The trapping flask was fitted with a glass distribution rod, which was immersed in a trapping solution of 75 ml of 2% boric acid-mixed indicator to capture the release of NH_3-N. The chamber was filled with 300 g of dried soil. The soil was wetted and the equivalent of 400 µg/g of urea fertilizer was added to each soil sample. The extracted solution was titrated with a solution of 0.1 N HCL once each week until 6 week.

RESULTS AND DISCUSSION

Morphology of the Surface and Elemental Analysis:-

granules were collected randomly and examined under optical microscope at magnifications of 2000X. Sample images in Fig. 1(from A to -D) shows the uncoated (UCU) and coated urea (ARCCU). Fig 1 (C and D) shows clearly the change in surface morphology due to the coating which gave more uniform surface as compared to uncoated Fig. 1(A and B) which formed an irregular surface like a membrane with disordered shape. EDX analysis showed no remarkable presence of any further elementals ruther than the pure urea Fig2 (A); while the elemental composition of Aswan Red Clay was attained on surface ofcoated urea Fig 2(B)

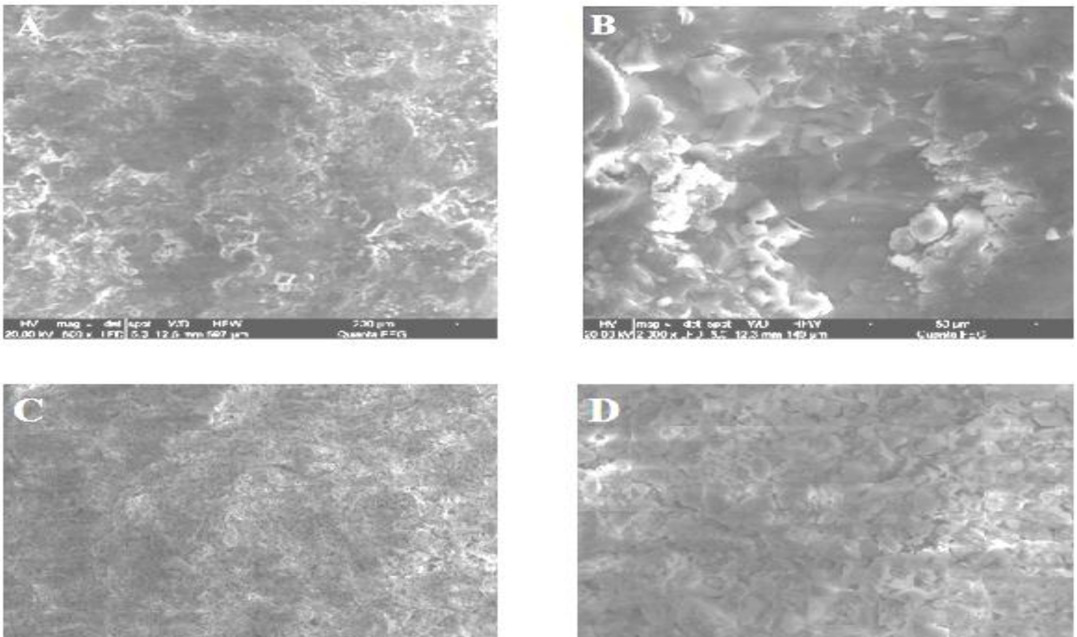

Figure 1. Optical Images of UCU (A, B) and (ARCCU) (C,D) at Magnifications 2000x

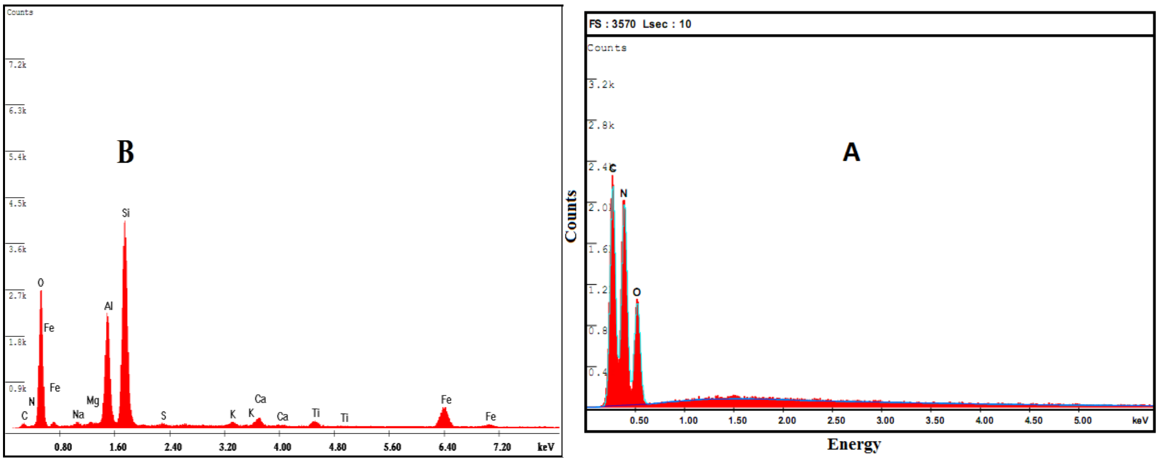

Fig. 2. EDX Diagram of (UCU) (A), and (ARCCU) (B) Materials.

Release Urea from coated urea(ARCCU):-

The refractive index technique is used to measure the concentration of urea in solution directly which possesses advantages, like fast analysis, high efficiency, without any chemicals or reagent consumped as well as pollution-free (Xie *et al*., 2011).Urea release % and N content for coated urea was estimated and compared with (UCU). The results are listed in the Table 3 and shown in figure (3) that shows a variation in urea release of (UCU) and ARCCU at various time. The results indicated 100% and 9.78 % released from(UCU) and ARCCU resectivily in the water during the first day. The uncoated urea released all its nitrogen in the first day (Muslimet *et al*., 2015) and the maximum of release appeared after 24 day which gave 95.36% for (ARCCU). Similar results were obtained by (Shaohua *et al*. 2012).

Table 3. Urea Released of Coated Urea and Uncoated within 21- Day.

Sample	Urea Release, %	
	1 day	24 day
UCU	100	
ARCCU	9.78	95.36

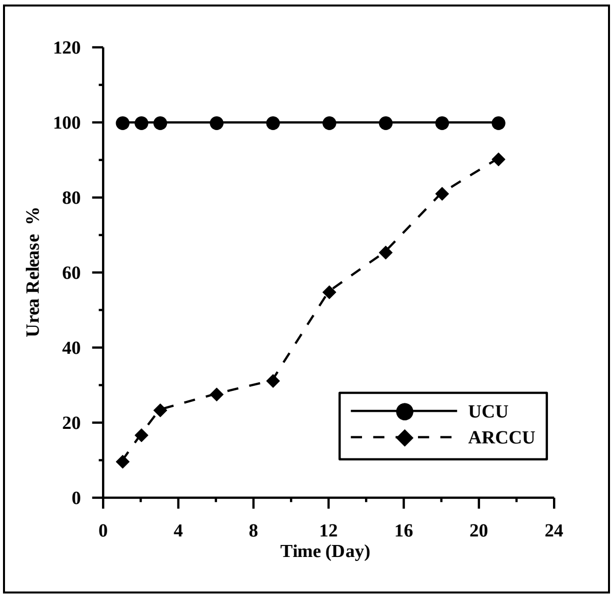

Fig. 3. Urea Release % of Uncoated and Different Coated Urea.

Ammonia Volatilization from Uncoated and Coated Urea:-

Ammonia volatilization or emission from agricultural fields not only decreases N uptake efficiency and increases production costs but also causes environmental concerns ((Fan *et al*., 2011). The cumulative percent of NH_3 losses are shown in Figure(4). The NH_3 loss of uncoated urea (UCU) was consistently higher than that of Aswan red clay coated urea (ARCCU). The percent of NH_3-N loss for UCU and (ARCCU) was 59.5 and 43.8 % after 6 week, respectively. The coated urea effectively reduced the ammonia loss in comparison to the uncoated urea. Similar results were obtained by (Lin *et al*., 2007; Zhaohui *et al*., 2012)..

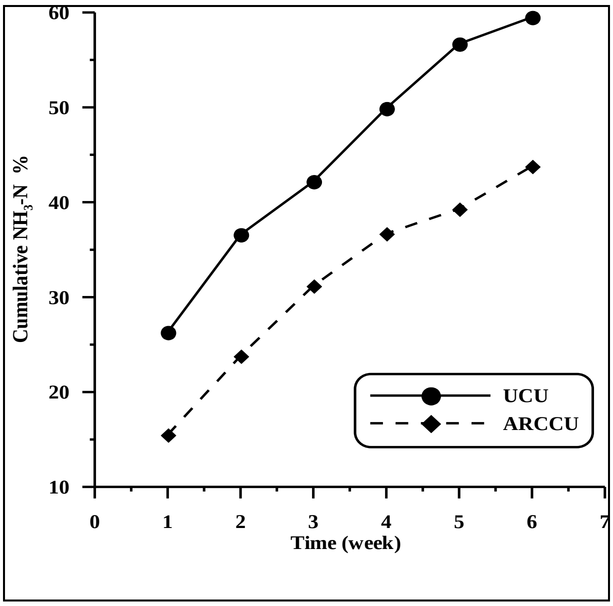

Fig. 4. The Cumulative NH3-N Loss from (UCU) and (ARCCU).

Le Monte *et al*. (2016) found thatammonia loss was always significantly lower for coated urea than uncoated urea with a range of 64 to 57.4% less volatilization and a highly significant 30.0% average. The addition of urea to soil increases the soil pH and microbial activity, which increases its hydrolysis in the soil as well as its affected to ammonia volatilization losses. When urea was encapsulated by coatings, it delayed its reaction in the soil, which positively affected its loss from the soil(Junejo *et al*., 2011). It is evident that the efficacy of (ARCCU) coated urea fertilizer is higher than that of common (UCU). Similar results were obtained by (Liao *et al*,. 2016)

4. Application:-

Application of slow release urea (ARCCU) and fast release urea (UCU) on yield of maize crop at harvest during 2014/2015 summer season and the statistical analysis done by ANOVA using least significant difference at P ≤ 0.05 as well reveled the following. Data in table 4 show that, the application of different source of (ARCCU and UCU) gives high significant increase grain yield than control (1.7 ton / fad) while uses (ARCCU) as a source of nitrogen fertilizer gives the high of grain Yield (3.45 ton /fad) than treatment of UCU (3.23 ton /fad), Similar finding were obtained by (Fan *et al*., 2011). Guan *et al*. (2014) was found attapulgite clay coated fertilizer increased the grain yield by 15 - 18%.

Table 4. Effect of ARCCU and UCU Fertilizers on Total Grain Yield.

Treatments	Total Grain Yield (Ton /Fad)
Control	1.71
UCU	3.23
ARCCU	3.45
Significance	**
LSD 0.05%	0.28

CONCLUSION

A new (SRF) was developed by coating urea with Aswan red clay (ARCCU) and biodegradable chitosan. The release of (ARCCU) gave of 9.7 at the first day and 90.36% at 24 days in the same condition. The ammonia % loss for UCU and ARCCU was 59.5 and 43.8 %, respectively. Also, significant increase in grain of maize crop by using Aswan red clay coated urea (ARCCU) than those of common urea (UCU).

Therefore, this approach showed a promise in the utilization of abundant, low cost, and natural resource such as Aswan Red Clay and polysaccharides as chitosan in the production of the coating material, which could significantly reduce the production cost and make the technique quite ecofriendly.

REFERENCES

Ariyathilaka, G. A. Buddhika, A. N. and Karunarathana, K. D. (2008). Urea Manufacturing Plant, Sri Lanka, 2-30.

Blouin, G. M.; Rindt, D. W and Moore, O. E. (1971). Sulfur Coated Fertilizers for Controlled Release Pilot Plant Production. J. Agr. Food Chem., 19(5), pp 808-

Cancellier, E. L; Silva, D. R; Faquin, V; Gonçalves, B. d; and Spehar, C. R (2016). Ammonia volatilization from enhanced-efficiency urea on maize in brazilian cerrado with improved soil fertility, Ciência e Agrotecnologia 40(2), 133-144.

Chassary P, Vincent T, Guibal E (2004). Metal anion sorption on chitosan and derivative materials: a strategy for polymer modification and optimum use. React Funct Polym, 60:137–49.

Chopra, H and Ruhi, G (2016) Eco friendly chitosan: An efficient material for water purification, The Pharma Innovation Journal, 5(1): 92-95.

Du, J. J.; Wu, Y. L.; Tian, J. L.; Wang, Y. Q. and Cui, Y. D. (2007). “Effect of Several Slow-Release Fertilizers on Decreasing Ammonia Volatilization and N Leaching,” Journal of Soil and Water Conservation, vol. 21, No. 2, pp. 49–52.

Fan, X. H.; Li, Y. C and Alva, A. K (2011). Effects of Temperature and Soil Type on Ammonia Volatilization from Slow-Release Nitrogen Fertilizers, Soil Science and Plant Analysis, 42:10, pp.1111-1122,DOI:10.1080/ 00103624. 2011.566957.

Guan, Y; Song, C; Gan, Y and Li, F (2014). Increased Maize Yield Using Slow-Release Attapulgite Coated Fertilizers, Agron. Sustain. Dev. 34:657–665.

Junejo, N;Khanif, M. Y;Hanfi, M. M;Dharejo, K.A and Wan, Z. W. Y(2011). Reduced loss of NH3 by coating urea with biodegradable polymers, palm stearin and selected micronutrients,African Journal of Biotechnology Vol. 10(52), pp. 10618-10625.

Kent, A. and Riegel's (2007). Handbook of Industrial Chemistry and Biotechnology, 11th ed.,. 1&2, Verlag, Springer.

Kjeldahl, J. (1883) A new Method for The Estimation of Nitrogen in Organic Compounds, Z. Anal. Chem., vol. 22,pp 366.

LeMonte, J. J, Jolley, V. D, Summerhays, J. S,Terry, R. E, Hopkins, B. G (2016).Polymer Coated Urea in Turfgrass Maintains Vigor and Mitigates Nitrogen's Environmental Impacts. PLoS ONE 11(1): e0146761.

Liao, Z. W.; Liu, K. X. and Wang, D. H. (2001). Develop slow Release Fertilizer with Chinese Characteristics. Review of China Agr. Sci. and Tech., 3, 71-75.

Lie, L; Sun, Y; Cao, B; Song, H; Xiao, Q and Yi, W (2016). Preparation and performance of polyurethane/mesoporous silica composites for coated urea, doi: 10.1016/j.matdes.2016.03.043

Lundt, O. R. (1971). Controlled Release Fertilizers Achievments and Potential" J. Agro. Food Chem. vol- 5- pp797- 800.

Mikkelesen, R. L.; Williams, H. M.; and Behel, A. D. (1994). Nitrogen Leaching and Plant Uptake from Controlled Release Fertilizaers. Fert. Res.,Vol 37:pp 43-50.

Mukerabigwi, J. F; Wang, Q; Ma, X; Liu, M; Lei, S; Wei, H; Huang, X and Cao, Y (2015). Urea fertilizer coated with biodegradable polymers and diatomite for slow release and water retention, J. Coat. Technol. Res., 12 (6) 1085–1094.

Muslim, S.; Salman, Fitriani, L.; Netty Suharti.; Erizal, Z.; Febriyenti .; Aldi Y and Akmal, D. (2015). Use of Bioblend Polystyrene/Starch for Coating Urea Granules as Slow Release Fertilizer, J Chem Pharm Res. 7 (11): 478-484.

Novoa, R. S; Tejeda, H. R (2006). Evaluation of the N_2O emissions from N in plant residues as affected by environmental and management factors. Nutrient Cycling in Agroecosystems, 75:29-46.

Pan, Y. F.; Xie, H. L.; Zhou, C. H.; Li, J.; Ge, Z. H and Li, X. N. (2006). Preliminary Study on Features of Controlled Release of Bentonite-Coated Compound Fertilizers. Journal of Zhejiang Univ. of Tech., 34, 393-397.

Salman, O. A (1988). Polymer Coating on Urea Prills To Reduce Dissolution Rate, J. Agric. Food Chem, 36, 616-621.

Shaohua, Qin.; Zhansheng, Wu.; and Chun, L. (2012). Synthesis& Characterization of Slow-Release Fertilizer with Water Absorbency: Based on Poly (acrylic amide)/Na-Bentonite Journal of Applied Polymer Science, Vol.10, No10.

Stehfest, E; Bouwman, L (2006). N_2O and NO emission from agricultural fields and soils under vegetation: Summarizing available measurement data and modeling of global annual emissions. Nutrient Cycling in Agro ecosystems, 74:207-228.

Vashishtha, M; Dongara, P and Singh, D (2010). Improvement in Properties of Urea by Phoshogypsum Coating. International Journal of ChemTech Research, Vol.2, No.1, pp 36-44.

Vilain, G; Garnier, J; Decuq, C and Lugnot, M (2014). NO production from experiments: Denitrification prevails over nitrification. Nutrient Cycling in Agro ecosystems, 98:169-186.

Wang, X.; Lü, S.; Gao, C.; Xu,.; Liu, M. and Wu, L. (2014). "Highly Efficient Adsorption of NH3 onto Palygorskite Nanocomposite and Evaluation of its Recovery as Slow-Release Fertilizer," ChemEng. J., vol. 252, pp. 404–414.

Wu, L. and Liu, M. (2008). Preparation and Properties of Chitosan coated Compound Fertilizer and Water-Retention. Carbohydr. Polym. Vol.72 pp 240–247.

Xie, L.; Liu, M.; Ni, B.; Zhang,X and Wang Y (2011).Chem Eng J; 167: 342-8.

Yang, Y. C.; Zhang, M.; Zheng, L.; and Geng, Y. Q (2011). Controlled Release Urea Improved N Use Efficiency, Yield and Quality of Wheat. Ag. vol. 103 pp479–485.

Zhang, M.; Gao, B.; Chen, J.; and Chen, H. (2014). "Slow-Release Fertilizer Encapsulated by Graphene Oxide Films,"Chem.Eng. J.,vol. 255, No.1, p.17- 19

Zou, H. T.; Zhang, Y. L.; Huang, Y.; Yang, Y and Yu. N. (2006). Inhibiting Effect of N-volatilization from Different Coated Fertilizers. Chinese J of Soil Scie, vol:37 pp(519-521).

Zou, H. T.; Wang, Y. S.; Song, H. W. and Hany. Y, (2009). "The production of Organic-Inorganic Compound Film-Coated Urea and The characteristics of its Nutrient Release," Agricultural Sciences in China,vol. 8, No. 6, pp. 703–708.

إعداد وتوصيف وتطبيق ليوريا جديدة مغلفة بطفلة أسوان الحمراء كسماد بطيئ الأنطلاق

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لتعزيز فعالية سماد اليوريا، تم تطوير أسمدة بطيئه الاطلاق بأستخدام طفله أسوان الحمراء مع الشيتوزان كمواد مغلفة لتحسين ميكانيكية الأطلاق وأختزال الأمونيا المتطايرة. تم دراسة خصائص ومميزات اليوريا قبل وبعد التغليف بأستخدام الماسح الالكترونى المزود بجهاز اكس (SEM- EDX). أما تاثير التغليف على إطلاق اليوريا المغلفة فقد تم دراستة بأستخدام معامل الأنكسار (refractive Index)) حيث أعطت ٩.٧٩ و ٩٠.٣٦ % فى اليوم الاول والحادى والعشرون على التوالى، كما تم دراسة الامونيا المتطايره على اليوريا اليوريا المغلفة والغير مغلفة لمدة ستة اسابيع باستخدام تجربة ال (forced-draft technique) حيث اعطث اليوريا المغلفة والغير مغلفة نسبه فقد ٤٣.٨ و ٥٩.٥ % على التوالى.