CHITOZAN-ZEOLITE COMPOSITE FERTILIZER FORMULATIONS FOR ENHANCING NUTRIENT USE EFFICIENCY

Abstract

The experiment was carried out in the Department of Soil Science and Agricultural Chemistry at the College of Agriculture, Vellayani, Kerala, from January to May 2024. Slow release fertilizer formulations (SRF) containing all the major (N, P,K), secondary (Ca, Mg, S) and micronutrients (Zn, B) were prepared using compatible fertilizer materials(urea, diammonium phosphate, muriate of potash, phosphogypsum, magnesium sulphate, zinc sulphate and borax), carrier materials (zeolite and chitosan) which are mixed in five ratios (1:1,1:2,1:3,2:1,3:1) and prepared by two methods namely solid impregnation and solute impregnation. Ten formulations were prepared with different combinations of fertilizer mix, carrier materials and impregnation methods. These formulations were prepared to meet the specific nutrient needs of solanaceous crops (75:40:25 N:P:K kgha^{-1}) and the soil nutrient status.The formulations were characterized for their physical (hygroscopicity, moisture content and stability) and electro-chemical properties (pH, EC) and observed that they are non hygroscopic, non caking and are highly stable. The moisture content of formulations ranged from 2.57 % to 3.92 %, pH 6.30 to 6.81 and EC 10.06 to 16.29 dS m^{-1}.The nutrient content in these formulations were 10.21 to 12.02 % nitrogen, 3.82 to 4.63 % phosphorus, 2.65 to 5.28 % potassium, 5.58 to 6.58 % calcium, 2.46 to 3.08% magnesium, 2.58 to 3.46% sulphur, 1.06 to 1.23% zinc and 0.15 to 0.24% boron. The highest nutrient content was obtained in formulation containing fertilizer mix + C-Z (1:1) prepared by solid impregnation method.

Keywords*: Fertilizer; Chitosan; zeolite ; slow release fertilizer ; solid impregnation ; solute impregnation*

INTRODUCTION

Achieving sustainable food production faces challenges such as declining soil organic matter, imbalanced fertilizer use, emerging multi-nutrient deficiencies, and low nutrient use efficiency. A major issue in agriculture is nutrient loss from conventional fertilizers, with only 10–30% of nutrients being absorbed by plants, resulting in economic losses and environmental damage. Most widely used fertilizers are highly water-soluble. In a state like Kerala where rainfall is abundant and well-distributed, the efficiency of these fertilizers tends to be low due to significant nutrient losses. The increasing demand for sustainable agricultural practices has led to the development of innovative smart fertilizer formulations that ensure enhanced nutrient efficiency and minimize environmental impacts[1].Slow-release fertilizers (SRFs) offer a solution by gradually releasing nutrients in accordance with plant needs, minimizing losses from leaching, volatilization and runoff and promoting sustainable yield improvements. SRFs and controlled-release fertilizers (CRFs) are designed to optimize nutrient use, with materials such as zeolite, bentonite, nanoclays, biochar, and chitosan serving as carriers for nutrients. These smart fertilizers not only enhance crop production but also reduce the environmental impact compared to conventional fertilizers.

Synthetic polymers used in SRF production can become pollutants due to their slow decomposition, leading to soil accumulation. Natural polymers like starch, cellulose, and lignin offer a more eco-friendly alternative but, due to their hydrophilic nature, need to be combined with other materials for effective use[2]. Chitosan and zeolite, as natural adsorbents, hold potential for producing slow-release fertilizers, reducing nutrient loss and environmental pollution. Zeolite is a porous mineral with high cation exchange capacity, adsorption ability, large surface area, and catalytic properties, making it ideal for use as a slow-release fertilizer. It retains nutrients and gradually releases them through ion exchange, providing a steady supply to plants.They also improves water retention, enhances soil bioactivity, reduces evaporation, and minimizes nutrient leaching and pollution[3,4].Chitosan, a naturally abundant bio-based polymer, is biocompatible, biodegradable, and non-toxic. It acts as a physical barrier, slowing the diffusion of water into fertilizers and controlling nutrient release [5]. This sustained release ensures continuous plant nutrition, leading to better growth and improved performance. Therefore in this present study, slow release fertilizer formulations are made by using chitosan-zeolite composites as carriers (in different ratios) with fertilizer mix containing major, secondary and micronutrients by solid and solute impregnation methods to slow down the nutrient release and thus enhance the nutrient use efficiency of crops.

MATERIALS AND METHODS

Preparation of Chitosan-Zeolite Composite Fertilizer Formulations

A chitosan-zeolite based slow release fertilizer formulation containing major (N,P,K),secondary (Ca,Mg,S) and micronutrients (Zn and B) were prepared using compatible fertilizer sources like urea, DAP, muriate of potash , phosphogypsum, magnesium sulfate, zinc sulfate, and borax also the carrier materials like chitosan and zeolite.The C-Z were mixed in five ratios viz., 1:1, 1:2, 2:1, 3:1, and 1:3.The fertilizer materials was mixed different ratios of chitosan-zeolite by two methods mainly namely solid impregnation and solute impregnation. Nutrient formulations were prepared using these nutrient sources considering the nutrient requirement of solanaceous crops (N: P_2O_5 : K_2O @ 75:40:25 kg ha^{-1}) and the fertility status of the soil as given in table 1.

Table 1. Soil nutrient status

Sl no.	Soil parameters	Status	Rating
2	pH	5.72	Moderately acidic
3	EC (dS m^{-1})	0.36	Normal
4	Organic Carbon (%)	0.58	Medium
5	Available Nitrogen (kg ha^{-1})	273.45	Low
6	Available Phosphorus (kg ha^{-1})	46.62	High
7	Available Potassium (kg ha^{-1})	89.6	Low
8	Exchangeable Calcium (mg kg^{-1})	169.61	Deficient

9	Exchangeable Magnesium (mg kg^{-1})	48.32	Deficient
10	Available Sulphur (mg kg^{-1})	12.52	High
11	Available iron (mg kg^{-1})	17.30	High
12	Available Manganese (mg kg^{-1})	8.64	High
13	Available Zinc (mg kg^{-1})	2.29	Sufficient
14	Available Copper (mg kg^{-1})	0.98	Deficient
15	Available boron (mg kg^{-1})	0.26	Deficient

Solid impregnation

Solid impregnation was done by preparing fertilizer mix containing N, P, K, Ca, Mg, S, Zn and B using compatible fertilizer sources following nutrient ratio based on nutrient requirement of solanaceous cropsand mixing with chitosan-zeolite composite in solid form in the ratio of 1:0.5. For 100g of formulation, the fertilizer sources included urea (22g), DAP (10g), MOP (10 g), Phosphogypsum (10 g), $MgSO_4$ (10 g), zinc sulfate (4 g) and borax (4 g) while the carrier materials consisted chitosan – zeolite composites (30 g) mixed thoroughly in solid form.

Solute impregnation

Solute impregnation was done by preparing percentage fertilizer solution by mixing compatible fertilizer forms containing N, P, K, Ca, Mg, S, Zn and B and with a chitosan-zeolite composite. For 100g of formulation, the fertilizer sources were urea (22g), DAP (10g), MOP (10 g), Phosphogypsum (10 g), $MgSO_4$ (10 g), zinc sulphate (4 g) and borax (4 g) and the carrier materials like chitosan – zeolite composites (30 g) were dissolved in 100 ml of water. They were stirred for 3 hr to attain maximum impregnation of these nutrients into the carriers. The resulting suspension was oven dried (105°C) for 2 hrs.The composite powder obtained was then ground with mortar, sieved and stored in air tight containers [6].

Ten formulations prepared were F1 (Fertilizer mix : chitosan-zeolite{1:1}-solid),F2 (Fertilizer mix : chitosan-zeolite {2:1}-solid),F3 (Fertilizer mix : chitosan-zeolite{1:2}-solid),F4 (Fertilizer mix : chitosan-zeolite{3:1}-solid),F5 (Fertilizer mix : chitosan-zeolite{1:3}-solid), F6 (Fertilizer mix : chitosan-zeolite {1:1}-solute),F7(Fertilizer mix : chitosan-zeolite {2:1}-solute),F8 (Fertilizer mix : chitosan-zeolite{1:2}-solute),F9 (Fertilizer mix : chitosan-zeolite{3:1}-solute), F10 (Fertilizer mix : chitosan-zeolite{1:3}-solute).The flow chart showing the preparation of these formulations are presented in plate 2.

Characterization of Chitosan-Zeolite Composite Fertilizer Formulations

The slow release nutrient formulations prepared were characterized for physical and chemical properties viz. moisture content by oven dry method, hygroscopicity, caking and stability (compatibility study) and electrochemical pH and EC were determined in a 1:10 sample to water extract using pH and EC meter respectively. The nitrogen (N) content was assessed using the Micro-Kjeldahl method, following digestion in concentrated sulfuric acid (H_2SO_4) [7]. The phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), zinc (Zn), and copper (Cu) levels were analyzed through acid digestion of the samples with a nitric-perchloric acid mixture (9:4) and subsequently measured using various methods: the vanadomolybdate method for phosphorus, flame photometry for potassium, the versanate titration method for calcium and magnesium, turbidimetry for sulfur [8] and atomic absorption spectrometry for the micronutrients. Boron (B) content was determined by dry ashing, followed by acid extraction of the ash and determined by spectrophotometric analysis [9].

Statistical Analysis

The data from the characterization study were statistically analyzed using standard methods with the GRAPE 1.0.0 software (General R-Shiny based Analysis Platform Empowered by Statistics). The means of various treatment combinations were compared using the least significant difference (LSD) at a significance level of 0.05. Principal Component Analysis (PCA) was conducted to identify the most effective slow release formulations [10].

RESULTS AND DISCUSSION

Properties of Chitosan – Zeolite Composite Fertilizer Formulations

The prepared properties of C-Z based slow release fertilizer formulations (Table 1) revealed that they were formulations found to be stable, non caking, non hygroscopic and no noxious gas formation was observed. The formulation prepared in F4 (Fertilizer mix : chitosan-zeolite{3:1}-solid) were found to be hygroscopic.The moisture content ranged from 2.57% (F2) to 3.92% (F6) and this low moisture content ensures that the prepared fertilizer formulations are more stable, less caking tendency and hygroscopicity. Significant variation was observed between different formulations with respect to electro- chemical properties like pH and EC (Table 3).The pH was found to be slightly acidic in nature (pH 6.30 to 6.81).The acidic nature of slow release formulation might be due to the presence of acidic ions [11]. The highest value of pH was obtained for the formulation containing more zeolite which may be due to slight alkaline nature of zeolites [12]. Electrical conductivity varied between 10.06 dS m^{-1} (F4) to 13.41 dS m^{-1} (F10). This might be attributed to the presence of soluble salts in the formulations from fertilizers used. An increased electrical conductivity of leachates from controlled release fertilizers is reported by [11] due to the release of dissolved salts from the fertilizers.

Nutrient Content of Chitosan – Zeolite Formulations

Nutrient content in the formulations was depicted in Table 2. The formulations contain 8.97 to 11.50% nitrogen,3.62 to 5.63% phosphorus,2.26 to 5.26% potassium,5.47 to 6.68 % calcium, 2.46 to 3.08% magnesium,2.58 to 3.46% sulfur,1.06 to 1.23% zinc and 0.15 to 0.24% boron. The highest concentration of nitrogen was recorded in formulation containing fertilizer mix + chitosan:zeolite {3:1} prepared by solute impregnation (11.50%).This might be due to presence of high nitrogen content in chitosan used in the formulation (9.86%). Phosphorus content was the highest in formulation containing fertilizer mix : chitosan-zeolite {1:3} prepared by solid impregnation (5.63 %) which might have contributed by zeolite used in the formulation that contained about 2.64% phosphorus. The highest potassium content was observed in formulation containing fertilizer mix : chitosan-zeolite {1:3} prepared by solid impregnation (5.26%) which may be due to the high content of potassium in zeolite (0.14%). Similar findings were reported by [13] in a multinutrient formulation which contained 17.9% N ,11.3% P_2O_5 and 8.2% K_2O.The highest content of 6.68 % Ca was observed in formulation prepared using fertilizer mix : chitosan-zeolite {3:1} prepared by solid impregnation F4), 2.83 % Mg and 3.37 % S in fertilizer mix : chitosan-zeolite {1:3} prepared by solid impregnation. Highest content of zinc (1.23 %) and boron (0.24 %) was obtained in F4 (Fertilizer mix : chitosan-zeolite{3:1} prepared by solid impregnation. This may be attributed to the presence of these nutrients in the fertilizer materials and also carrier materials used for the development of these formulations.

Plate 1. Materials used for preparation of fertilzer formulations

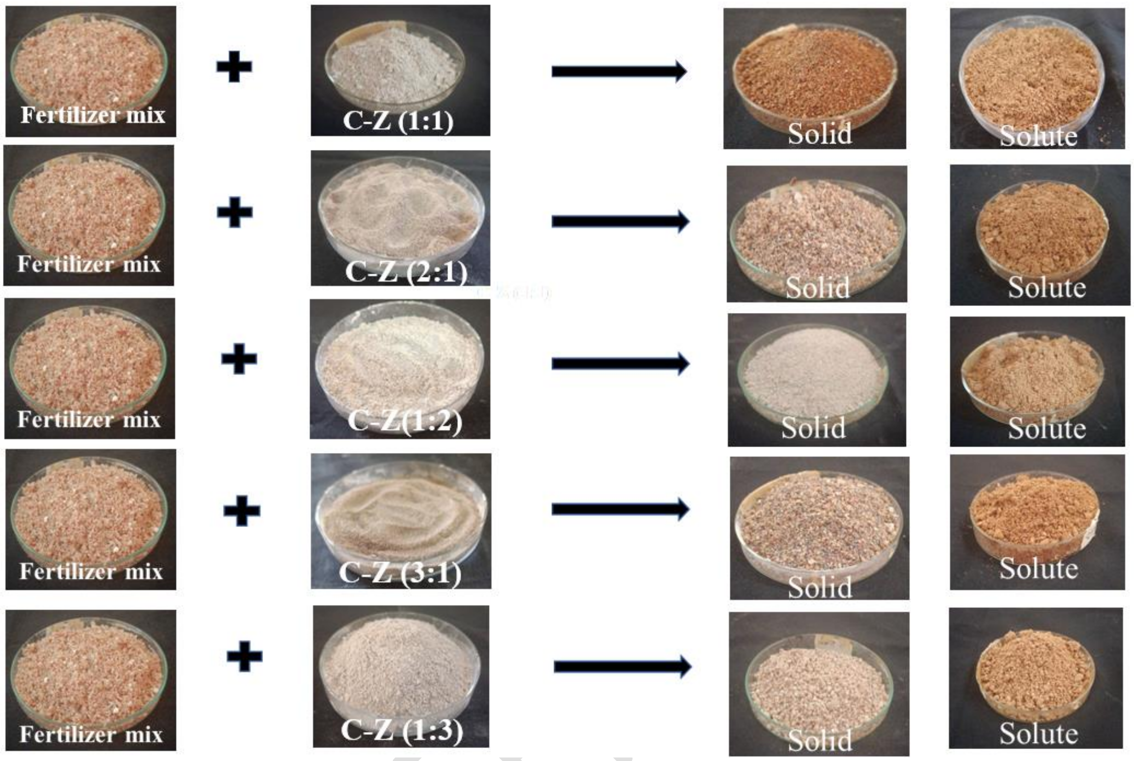

Plate 2. Preparation of chitosan-zeolite composite fertilizer formulations

Table 1. Properties of chitosan -zeolite fertilizer formulations

Treatment details		pH	EC (dSm^{-1})	MC (%)	Hygroscopity	Stability
F1	Fertilizer mix + C-Z (1:1) [Solid]	6.63	11.04	3.88	Nil	Highly stable
F2	Fertilizer mix + C-Z (2:1) [Solid]	6.41	10.96	2.57	Nil	Stable
F3	Fertilizer mix + C-Z(1:2) [Solid]	6.72	12.01	3.05	Nil	Stable
F4	Fertilizer mix + C-Z(3:1) [Solid]	6.30	10.06	2.59	Slightly hygroscopic	Stable
F5	Fertilizer mix + C-Z (1:3) [Solid]	6.81	12.82	3.07	Nil	Stable
F6	Fertilizer mix + C-Z(1:1) [Solute]	6.66	13.41	3.92	Nil	Highly stable
F7	Fertilizer mix + C-Z (2:1) [Solute]	6.34	11.12	2.73	Nil	Stable
F8	Fertilizer mix + C-Z (1:2) [Solute]	6.69	15.97	3.31	Nil	Stable
F9	Fertilizer mix + C-Z (3:1) [Solute]	6.34	10.85	2.94	Nil	Stable
F10	Fertilizer mix + C-Z (1:3) [Solute]	6.83	16.29	3.44	Nil	Highly stable

C-Chitosan, Z-Zeolite

Table 2. Nutrient content of chitosan zeolite composite fertilizer formulations

Treatment details		N(%)	P (%)	K(%)	Ca (%)	Mg (%)	S (%)	Zn (%)	B (%)
F1	Fertilizer mix + C-Z (1:1) [Solid]	10.51	4.14	2.76	5.58	2.60	3.11	1.13	0.17
F2	Fertilizer mix + C-Z (2:1) [Solid]	11.12	3.62	3.24	6.37	2.46	2.87	1.20	0.19
F3	Fertilizer mix + C-Z (1:2) [Solid]	8.97	4.87	3.76	5.66	2.75	3.19	1.11	0.15
F4	Fertilizer mix + C-Z (3:1) [Solid]	11.30	3.95	3.03	6.68	2.13	2.58	1.23	0.24
F5	Fertilizer mix + C-Z (1:3) [Solid]	9.02	5.63	5.26	5.60	2.83	3.37	1.06	0.14
F6	Fertilizer mix +C-Z(1:1) [Solute]	10.65	4.19	2.26	5.85	2.66	3.12	1.15	0.18
F7	Fertilizer mix + C-Z (2:1) [Solute]	11.16	3.90	3.31	6.11	2.50	2.76	1.21	0.13
F8	Fertilizer mix + C-Z (1:2) [Solute]	9.25	4.67	4.52	5.72	2.795	3.25	1.13	0.15
F9	Fertilizer mix + C-Z (3:1) [Solute]	11.50	3.88	3.53	6.49	2.215	2.60	1.19	0.17
F10	Fertilizer mix + C-Z (1:3) [Solute]	8.78	5.20	4.76	5.47	3.08	3.46	1.08	0.15

Principal Component Analysis

The results on the nutrient content of the slow release nutrient formulations were evaluated using principal component analysis (PCA) (Table 3, Plate 3) to identify the most effective formulations. The PCA focused on the content of N, P, K, Ca, Mg and S within the formulations and successfully extracted six principal components.

Index values were calculated based on these variables, and a one-way analysis (completely randomized design) was performed on the index values (Table 4). Among the formulations, F1 and F6 exhibited the highest index values of 12.29 and 12.20 respectively, which was found to be significantly higher to the other formulations. While, formulations F4 and F9 recorded the lowest index values of 10.42 and 10.33 respectively. This suggests that formulation F1 (Fertilizer mix + C-Z (1:1) [Solid]) having 10.51% N, 4.14% P, 2.76 % K, 5.58% Ca, 2.60 % Mg,3.11% S,1.13% Zn, 0.17% B is the best formulation, demonstrating superior nutrient content, while formulation F9 (Fertilizer mix + C-Z (3:1) - Solute] is the least advantageous, having the lowest nutrient content. Based on the index values, the formulations were obtained in the order 12.29 (T_1) > 12.20 (T_6) > 12.17 (T_5) >12.07 (T_3) > 12.06 (T_2) > 11.25 (T_{10}) > 10.90 (T_8) >10.87 (T_7) > 10.42 (T_4) and 10.33 (T_9).

Table 3. Principal component analysis

Variables	PC1	PC2	PC3	PC4	PC5	PC6
N	-0.444	0.198	0.218	0.822	-0.031	-0.208
P	0.343	0.571	0.729	-0.124	-0.011	0.096
K	0.268	-0.77	0.505	0.191	-0.211	0.013
Ca	-0.442	-0.203	0.344	-0.276	0.748	-0.097
Mg	0.456	-0.007	-0.189	0.439	0.578	0.479
S	0.462	0.024	-0.11	0.067	0.246	-0.842

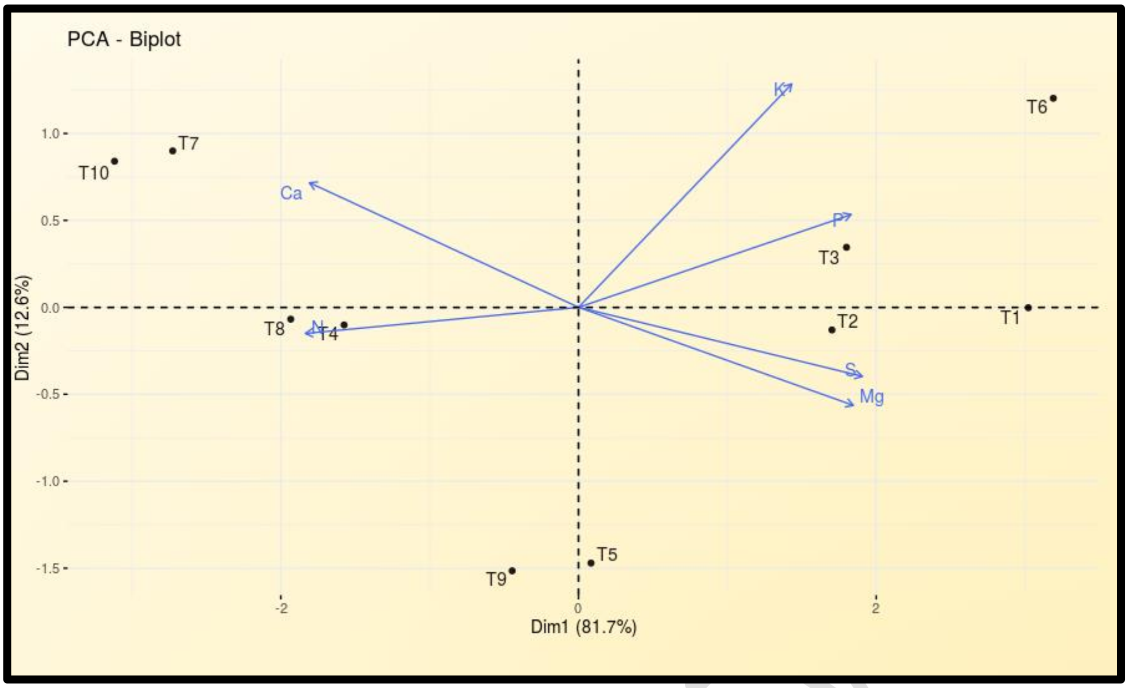

Plate 3. Principal component analysis biplot with nutrient content of slow release fertilizer formulations

Table 4. One-way ANOVA of index values

Treatment	Mean
F1	12.29
F2	12.06
F3	12.07
F4	10.42
F5	12.17
F6	12.20
F7	10.87
F8	10.99
F9	10.33
F10	11.25
SEm(±)	0.07
CD (0.05)	0.205

CONCLUSION

The results of PCA revealed that formulations F1 and F6 containing fertilizer mix +chitosan-zeolite {1:1} prepared by solid and solute impregnation respectively found to have superior quality followed by F5 (fertilizer mix + chitosan-zeolite{1:3}) and F3 (fertilizer mix + chitosan-zeolite{1:2}) prepared by solid impregnation technique. The formulation F1 has moisture content (3.8%), desirable electro-chemical properties of pH by 6.63 and EC by 11.04 dSm^{-1}. It contains sufficient amount of nutrients with 10.51% N, 4.14% P, 2.76 % K, 5.58% Ca, 2.60 % Mg, 3.11% S, 1.13% Zn, 0.17% B and also contains balanced composition of chitosan and zeolite. The best five fertilizer formulations are the ones having chitosan and zeolite in the ratios 1:1,1:2 and 1:3.The results also shown that all the slow release fertilizer formulations prepared using inorganic nutrient sources mixed with chitosan and zeolite have the ability to provide the essential major nutrients and micronutrients for plant growth and are suitable to use as a good slow release formulation for enhancing the nutrient use efficiency of crops

Disclaimer (Artificial intelligence)

Option 1:

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

REFERENCES

1. Karthik A, Maheswari MU. Smart fertilizer strategy for better crop production. Agricultural Reviews. 2021;42(1):12-21.

2. B. Azeem., K. KuShaari., Z.B Man., A. Basit., and T.H. Thanh “Review on Materials & Methods to Produce Controlled Release Coated Urea Fertilizer”. 2014. Journal of Controlled Release, 181: 11–21.

3. Mihok F, Macko J, Oriňak A, OriňakováR, Kovaľ K, Sisáková K, Petruš O, Kostecká Z. Controlled nitrogen release fertilizer based on zeolite clinoptilolite: Study of preparation process and release properties using molecular dynamics. Current Research in Green and Sustainable Chemistry. 2020;3:200-209.

4. Lateef, A., Nazir, R, Jamil, N., Synthesis and Characterization of Zeolite Nanocomposites : An Environment friendly Slow Release Fertilizer, Microporous and Miesoporous Material.2016; 232: 174-183.

5. Wu, L and Liu, M., Preparation and Properties of Chitosan-coated NPK Compound Fertilizer With controlled Release and water Retention, Carbohydrate Polymers, 2008;72:240-247.

6. Maharani, D.K., Dwiningsih, K., Savana, R.T., and Andika, P.M.V. Usage of zeolite and chitosan composite as slow release fertilizer. International Conference on Science and Technology.2018;14(2): 179-182.

7. Jackson ML. Soil Chemical Analysis. 2nd ed. New Delhi: Prentice hall of India; 1973.

8. Tabatabai MA. Sulfur. In: Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties, Agronomy Monograph *9.2,* ed. A. L. Page, 2nd ed.ASA-SSSA, Madison, USA. 1982.

9. Roig A, Lax A, Costa F, Cegarra J, Hernandez T. The influence of organic materials on the physical and physio- chemical properties of soil. *Agric. Medit*.1996;117:309-318.

10. Gopinath, P. P, Parsad, R, Joseph, B, Adarsh, V. S. GRAPES: General Rshiny Based Analysis Platform Empowered by Statistics.2020.

11. Merhaut DJ, Blythe EK, Newman JP, Albano JP. Nutrient release from controlled-release fertilizers in acid substrate in a greenhouse environment: leachate electrical conductivity, pH, and nitrogen, phosphorus, and potassium concentrations. Hort. Science. 2006;41(3): 780-7.

12. Shi, W.Y., Li, H., Du, S., Wang, K.B. and Shao, H.B. Immobilization of lead by application of zeolite: Leaching column and rhizobox incubation studies. *Applied Clay Science.* 2013; *85*.103-108.

13. Ni,B.,Lu,S., and Liu,M. Novel multinutrient fertilizer and its effect on slow release ,water holding and soil amending. Ind.Eng.Chem. Res.2012. 51(40):12993-13000.