DEVELOPMENT AND CHARACTERISATION OF CHITOZAN-ZEOLITE COMPOSITE FERTILIZER FORMULATIONS FOR ENHANCING NUTRIENT USE EFFICIENCY

Abstract

The objective of the study was to develop slow release fertilizer formulations using chitosan and zeolite as carrier materials. A completely randomized design was selected, containing 10 treatments with 3 replications. 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. Chitosan and zeolite based slow release fertilizer formulations (SRF) containing all the major, secondary and micronutrients were prepared using compatible fertilizer materials (urea, diammonium phosphate, muriate of potash, phosphogypsum, magnesium sulphate, zinc sulphate and borax), carrier materials (zeolite, and chitosan) in which carrier materials are mixed in five ratios (1:1,1:2,1:3,2:1,3:1) in two methods namely solid impregnation and solute impregnation. These formulations were prepared to meet the specific nutrient needs of solanaceous crops (75:40:25 kgha^{-1}) and the soil nutrient status. The formulations were characterized for their physical and chemical properties and observed that they are non hygroscopic, non caking and are highly stable. On the basis of character analysis and principal component analysis the formulation F1 containing fertilizer mix + C-Z (1:1) [SD] and F6 containing fertilizer mix + C-Z (1:1) [ST] were found to be the best among the ten formulations. Formulation F1 had 3.88% moisture content, 6.63 pH,11.04 dsm^{-1} EC, 10.51% N, 4.14% P, 2.76 % K, 5.58% Ca, 2.60 % Mg, 3.11% S, 1.13% Zn, 0.17% B. The best five formulations which are selected on the basis of principal component analysis are F1(Fertilizer mix + C-Z {1:1}[SD]), F3 (Fertilizer mix + C-Z {1:2} [SD], F5 (Fertilizer mix + C-Z {1:3} [SD]), F8 (Fertilizer mix + C-Z {1:2}[ST]) and F10 (Fertilizer mix + C-Z {1:3} [ST]), SD and ST represents the solid and solute impregnated formulations. Hence chitosan – zeolite based slow release fertilizer formulations can be recommended as a nutrient source for solanaceous crops.

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Keywords: Fertilizer; Chitosan; zeolite

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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

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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 by solid and solute impregnation methods to slow down the nutrient release and thus enhance the nutrient use efficiency of crops.

MATERIALS AND METHODS

2.1 Experimental Site

Experiments were conducted in the laboratory at the Department of Soil Science and Agricultural Chemistry, College of Agriculture, Vellayani,Kerala during the month between January to May 2024.

2.2 Preparation of Chitosan-Zeolite Composite Fertilizer Formulations

A fertilizer formulation of chitosan-zeolite composites containing major, secondary, and micronutrients were prepared using compatible fertilizer sources like urea, DAP, muriate of potash (MOP), phosphogypsum, magnesium sulfate, zinc sulfate, and borax and the carrier materials included chitosan and zeolite, mixed in five ratios- 1:1, 1:2, 2:1, 3:1, and 1:3.The mixing of these fertilizer materials with chitosan was done by mainly two methods namely solid impregnation and solute impregnation. Nutrient formulations were prepared using these nutrient sources considering the nutrient requirement of the crop brinjal (N: P_2O_5 : K_2O @ 75:40:25 kg ha^{-1}) and the fertility status of the soil of agro-ecological unit 8 of Kerala.

<u>2.2.1 Solid impregnation (1:0.5)</u>

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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 brinjal crop nutrient requirement and mixing with chitosan-zeolite composite in solid form in the ratio of 1:0.5. For 100g of formulation, the fertilizer sources like 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 mixed in solid form.

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2.2.1 Solute impregnation (1:1)

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 mixing with chitosan-zeolite composite. For 100g of formulation, the fertilizer sources were same as for solid impregnation and the carrier materials like chitosan – zeolite composites (30 g) were dissolved in 100 ml of water. They were stirred for 3 hr for 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].

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The experimental design selected was CRD with 10 treatments and 3 replications. The formulations prepared were F1 (Fertilizer mix : chitosan-zeolite{1:1}),F2 (Fertilizer mix : chitosan-zeolite{2:1}),F3 (Fertilizer mix : chitosan-zeolite{1:2}),F4 (Fertilizer mix : chitosan-zeolite{3:1}),F5 (Fertilizer mix : chitosan-zeolite{1:3}), F6 (Fertilizer mix : chitosan-zeolite {1:1}),F7(Fertilizer mix : chitosan-zeolite {2:1}), F8 (Fertilizer mix : chitosan-zeolite{1:2}),F9 (Fertilizer mix : chitosan-zeolite{3:1}), F10 (Fertilizer mix : chitosan-zeolite{1:3}).The first five treatments were prepared by solid impregnation and the remaining five treatments were prepared by solute impregnation technique. The materials used and the prepared slow release formulations were presented in plate 1 and 2 respectively.

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2.3 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, 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 the samples at 550°C in silica crucibles, followed by extraction of the ash with 10 ml of 0.36 N NH_2SO_4 for one hour at room temperature, and then filtered using Whatman No. 42 filter paper before spectrophotometric analysis [9].

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2.4 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].

3. RESULTS AND DISCUSSION

3.1 Properties of Chitosan – Zeolite Composite Fertilizer Formulations

Properties of slow release fertilizer pellets (Table 1) revealed that the formulations prepared were stable, non caking , no noxious gas formation and non hygroscopic (except F2 and F4) in nature. 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 to slightly alkaline in nature (6.30 in F4 to 6.81 in T5).The alkaline or acidic nature of slow release formulation might be due to the presence of basic or acidic ions [11]. The highest value of pH was obtained for the treatment containing more zeolite which may be due to 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.

3.2 Nutrient Content of Chitosan – Zeolite Formulations

Nutrient content in the formulations are depicted in Table 2. The formulations contains 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% sulphur, 1.06 to 1.23% zinc and 0.15 to 0.20% boron.The highest concentration of nitrogen was recorded in F9 (11.50%), this might be due to presence of high nitrogen content in chitosan used in the formulation (9.86%). Phosphorus content was highest in F5 (5.63 %) which might be contributed from zeolite used which contained about 2.64% phosphorus. The highest potassium content was observed in F5 (5.26%) that may be due to the high content of potassium in zeolite (0.14%). Similar findings were given by [13] in a multinutrient formulation which contain 17.9%N ,11.3% P_2O_5 and 8.2% K_2O.Highest content of calcium was obtained on F4 ,magnesium and sulphur on F5,zinc and boron on F4.

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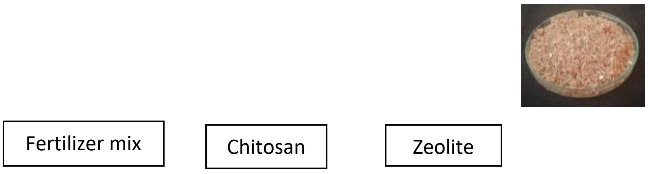

Plate 1. Materials used for preparation of fertilzer formulations

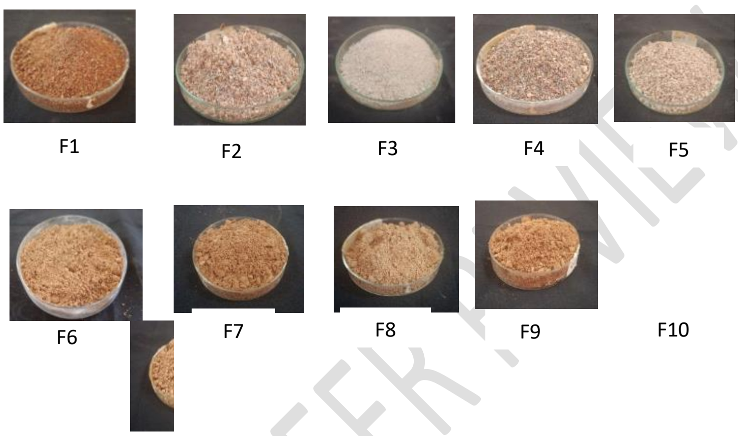

Plate 2. Prepared slow release fertilizer formulations

Table 1. Properties of chitosan -zeolite fertilizer formulations

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

Treatment details	N(%)	P (%)	K(%)	Ca (%)	Mg (%)	S (%)	Zn (%)	B (%)

F1	Fertilizer mix + C-Z (1:1) [SD]	10.51	4.14	2.76	5.58	2.60	3.11	1.13	0.17
F2	Fertilizer mix + C-Z (2:1) [SD]	11.12	3.62	3.24	6.37	2.46	2.87	1.20	0.19
F3	Fertilizer mix + C-Z (1:2) [SD]	8.97	4.87	3.76	5.66	2.75	3.19	1.11	0.15
F4	Fertilizer mix + C-Z (3:1) [SD]	11.30	3.95	3.03	6.68	2.13	2.58	1.23	0.20
F5	Fertilizer mix + C-Z (1:3) [SD]	9.02	5.63	5.26	5.60	2.83	3.37	1.06	0.14
F6	Fertilizer mix + C-Z(1:1) [ST]	10.65	4.19	2.26	5.85	2.66	3.12	1.15	0.18
F7	Fertilizer mix + C-Z (2:1) [ST]	11.16	3.90	3.31	6.11	2.50	2.76	1.21	0.13
F8	Fertilizer mix + C-Z (1:2) [ST]	9.25	4.67	4.52	5.72	2.795	3.25	1.13	0.15
F9	Fertilizer mix + C-Z (3:1) [ST]	11.50	3.88	3.53	6.49	2.215	2.60	1.19	0.17
F10	Fertilizer mix + C-Z (1:3) [ST]	8.78	5.20	4.76	5.47	3.08	3.46	1.08	0.15

Table 2. Nutrient content of chitosan zeolite composite fertilizer formulations

3.3 Principal Component Analysis

The laboratory analysis results 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.

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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 mean value of 12.29 and 12.20, significantly over the other formulations. While, formulation F4 and F9 recorded the lowest mean value of 10.42 and 10.33 respectively. This suggests that formulation F1 (Fertilizer mix + C-Z (1:1) [SD]) 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) [ST]) is the least advantageous, having the lowest nutrient content. So for selecting six best treatments, F1(Fertilizer mix + C-Z {1:1}[SD]),F3 (Fertilizer mix + C-Z {1:2} [SD],F5(Fertilizer mix + C-Z {1:3} [SD]) ,F8

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(Fertilizer mix + C-Z {1:2}[ST]) and F10 (Fertilizer mix + C-Z {1:3} [ST]) was taken based on highest index mean values. ?

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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

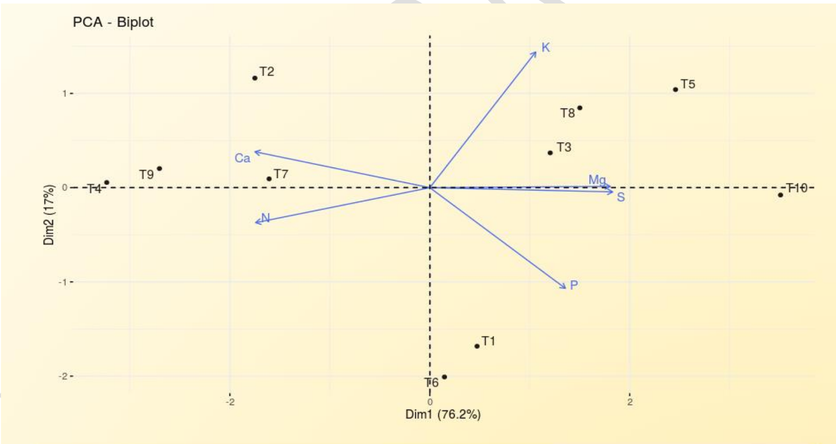

Plate 3. Principal component analysis biplot with nutrient content of slow release fertilizer formulations

Table 4. One-way ANOVA of index values

Treatment	Mean
F1	12.29

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

4. CONCLUSION

The results of the characterization study have 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. However, after the conduct of PCA, formulation F1 and F6 containing fertilizer mix +chitosan-zeolite {1:1} made by solid and solute impregnation respectively was found to have superior quality followed by F5(fertilizer mix + chitosan-zeolite{1:3})and F3 (fertilizer mix + chitosan-zeolite{1:2}) both made by solid impregnation technique. Formulation F1 has moisture content (3.8%). It has desirable electro-chemical properties with 6.63 pH and 11.04 dSm^{-1} EC. 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 it 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.

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