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ORIGINAL PAPER

Organic acid and amino acid coated multi-nutrient fertilizer granules (MNFG): synthesis and characterization

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Abstract

Organic and amino acids are used as coating material in developing controlled release fertilizers (CRF) due to their low cost and favorable properties that effectively controls the nutrient release rate. In this study, fertilizer grades of gypsum, ferrous sulphate, zinc sulphate, copper sulphate and borax were used to prepare multi-nutrient fertilizer granules (MNFG). Five different polymers, namely citric acid (CA), humic acid (HA), fulvic acid (FA), salicylic acid (SA) and glycine (GY), were used in various concentrations (0,3,5 & 10% w/v) for fabricating coated MNFG by spraying. The fabricated MNFGs were characterized for particle size distribution (PSD), single grain weight, bulk density, solubility, moisture content, structural stability, crushing strength, pH, EC and elemental analysis, FTIR and surface properties through scanning electron microscopy (SEM). The physico-chemical properties of coated MNFG were strongly influenced by coating materials and their concentrations. The MNFG coated with 10% fulvic acid was found to be structurally stable with moderate crushing strength. However, the MNFG coated with 10% salicylic acid had high bulk density (0.95 Mg m^{-3}), low solubility (70 g L^{-1}) and moisture content (0.50%). The uncoated MNFG has lesser bulk density (0.80 Mg m^{-3}), higher solubility (260 g L^{-1}) and moisture content (2.04%). The SEM analysis revealed that, coated MNFG has smooth surface and tiny pores compared to uncoated MNFG. This newly developed organic acids and amino acids coated MNFG could be a potential fertilizer with controlled release properties for achieving higher crop productivity.

Keywords Properties · Physico-chemical properties · Multi nutrient fertilizer granules · Biopolymers · Coating concentrations · Surface properties

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Introduction

Fertilizers are defined as sources of macro and micronutrients, which are essential inputs to get higher crop productivity. Macronutrients are fundamental building blocks of plant structures. On the contrary, micronutrients are required in much smaller quantities by plants, but still limit crop production and yields considerably. Much of the applied fertilizers are gradually rendered unavailable to plants over time as it reacts with soil constituents through various processes like precipitation, adsorption and sorption on soil matrix which contributes to lesser fertilizer use efficiency [1]. Though various management options are available to improve the nutrient use efficiency, controlled release of fertilizers (CRF) using various coated materials is proved to be the most effective one [2] which consists of an inert layer [3]. At present various polymer coated fertilizers are produced with different kinds of polymers and manufacturing technology. Application of sulphur coated fertilizers may increase the acidity of soil and the fertilizers coated with plastic resin may leave undesired residues of synthetic materials on soil, resulting in environmental pollution [4]. In this context, use of quickly degrading polymers like organic acids and amino acids to produce the controlled release fertilizer is a short-term viable option to avoid soil contamination [5].

Coating of fertilizer granules changes the nutrient solubility characteristics and controls nutrient release. The coating of fertilizers using organic acids helps to improve the fertilizer use efficiency and also reduces the losses of essential plant nutrients. Humic acids (HA) and fulvic acids (FA) are natural bio-stimulants that improved the growth of plants as a soil conditioner and enhanced the ability of soil to hold more nutrients [6, 7]. Humic acid coated urea is a good alternative nitrogen source to neem oil-coated urea in the future [8]. Citric acid is considered as one of the important organic acids that have a wide commercialization potential. Recently, major production of citric acid was achieved via microbial fermentation, as it is economical and easy to handle. Thus, using citric acid reduces the production cost of controlled release fertilizer [9, 10]. Salicylic acid enriched polymer coating of phosphatic fertilizers improved the phosphorus release in soils and its positive effect depends upon plant growth stage, its concentration and environment [11]. Amino acids also be of an interesting agent for coating due to their higher bio-compatibility [12, 13]. Amine functionalization increases the chance of surface interactions. It has also been reported that, amino acids like cysteine, glycine and glutamine could easily attach to the surface of ions through their carbonyl groups and resulted in controlled release of added nutrients [14].

An increase in the effectiveness of plant nutrient assimilation and decrease in material losses can be achieved through the production and application of coated multi-nutrient fertilizers which provide many nutrient elements for plants due to their abundant concentrations. Many research findings reported that, the production and use of novel controlled-release multi-nutrient fertilizers effectively reduce the nutrient loss as runoff or leaching and improved the nutrient use efficiency [4].

Physico-chemical properties used to predict the behavior of coated fertilizer granules are very much essential. Water sorption from soil or free water into fertilizer granules is important since the granule water content determines the rate of slaking and chemical diffusion [15, 16]. The stability in water by measuring the potentials of solubility, swelling and slaking in water, consequently affecting the efficiency and duration of nutrient release [17]. Coating uniformity and nutrient release rate depend on particle size distribution, drying temperature and quantity of coating materials used [18]. As the film thickness of the coating material increases, the slow-release properties of coated products are also increased [19]. However, limited studies have focused on characterizing the coated fertilizer granules and their suitability [20].

The quality of coating was important in controlling nutrient release and was determined by the polymer source used and its concentrations. The thickness, solubility and biodegradability of coating play important roles in the release of nutrients. Hence, the present study aimed to produce materials with controlled release properties by coating the granules of multi-nutrient fertilizer with a layer of quickly degradable polymers such as organic acid and amino acid under laboratory conditions. The main objective of the work was to develop organic acid and amino acid coated fertilizer granules and to characterize the multi-nutrient fertilizer granules for their nutrient release potentials.

Materials and methods

Materials

The fertilizer grades of gypsum, ferrous sulphate, zinc sulphate, copper sulphate and borax were used to prepare multi-nutrient fertilizer granules. For effective granulation, starch was used as a binding agent. The organic acids and amino acids such as citric acid (CA), humic acid (HA), fulvic acid (FA), salicylic acid (SA) and glycine (GY) were selected as coating materials. All polymers used were analytical grade and used as received. Sprayer is used to spray the coating material; a shaker is used for rotations so that the coating becomes homogenous. The hot air oven is used to dry the coated fertilizer granules.

Fabrication of coated multi-nutrient fertilizer granules (MNFG)

As a source of active mineral components, the granulated multi-nutrient fertilizer was prepared using straight commercial fertilizers of sulphur as well as micronutrients (Zinc, Iron, Copper and Boron). All the fertilizer materials at specified composition based on the weightage of crop demand were physically mixed together in a solid form until they became homogenous. Starch, a biodegradable binder, has been used to improve the granulation and to increase the stability of the fertilizer granules. The homogenized fertilizers mixture was transferred into a horizontal shaker and added with starch at 3% w/v. It was shaken at 250 rpm in a horizontal shaker for 30 min until gets complete granulation (Fig. 1). The granules were sieved to

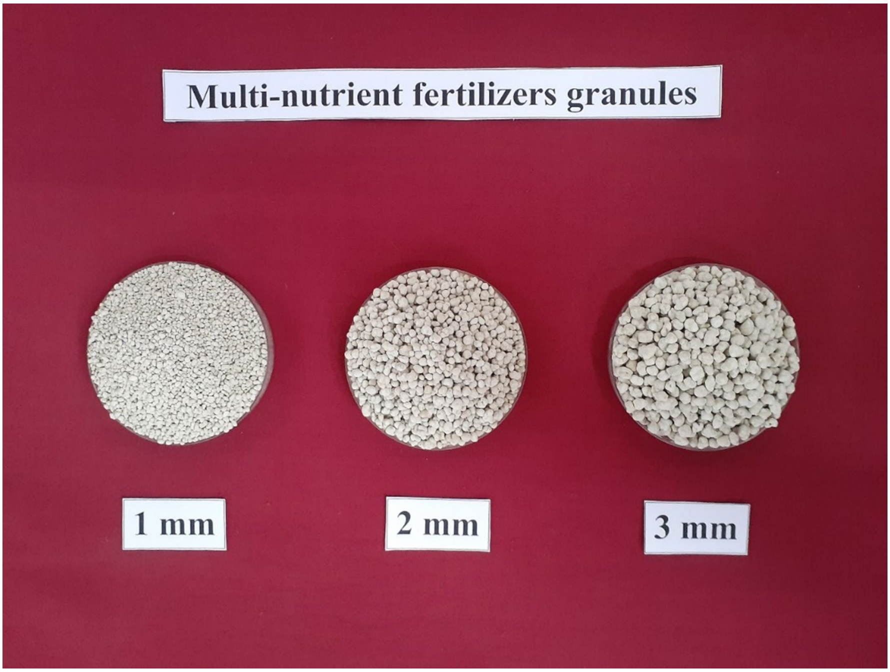

Fig. 1 View of multi-nutrient fertilizer granules of various sizes

segregate into different sizes and shade dried. The prepared granules were kept in an airtight container for further analysis and investigations.

Analar grade organic acids and amino acids such as citric acid, humic acid, fulvic acid, salicylic acid and glycine were used as coating agents. The coating solution of different concentrations (3,5 and 10%) was prepared by dissolving the known weight of coating material in 100 ml of double distilled water (w/v) and stirred continuously until it was dissolved. For coating, the fertilizer granules (100 g) were placed in the coating vessel which was kept on the shaker. As a result, the granules were forced to follow the circular vibration pattern. The coating material was pumped from a container to the nozzle with the aid of manual pump and sprayed over the fertilizer granules. The prepared 100 ml of coating material was completely sprayed over the granules with repetitive spraying after drying. The coated products were dried completely in a hot air oven at 40 °C for 2 h. After drying, the coated granules were taken out for analysis and further investigations (Fig. 2).

Characterization of MNFG

Physical characteristics

The particle size distribution was determined by using sieves of 1, 2, 3 and 4 mm which were stacked together from top to bottom. The fertilizer granules were

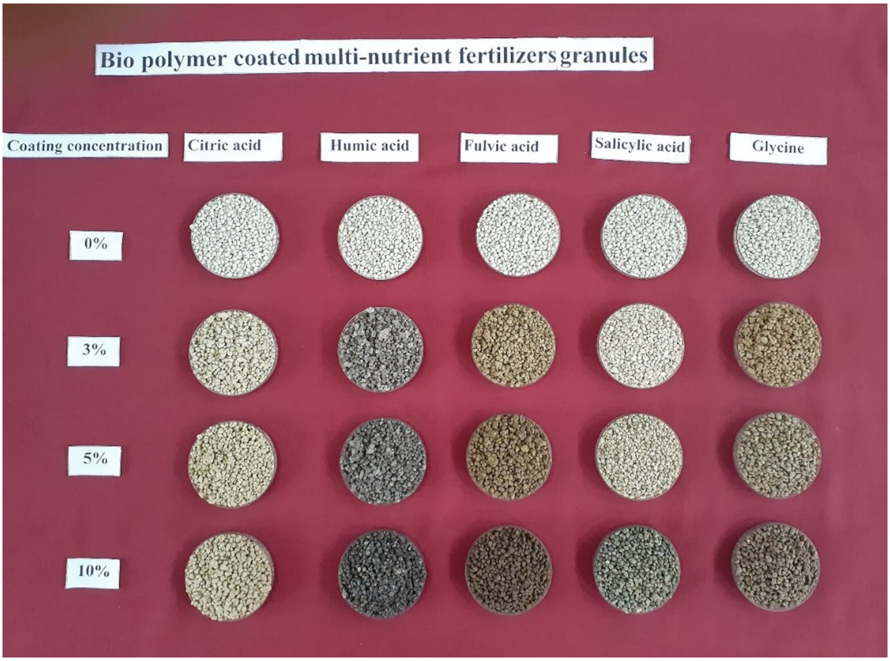

Fig. 2 View of multi-nutrient fertilizer granules (MNFG) coated with various concentrations of bio degradable polymers

placed on the upper most sieve and shaken at 250 rpm. During shaking, fertilizer granules gravitate downward through sieves and were weighed individually. The particle size distribution was calculated as follows [21].

$$\text{Material retained on a sieve (\%)} = \frac{\text{Weight retained on sieve (g)}}{\text{Total weight of sample (g)}} \times 100$$

The individual grain weight was measured using digital weighing balance and expressed in grams. The bulk density of the fertilizer granules was measured using standard protocol of International Fertilizer Development Center [21]. It represents the mass to volume ratio of granules, including voids between the particles and reported as Mg m^{-3}. The bulk density was calculated using weight and volume of the test sample. The angle of repose is the angle at the base of the cone of fertilizer heap obtained by allowing a material to fall onto a horizontal flat surface. Standard protocol of International Fertilizer Development Center [21] was used to measure the angle of repose for the material. About 100 g of fertilizer granules was passed through the funnel to form a cone on the flat surface. The circumference of the cone was measured at four corners and the angle of repose was estimated using the following equation:

$$\text{Angle of repose (degree)} = \text{Arctangent}\frac{2h}{\bar{d} - d_i}$$

where ‘h’ is the height of the cone, $\bar{d}$ is the arithmetic mean of the four diameters (cm), ‘d_i’ is the internal diameter of the funnel spout (cm).

The crushing strength is defined as the resistance of granules to deform or fracture under pressure. A simple finger test was used to evaluate the crushing strength of the fertilizer granules. A granule which crushed between the thumb and forefinger was classified as “soft”. If it crushed with the fore finger on a hard surface it was regarded as “medium hard”. If it remained intact when subjected to pressure by the fore finger against a hard surface, it was grouped as “hard” [22]. The moisture content of the multi-nutrient fertilizer granules was determined by drying 20 g of granules in hot air oven at 40˚Cuntil there was no appreciable change in its weight and expressed in percentage [23]. The solubility of a fertilizer is defined as the maximal amount of fertilizer that can be soluble in a litre of water. The solubility of the multi-nutrient fertilizer granules was determined by continuously dissolving a known quantity of granules in one litre of water until they attain saturation and expressed in g L^{-1} [24]. The fertilizer granules were tested for structural stability as suggested by [25]. About 2 g of fertilizer granules were soaked in 100 ml of distilled water for about 24 h and visually observed for deformation in the shape of the granules at regular intervals of time.

Chemical characteristics

The pH and EC of the coated multi-nutrient fertilizer granules were determined in a sample: water ratio of 1:100 using the pH meter and conductivity bridge as suggested by [26]. The total amount of nutrients present in the materials was determined by elemental analysis in triplicates using the standard procedures [27]. Sulphur content was analyzed by barium chloride gravimetric analytical method where 1 g of fertilizer sample was dissolved in 50 ml of water and filtered using Whatman No.1 filter paper and the volume was made up to 250 ml. About 10 ml of the aliquot was taken and added with 10 ml of 1:1 hydrochloric acid and a pinch of ammonium chloride. The contents were heated at 80–90˚C and 10 ml of 2% barium chloride was added and digested in a water bath to promote granulation and precipitation. Then filtered and washed till it became free of chloride. The filter paper was transferred to weighed silica crucible and ignited until the substance turns white and weighed to calculate the sulphur content.

For determining the micronutrients content, 2 g of fertilizer sample was dissolved in 20 ml of water and filtered through Whatman No. 42 filter paper then the volume was made up to 50 ml. The nutrient content in the solution was estimated using an Atomic Absorption spectrophotometer (Model GBC Avanta PM). Boron was estimated by azomethine- H method where 2.5 g of fertilizer sample was dissolved in 20 ml of water and boiled for 15 min. It was filtered through Whatman No. 40 filter paper and 5 ml of the extract was added into a volumetric flask then with 4 ml buffer and 4 ml of azomethine and the volume was made up to 25 ml using double distilled water. After one hour, the reading was taken at 420 nm using the spectrophotometer [28].

Structural characteristics

Thickness of the coating material plays an important role in determining the release rate of the nutrients. The morphology and cross-sectional characterization of fertilizer granules was carried out by scanning electron microscopy (SEM Model—S-3000 N Bruker, Germany). Single granule was cut down into two-halves with the help of a sharp knife and coated with thin layer of platinum to prevent charging under the electron beam. Image was taken at an operating voltage of 20 kV. The same samples were used for surface elemental analysis using energy dispersive X-ray spectroscopy (EDS). Which was carried out simultaneously with the SEM for rapid quantification.

The FTIR spectra of coated MNFG were recorded using a Model 8400S (Kyoto, Japan) equipped with attenuated total reflectance (ATR) technique having a wavelength source 400–4000 cm^{-1}. The powdered samples were loaded in FTIR spectrophotometer with scam range from 400 to 4000 cm^{-1} and spectrum was recorded which provides information on the nature of surface hydroxyl groups and identifying types of chemical bonds in a molecule.

Statistical analysis

The data obtained from the investigations were subjected to the analysis of variance using IBM Statistical Package for the Social Science Software version 22 to determine the significance. Wherever the treatment differences were found significant, critical differences (CD) were worked out at 5% level of significance and denoted by symbol * and ** for 1%. Non-significant comparisons were indicated as NS [29].

Results and discussion

Characteristics of MNFG

The granules of multi-nutrient fertilizer are of regular, spherical shape and white in colour with a slightly grey shade (Fig. 1). The granules of 2 mm size were used as the base material in the fabrication of polymers coated multi-nutrient fertilizer granules. They are soft, adequate crushing force easily crumbled the granules into small pieces. The multi-nutrient fertilizer granules coated with the different organic acids and amino acids vary in their appearance, surface structure and morphology. The picture of multi-nutrient fertilizer granules coated with the layer of organic acids and amino acids is presented in Fig. 2. The colour of the granules changed from light brown to dark brown in citric acid, fulvic acid and glycine coating, from light black to dark black in humic acid coating and in salicylic acid coating, it varied from white grey to slightly greenish grey which was majorly associated with coating concentrations of polymers. Many research studies demonstrated that polymer coatings change the colour of fertilizer granules which depends on the nature of polymers used for coating [30].

Table 1 shows the selected properties of MNFG. The pH, EC, grain weight and bulk density of MNFG were 4.04, 6.48 dS m^{-1}, 0.07 g and 0.80 Mgm^{-3}, respectively. In case of angle of repose, average bottom diameter of heap was 15.1 cm, whereas the height of the heap was 3 cm. Since the inner diameter of the funnel was 6 cm, the angle of repose for MNFG was 33.4°. The sulphur content was 17.1% in the tested MNFG with the iron, zinc, copper and boron contents of 4692, 869, 725 and 98.1 mg kg^{-1}, respectively. The solubility and moisture content were observed as 260 g L^{-1} and 2.04% in fabricated MNFG. The physico-chemical properties of MNFG were altered significantly by the coating materials and their concentrations. The coating of MNF granules with various concentrations of organic acids and amino acids increased the grain weight, bulk density, electrical conductivity and stability whereas it decreased the moisture content, solubility, pH, and release of water soluble nutrient contents. Among coating concentrations, irrespective of all sources 10% coating concentration significantly improved the physico-chemical properties of MNFG than 3 and 5% coating concentrations.

Physico-chemical properties

Table 2 shows the particle size distribution (PSD) of the coated multi-nutrient fertilizer granules which was observed by taking the weight of the granules retained in the sieves of various sizes. The PSD results indicated a grain size of 1 to 4 mm which was in accordance with the European regulation [31, 32]. The recovery percentage showed, 84.8% of the granules were with a size of 2 mm, 14% of 3mmand 1.2% in the size of 1 mm. The required specifications are that at least 85% of the granules to be with sizes between 1.0 to 4.0 mm. In the prepared products all

Table 1 Selected properties of multi-nutrient fertilizer granules (MNFG)

Properties	MNFG
Particle size (mm)	2.00
Colour	Greyish white
Grain weight (g)	0.07
Bulk density (Mg m^{-3})	0.80
Crushing strength	Soft
Moisture content (%)	2.04
Solubility (g L^{-1})	260
Angle of repose (°)	33.4
pH	4.04
Electrical conductivity (dS m^{-1})	6.48
Sulphur (%)	17.1
Iron (mg kg^{-1})	4992
Zinc (mg kg^{-1})	869
Copper (mg kg^{-1})	725
Boron (mg kg^{-1})	98.1

Table 2 Particle size distribution (PSD) of multi-nutrient fertilizer granules

Size (mm)	Recovery (g kg^{-1})	Particle size distribution (%)
1	12	1.20
2	848	84.8
3	140	14.0
SEd	10.2	1.26
CD(p = 0.005)	24.5	3.09

granules have the size between 1 to 3 mm which meant that the specifications were well adhered [33]. The smaller sized granules can be effectively (< 4 mm diameter) used as the fertilizer core for preparing coated fertilizers [33]. Organic acids and amino acids of various concentrations were properly coated on the MNFG and uniformly distributed.

The single grain weight and bulk density were increased directly and proportionally to various coating concentrations irrespective of the polymers used (Table 3). The single grain weight and bulk density of all coated fertilizer granules were higher than raw material. The maximum grain weight was obtained at 10% coating concentration irrespective of the sources of organic acids and amino acids (0.09 g) used whereas lesser weight was noted in uncoated granules (0.07 g). Higher bulk density was noted in granules coated with salicylic acid at 10% concentration (0.95 Mg m^{-3}). Lesser bulk density was registered in uncoated MNFG (0.80 Mg m^{-3}). The single grain weight and bulk density increase as the fertilizer coating concentration increases for all the sources which were in agreement with those suggested by [35] and [36]. Concentrations of the coating solution brought slight changes in the mass of fertilizer granules [37].

The crushing strength of different coated MNFG is shown in Table 3. On comparing the crushing strength data, it is important to compare equi-size granules, because crushing strength increases with coating concentration which provides sufficient mechanical strength to withstand normal handling and storage without fracture [38, 39]. The results showed that, crushing strength of uncoated MNFG was soft which was due to the binding agent used during granulation. The polysaccharide based binding material (starch) absorbs moisture which leads to poor crushing strength in uncoated granules. The crushing strength was strongly influenced by adhesion between the matrix of fertilizer granules [17]. The granules coated with citric acid and glycine exhibited the highest tensile strength (Hard) whereas fulvic acid and salicylic acid coating showed moderate strength (Medium hard). On the contrary, the lowest strength (soft) was observed in humic acid coated MNFG. The mechanical strength of a granule is influenced by porosity, shape, crystal surface, moisture content and materials used for coating [39]. From the perspective of crushing strength, it is satisfactory to note that the samples had better strength which facilitate to withstand operational handling [39].

The percentage of moisture by weight in the fertilizer is known as the moisture content which was a crucial product quality indicator and management tool for its

Table 3 Physical properties of organic acids and amino acids coated MNFG

Sources	Coatingconcen-trations (%)	Grain weight(g)		Bulk density (Mg m^{-3})			Crushing strength
Citric acid	0	0.07		0.80			Soft
	3	0.08		0.82			Hard
	5	0.09		0.83			
	10	0.09		0.87			
Humic acid	0	0.07		0.80			Soft
	3	0.08		0.81			Soft
	5	0.09		0.82			
	10	0.09		0.84			
Fulvic acid	0	0.07		0.80			Soft
	3	0.08		0.82			Medium hard
	5	0.09		0.86			
	10	0.09		0.91			
Salicylic acid	0	0.07		0.80			Soft
	3	0.07		0.91			Medium hard
	5	0.08		0.94			
	10	0.09		0.95			
Glycine	0	0.07		0.80			Soft
	3	0.07		0.87			Hard
	5	0.08		0.91			
	10	0.09		0.92			
		S	L	S x L	S	L	S x L
	SEd	0.007	0.006	0.013	0.009	0.008	0.018
	CD (P = 0.05)	NS	0.012	NS	0.019	0.017	0.037

S−Sources of polymers; L− Coating concentrations; NS−Non−significant; MNFG−Multi nutrient fertilizer granules

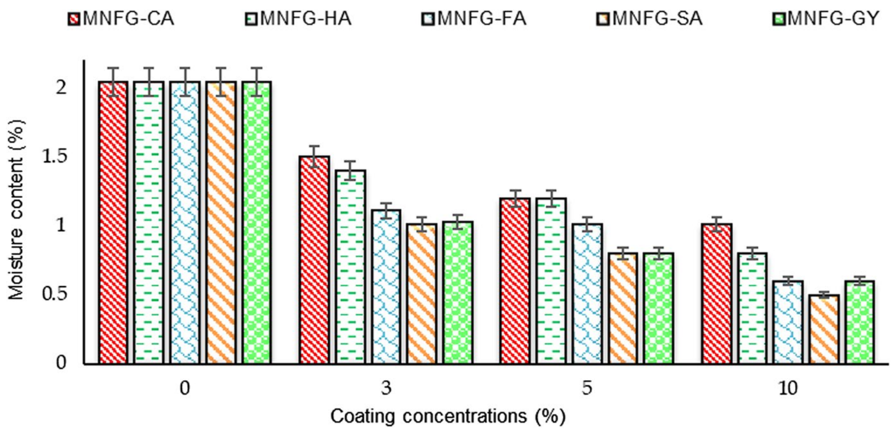

Fig. 3 Moisture content in the MNFG coated with different organic acids and amino acids at various concentration (MNFG-Multi Nutrient Fertilizer Granules, CA-Citric acid, HA-Humic acid, FA-Fulvic acid, SA-Salicylic acid, GY-Glycine, Error bars indicates significance level @ 5%)

storage and transport. If moisture content was high, fertilizers tend to form a coherent mass during their storage which reduces the flowability of fertilizers. Figure 3 illustrates the moisture content of coated and uncoated MNFG. The higher moisture content was recorded in uncoated MNFG as 2.04% followed by 3% citric acid coated MNFG (1.50%) and 3% humic acid coated MNFG (1.40%). Lesser moisture content was registered in 10% salicylic acid coated MNFG (0.50%) which was due to the highly hydrophobic nature of salicylic acid. The water absorption of coated polymers depends on number of hydrophilic groups and elasticity of the polymer networks [25]. The moisture content of all coated MNFG decreases with increasing coating concentrations of organic acids and amino acids. Similar findings were reported by [33], where the absorption of moisture decreased with the increase in percentage of coating concentration. The lesser moisture content has been recognized as a factor favoring satisfactory physical condition of fertilizer. There is an acceptation of the fact that caking is directly related to the moisture content of the fertilizers. About 1.5 to 2.0% moisture has been recommended as the maximum moisture content to prevent caking in fertilizers [42]. The newly developed products in the study had only 0.5 to 1.40% which was within the recommended range and proved their better suitability.

To make a good controlled release fertilizer coating, knowledge on water solubility is highly essential. The water permeability and solubility of polymers determine their rate of hydrolysis [43]. Higher solubility was discerned as 260 g L^{-1} in uncoated MNFG followed by 3% citric acid coated MNFG (250 g L^{-1}) and 3% humic acid coated MNFG (200 g L^{-1}). The solubility was lesser (70 g L^{-1}) in MNFG coated with 10% salicylic acid (Fig. 4) which was mainly due to the poor solubility of salicylic acid (<2 g L^{-1}) in water. The solubility of the citric acid in water at a room temperature of 25˚C was 59.2%. It resulted in higher solubility in citric acid coated fertilizer granules. Moreover, the solubility of coated MNFG proportionally decreases with increasing coating concentration of polymers irrespective of all sources [44]. The coating thickness and the solubility of polymers were

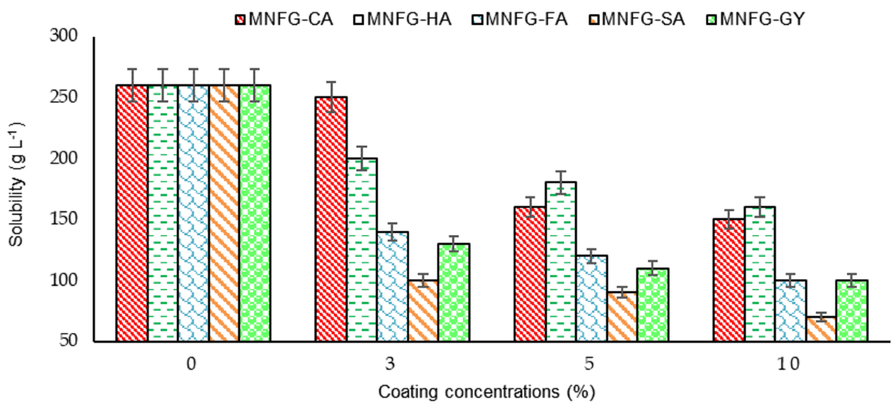

Fig. 4 Solubility of MNFG coated with different organic acids and amino acids at various coating concentration (MNFG-Multi Nutrient Fertilizer Granules, CA-Citric acid, HA-Humic acid, FA-Fulvic acid, SA-Salicylic acid, GY-Glycine, Error bars indicates significance level @ 5%)

considered as controlling factors for the slow release. Higher the coating thickness lesser was the solubility and resulting in the best slow-release outcome [45]. Several researchers reported that nutrient diffusion through the polymer coating and hydrolysis was greatly influenced by coating materials and their concentrations [46, 47].

During the first 2 min of submersion, the granules tend to swell, resulting in an increase in their mean weight diameter. Thereafter, the salts began to dissolve resulting in slaking. The multi-nutrient fertilizer granules were broken within 5 min of soaking in deionized water (Fig. 5a). Among the coated MNFG, 10% fulvic acid coated MNFG emerged as structurally stable as no breakage or burst of granules was observed over 24 h of soaking. Due to its high viscosity, granules swelled instead of caking (Fig. 5b). Few tiny cracks and pores were noticed in 10% salicylic acid coated MNFG and 5% fulvic acid coated MNFG which may increase the possibility of burst and further release of nutrients (Fig. 5c & d). The 10% humic acid coated MNFG (Fig. 5e) maintained its physicality for up to 20 min. All other coated granules were swollen and deformed in deionized water. The mechanism of nutrient release from coated MNFG is presented in Fig. 6.

The release of nutrients from polymer coated fertilizer is a three-step process involving the water transport by dissolving polymers, dissolution of fertilizer components and gradual release of nutrients. The organic acids and amino acids used for coating act as a physical barrier that controlled the nutrient release.

The pH and EC of the polymer coated MNFG at various coating concentrations are given in Figs. 7 and 8. The polymers and their coating concentrations barely altered the pH and EC of the fertilizer granules. The EC is an indicative of the

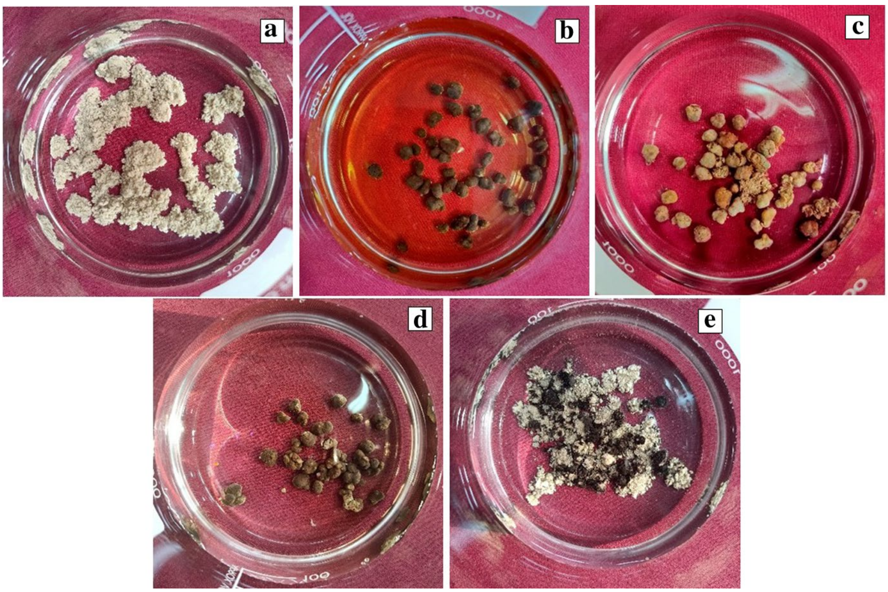

Fig. 5 Structural stability of different organic acids and amino acids coated MNFG after 24 h of soaking **a** MNFG, **b** 10% fulvic acid coated MNFG, **c** 10% salicylic acid coated MNFG, **d** 5% fulvic acid coated MNFG and 10% humic acid coated MNFG

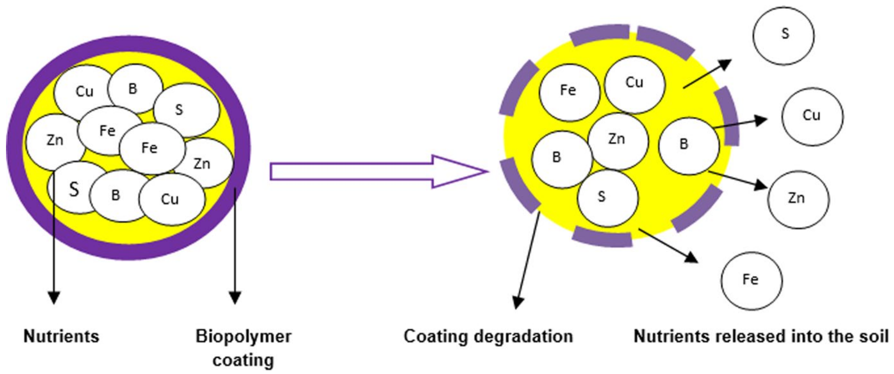

Fig. 6 Thematic view on the mechanism of nutrient release from MNFG coated with organic acids and amino acids

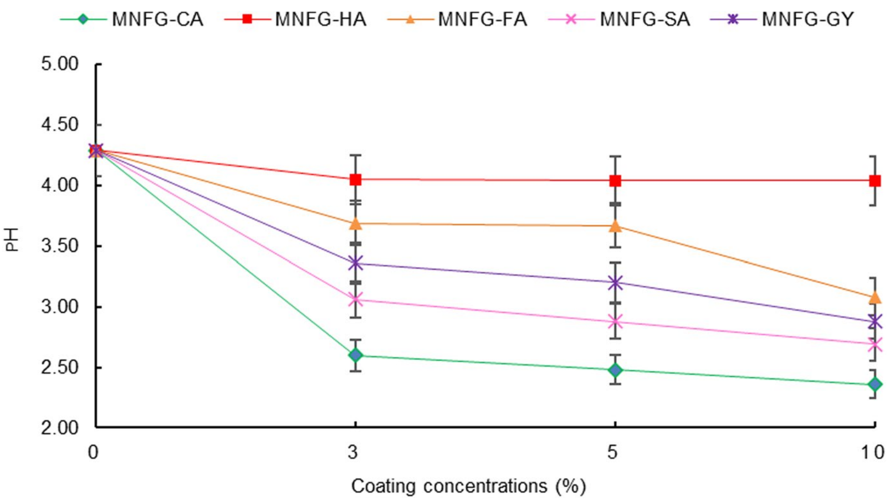

Fig. 7 pH of MNFG coated with different organic acids and amino acids at various coating concentration (MNFG-Multi Nutrient Fertilizer Granules, CA-Citric acid, HA-Humic acid, FA-Fulvic acid, SA-Salicylic acid, GY-Glycine, Error bars indicates significance level @ 5%)

fertilizer's soluble salts, which slightly increased owing to increasing coating concentration of all organic acids and amino acids. The pH also had significant variations (2.36 to 4.29) as a result of coating with different polymers at various concentrations. Higher EC (8.56 dS m^{-1}) and lesser pH (2.36) in MNFG have recorded with10% citric acid coating whereas lesser EC (6.48 dS m^{-1}) and higher pH (4.29) was registered in uncoated MNFG. The coating of various polymers increased the pH and electrical conductivity of the coated MNFG [39].

The elemental composition of MNFG coated with organic acids and amino acids at various concentrations is analyzed and given in Table 4. The Fe, Zn, Cu, B and S content of uncoated MNFG were found to be 4962, 869, 725, 98.1 mg kg^{-1} and

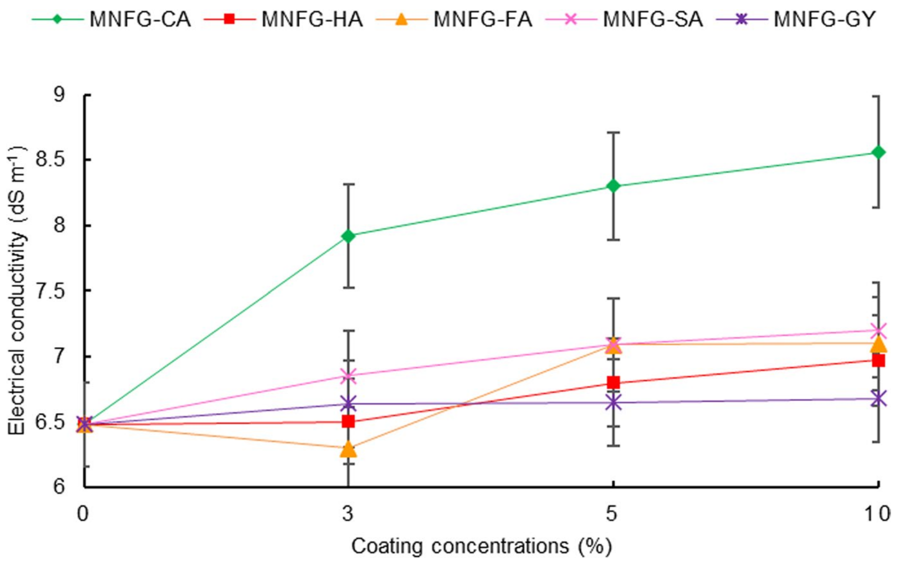

Fig. 8 Electrical conductivity of MNFG coated with different organic acids and amino acids at various coating concentration (MNFG-Multi Nutrient Fertilizer Granules, CA-Citric acid, HA-Humic acid, FA-Fulvic acid, SA-Salicylic acid, GY-Glycine, Error bars indicates significance level @ 5%)

17.1%, respectively. Irrespective of all polymers used, increasing coating concentration slightly decreased the nutrient contents which might be due to the nature of coating materials and their thickness. Similar findings were reported by various researchers, where increasing coating concentration slightly decreases the nutrient contents in the fertilizer granules [20].

Surface morphology and FTIR analysis

Based on the structural stability and solubility test, MNFGs coated at 10% coating concentration were selected for evaluating the surface morphology and FTIR analysis. Figure 9 shows the morphology and coating thickness of the MNFG and coated MNFG under scanning electron microscope (SEM). To examine the surface morphology, SEM micrographs were obtained at different magnifications on the cross-sectional view and profile of the coated fertilizers. Uncoated MNFG has compact rough surface and greater number of pores in the surface of the granules (Fig. 9a1, a2) which was due to lack of polymer coating on their surfaces. The coated MNFG, showed smooth surface with few small cracks and pores, but no large pores that permit free circulation of the solution between the interior and exterior of grains were noted. Similar finding was reported by researchers, who found that coating smoothens the surfaces by forming a cohesive film on the granules and there was a good interaction (adhesion) between the granule and coating agents [45, 48].

The chemical composition of organic acids and amino acids coated MNFG was confirmed by the FTIR spectroscopy (Fig. 10). The data revealed that uncoated MNFG spectra show strong absorption peaks in the range of 3900 to 3700 cm^{-1}

Table 4 Elemental composition of organic acids and amino acids coated MNFG

Sources	S (%)				Mean	Fe (mg kg^{-1})				Mean
	Coating concentration					Coating concentration				
	0	3	5	10		0	3	5	10	
Citric acid	17.1	15.1	13.7	13.5	14.8	4992	4217	4137	4127	4368
Humic acid	17.0	16.7	16.4	16.3	16.6	4987	4334	3690	3416	4106
Fulvic acid	17.2	16.7	16.5	16.4	16.7	4990	3715	3819	3658	4045
Salicylic acid	16.9	16.0	15.3	15.0	15.8	4988	3888	3716	3393	3996
Glycine	17.0	16.8	16.4	16.1	16.5	4993	4039	3956	3467	4113
Mean	17.0	16.2	15.6	15.4	16.1	4990	4038	3863	3612	4125
	S	L	SxL			S	L	SxL		
SEd	0.18	0.16	0.37			41.6	37.2	83.3		
CD (P = 0.005)	0.37	0.33	0.74			84.5	75.5	169		
Citric acid	868	783	747	700	774	725	670	662	642	674
Humic acid	870	855	805	755	821	720	689	657	649	678
Fulvic acid	865	786	783	750	796	728	613	608	601	637
Salicylic acid	872	780	765	725	785	724	694	674	645	684
Glycine	864	832	787	740	805	718	697	682	643	685
Mean	867	807	777	734	796	723	672	656	636	671
	S	L	SxL			S	L	SxL		
SEd	8.41	7.52	16.8			6.41	5.72	12.8		
CD (P = 0.005)	17.1	15.2	NS			13.0	11.6	26.0		
B (mg kg^{-1})										
Citric acid	98.0	96.8	96.1	92.5						
Humic acid	98.1	96.5	95.0	94.7						
Fulvic acid	97.8	97.9	94.1	93.7						
Salicylic acid	98.5	98.0	96.6	94.6						
Glycine	98.2	97.6	92.8	90.1						
Mean	98.1	97.3	94.9	93.1						
	S	L	SxL							
SEd	0.65	0.58	1.30							
CD (P = 0.005)	1.32	1.18	NS							

S− Sources of polymers; L− Coating concentrations; NS−Non−significant; MNFG−Multi nutrient fertilizer granules

due to the presence of characteristic asymmetric and symmetric stretching vibrations of (O–H) in MNFG. It showed that there might be no chemical reactions during the mixing process and mixture of fertilizers could contact with each other mainly by some physical attraction such as Vander Waals force, hydrogen bonding and electrostatic attraction [49]. In the spectra of all organic acids coated MNFG, there are strong stretching bands of 3197 cm^{-1}and 1990 at cm^{-1}were ascribed to the stretching of hydroxyl group (O–H) and carboxylic group (-COO^{-}), which could be observed clearly. It can be seen from the spectrum of 10% glycine coated MNFG

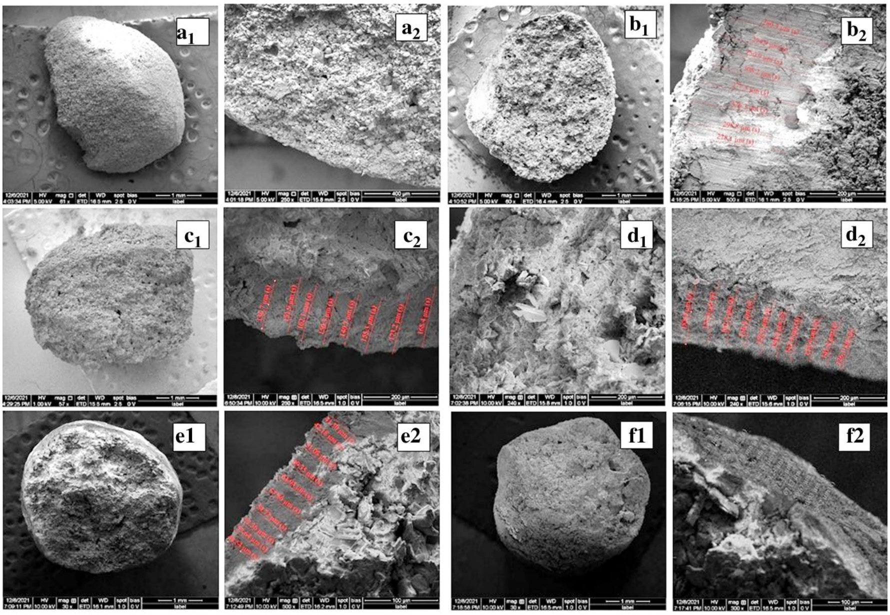

Fig. 9 Scanning electron microscope images of uncoated MNFG (a_1, a_2), 10% citric acid coated MNFG (b_1, b_2), 10% humic acid coated MNFG (c_1, c_2), 10% fulvic acid coated MNFG (d_1, d_2), 10% salicylic acid coated MNFG (e_1, e_2) and 10% glycine coated MNFG (f_1, f_2)

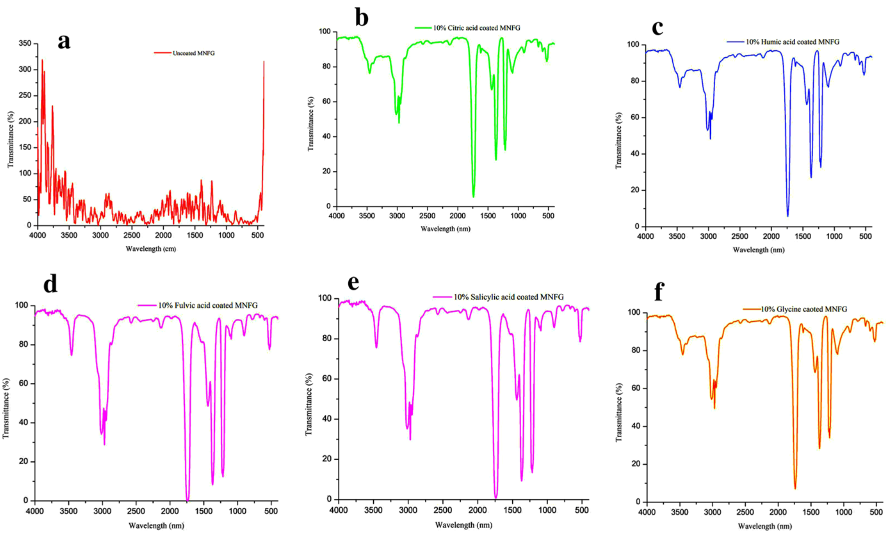

Fig. 10 Fourier transform infrared spectroscopy images of uncoated MNFG (**a**), 10% citric acid coated MNFG (**b**), 10% humic acid coated MNFG (**c**), 10% fulvic acid coated MNFG (**d**), 10% salicylic acid coated MNFG (**e**) and 10% glycine coated MNFG (**f**)

that there is a strong broad peak at 3052 cm^{-1} and 3986 cm^{-1}, representing the presence of stretching vibration region of -OH and -NH_2 and the intermolecular hydrogen bonding. The finger print zone of 1500–400 cm^{-1} all the peaks were similar for all sources. The -COO^- and -NH_2 stretching vibrations might be due to the layer of organic acids and amino acid coatings on the MNFG. Compared with the uncoated MNFG curve, organic acids and amino acid coating of MNFG shifted the absorption spectra and the shift of the characteristic peak may correspond to the intermolecular reactions between the MNFGs and coating agents which are physical but not chemical nature.

Conclusions

Multi-nutrient fertilizer granules were prepared by physical mixing of fertilizer grades of gypsum, ferrous sulphate, zinc sulphate, copper sulphate and borax. The controlled release properties of the multi-nutrient fertilizer granule were obtained as a result of coating with organic acids and amino acids at various concentrations. Depending on the nature of polymers and their coating concentrations, the morphological and physico-chemical properties of the obtained coated fertilizer materials differed from each other. Morphology and the thickness of the coating layer on the multi-nutrient fertilizer granules determined by SEM showed smooth surface with few cracks and pores as compared to uncoated which had large and more pores permitting the solutions to circulate and release the nutrients. The solubility, moisture content, pH and elemental composition were decreased with increasing coating concentrations of polymers. Lesser moisture content (0.50%) and solubility (70 g L^{-1}) were registered with 10% salicylic acid coated MNFG whereas higher moisture content and solubility were noted in uncoated MNFG as 2.04% and 260 g L^{-1}, respectively. The increase in grain weight, bulk density, electrical conductivity, stability and crushing strength was directly proportional to the coating concentration of polymers used. The bulk density was higher (0.95 Mg m^{-3}) in granules coated with salicylic acid at 10% coating concentration and lesser (0.80 Mg m^{-3}) in uncoated MNFG. The MNFG coated with 10% fulvic acid was found to be structurally stable with moderate crushing strength. The results indicated that variations in the characteristics of the polymer coated MNFG would be utilized in producing controlled release fertilizer that fit the requirement of growing plants.

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Declarations

Conflict of interest Authors declared that no competing interests exist among them.

Data availability Authors declare no data sharing as the research data cannot be shared.

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