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RESEARCH ARTICLE

Synthesis and characterization of nano phosphorus fertilizer from rock phosphate

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Abstract

Phosphorus is a vital macronutrient required for the growth and development of plants. The major concern regarding phosphorus (P) is low availability. Fertilizers are generally supplied to increase the crop growth. Rock phosphate (RP) is mainly used as the precursor for synthesizing phosphatic fertilizers. The applied phosphatic fertilizers are usually fixed in the soil and the excess fertilizers result in eutrophication and pollute the water bodies. To address these challenges nanofertilizer technology was created. In the present study, nano phosphorus fertilizer was developed using P-solubilizing bacteria (*Bacillus megaterium*) from RP. The nano RP was characterized using particle size analysis (PSA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM). The size of nano RP using a particle size analyzer was ~450 nm with a polydispersity index of 0.803. The FTIR spectra of RP show the presence of phosphate minerals, whereas some peaks of RP were altered after bios olubilization of RP. The XRD pattern indicated the presence of apatite and calcite and the number of peaks of nano RP was 13, while RP has 25 diffraction peaks. The scanning electron microscope image of nano RP indicated the reduction in the crystalinity of RP.

Keywords

Bacillus megaterium ; biosolubilization; nanofertilizer; rock phosphate

Introduction

An essential component of agricultural production is phosphorus. Phosphorus is a vital macronutrient that significantly influences seed germination as well as both vegetative and reproductive growth in plants (1). However, most soils don't contain enough of P to support adequate crop growth. Its absence drastically reduces the crop's ability to grow and develop (2). Additionally, P availability can enhance plants' ability to fix nitrogen and promote their growth throughout their life cycle (3).

Fertilizers are essential to crops because they supply the nutrients needed for growth and improve crop quality and yield. In agricultural soils, superphosphates such as single superphosphate (SSP) and triple superphosphate (TSP) are the predominant sources of P fertilizer. Interest in using RP has increased due to the high cost of these soluble phosphate fertilizers (2). Since phosphate rocks aren't ideal for producing phosphoric acid and other soluble fertilizers like TSP or SSP, interest in using them has grown because of their

relative affordability and potential for use, either with or without amendments. In addition to being expensive, phosphatic fertilizers are in short supply compared to demand. Therefore, it is imperative to investigate ways to preserve phosphatic fertilizers without compromising financial returns. However, the problem of eutrophication in surface waters is made worse by applying P fertilizers. Only a small soluble fraction of P is available for plant uptake, even though soils may contain P pools several thousand times higher than what is needed for plant growth. This is caused by intricate edaphic processes and interactions with the soil constituents, including calcium in alkaline soils and iron and aluminum hydroxides in acidic soils (4).

More emphasis has recently been paid to the bio-solubilization of RPs by various bacterial, fungal, and actinomycetes species. Microbial technology-based RP solubilization has been suggested as a low-cost, low-energy-input method to improve agronomic efficiency. Over the past ten years, they have received much attention in agronomic techniques and multiple reports have suggested that some microbes are effective at solubilizing RP (5).

Nonetheless, the availability of phosphatic fertilisers is insufficient to meet demand and costly. Therefore, investigating the potential for preserving phosphatic fertilizers without compromising economic returns is quite desirable. Nano and biophosphatic fertilizers may be crucial in reducing the reliance on chemical fertilizers by enhancing crops' availability to phosphorus and other nutrients. Thus, novel crop management methods may be made possible by nanotechnology, such as the use of nano-scale fertilizer. A mitigating technique for obtaining an effective fertilizer that lowers the danger of eutrophication is the nano-scaling of fertilizer (6).

Thus, applying novel techniques and fertilizers can be crucial to advancing the agricultural sector (2). Mitigation of fertilizer impact is believed to be accomplished through nano-scaling fertilizers, which concurrently reduces the risk of eutrophication. There has been a recent shift in how nano fertilizers are prepared and applied to improve fertilizer use efficiency, boost crop yield and quality, lessen the negative environmental effects of chemical fertilizers, and create a more environmentally friendly and sustainable agricultural sector (7). The technology of nano-fertilizers is a creative tactic. Nanofertilizers are crucial for boosting agricultural output and eliminating environmental and soil hazards.

Materials and Methods

Materials

Rock phosphate, *Bacillus megaterium* culture, all other reagents and glassware are laboratory-grade.

Synthesis of nano rock phosphorus from rock phosphate

Rock phosphate was initially subjected to high-energy planetary ball milling for around 30 min, with a ball-to-powder ratio of 10:1 and a speed of 150 rpm, facilitating the decrease of particle size from macro to nano. The ball milling was followed by the acidulation of the milled RP using sulphuric acid (10% acid utilized for 1 g of sample), leading to the acidulation of P from the RP. Then, the acidulated RP was neutralized with 1 N KOH using the back titration method, where a phenolphthalein indicator was added before titration and disappearance of pink colour was the endpoint. The nutrient broth was prepared and autoclaved for 20 mins at 121 psi. *B. megaterium* was inoculated in nutrient broth (Glucose: 5g, Peptone: 5g, Beef extract: 3g, NaCl: 5g, Distilled water: 1000 mL pH: 7.0) and allowed to grow for 48 hours in an incubator shaker at 30˚C at 150 rpm. Then, the grown culture was centrifuged, the supernatant solution was added to the neutralized RP solution 1:1 ratio and the culture was allowed to grow for 48 hours in an incubator shaker. Then, the solution and culture were centrifuged and the pellet was collected. The pellet was dried in a hot air oven for characterization and further analysis.

Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry is an analytical instrument used for elemental determination. Thermo Scientific TM iCAP™ RQ ICP-MS is outfitted with a quartz cyclonic spray chamber, a micro mist borosilicate glass nebulizer, an ICP torch, nickel sampler and skimmer cones, a quadrupole mass analyzer and a mass spectrometry detector. Under ideal auto-tune conditions of the apparatus straight from quality control with Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, all the samples were examined in Kinetic Energy Discrimination (He KED) mode with pure He as the collision gas in the collision/reaction cell (CRC) (8).

Dynamic light scattering (DLS) analysis

The mean droplet size, polydispersity index and zeta potential were measured using a Horiba scientific Nano particle analyzer SZ- 100. The particle size analyzer works based on dynamic light scattering. The polydispersity index determines sample heterogeneity and zeta potential determines sample stability. By measuring the rate of fluctuations in the laser light intensity scattered by the particles as they diffused through aqueous solution, DLS measurement estimated the size distribution and zeta potential of nano RP particles and the measurement was replicated thrice.

Fourier Transform Infrared Spectroscopy Spectra were normally acquired using 4 cm^{-1} resolution, yielding IR traces over the 400 - 4000 cm^{-1} range. The functional groups in the formulation were examined using the JASCO FT/IR-6800. FTIR identifies molecules through chemical bonding by creating an infrared absorption spectrum.

Structural property- X-ray diffraction (XRD)

One of the most effective analytical methods for determining the identity of unidentified crystalline materials is XRD spectrometry. The crystal structure of the nano RP particles was examined using XRD analysis. The structural property was identified using Ultima IV X-RAY DIFFRACTOMETER. XRD works on the principle of Bragg's law, i.e., scattering of waves from the crystalline structure, which helps to identify the arrangement of atoms in a molecule and the crystallographic nature of the sample. The XRD was operated at 40 kV and 30 mA with monochromated Cu Ka radiation. XRD data over the range of angle (2^{θ} =10 - 90^{o}) were collected with a step size of 0.02 degrees.

Scanning electron microscopy

The formulation's topography, morphology, composition and crystallographic information were identified through QUANTA 250 Scanning Electron Microscope.

Results and Discussion

Inductively coupled plasma mass spectrometry

Inductively Coupled Plasma Mass Spectrometry is an analytical technique that uses a high-temperature plasma to ionize elements in a sample and then measures the ions using a mass spectrometer. Rock phosphate was analyzed using ICP-MS before and after ball milling and the results are shown in Table 1. All elements of RP experienced a modest reduction post-ball milling; however, cobalt, barium, mercury and lead exhibited an increase, maybe attributable to the collision of RP with zirconium balls.

Particle size analyzer

The size of RP and biologically solubilized RP were analyzed by dynamic light scattering technique using a particle size analyzer and the results were shown in Fig. 1. and Fig. 2. respectively the comparison between their particle size and polydispersity index were given in Table 2. The dimensions of RP and biologically solubilized RP were approximately 1295.8 nm and 450.9 nm, respectively, indicating a reduction in the size of RP after ball milling and subsequent biological solubilization. The polydispersity index of RP and biologically solubilized RP were 1.322 and 0.803, respectively. The polydispersity index of biologically solubilized RP of 0.803 represents the reduction of RP's heterogeneous nature. The statistical analysis of DLS measurements for RP yielded a mean of 1295.8 nm, a mode of 1279.1 nm and a standard deviation of 181.1 nm. and the statistical analysis of biologically solubilized RP were mean 450.9 nm, mode 548.3 nm and the standard deviation of 116.1 nm.

Table 1. Inductively Coupled Plasma- Mass Spectroscopy results of Rock phosphate and Ball milled rock phosphate

Elements	RP (in ppm)	BMRP (in ppm)
7 Li (Lithium)	8.3224	7.6254
9 Be (Beryllium)	1.8396	1.2430
11B (Boron)	31.3220	29.0812
23Na (Sodium)	6426.6352	5931.9162
24Mg (Magnesium)	20380.0563	20232.6763
27 Al (Aluminium)	6589.5196	5818.2004
31P (Phosphorus)	136338.8464	122506.7287
39K (Potassium)	3092.5842	2722.4522
44Ca (Calcium)	150474.0432	137722.6801
48 Ti (Titanium)	805.6676	747.9710
51V (Vanadium)	154.5534	130.3043
52Cr (Chromium)	121.6373	109.4590
55Mn (Manganese)	650.9397	621.5681
57Fe (Iron)	14135.8917	12840.0574
59Co (Cobalt)	2.8599	201.6964
60Ni (Nickel)	23.7052	20.8044
63Cu (Copper)	12.9114	11.4329
66Zn (Zinc)	219.6781	204.5244
75As (Arsenic)	10.0506	9.2574
95Mo (Molybdenum)	10.0659	9.3286
107Ag (Silver)	0.0370	0.0519
111Cd (Cadmium)	4.3495	4.1101
118 Sn (Tin)	0.0737	0.0746
121Sb (Antimony)	0.2524	0.2445
133Cs (Cesium)	0.5215	0.4789
137 Ba (Barium)	97.5543	110.8146
202Hg (Mercury)	1.0181	7.0459
205Tl (Tellurium)	0.4561	0.4317
208 Pb (Lead)	17.7470	18.0326

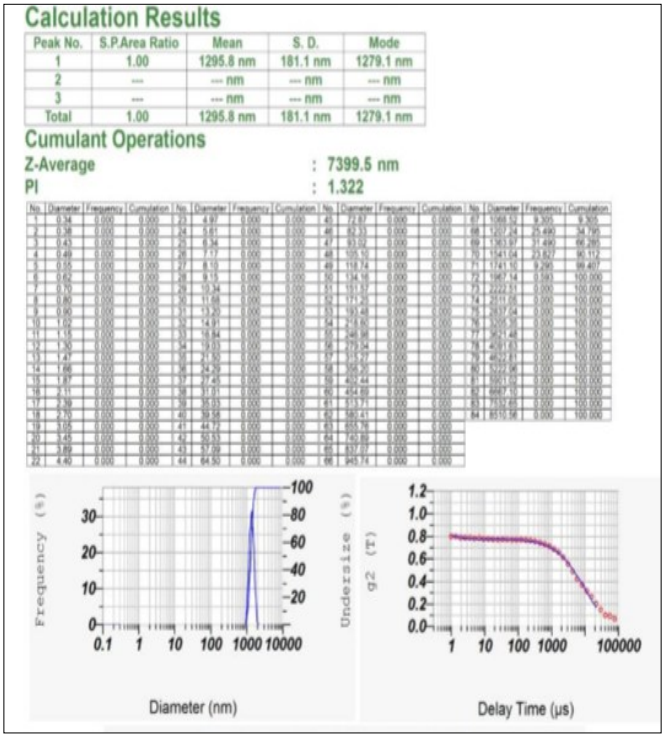

Fig. 1. Size of rock phosphate measured by DLS technique.

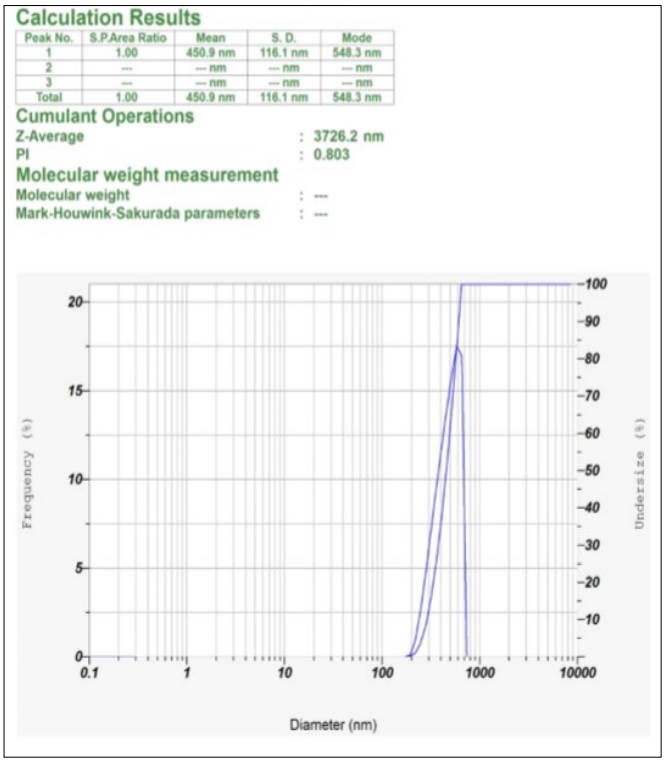

Fig. 2. Size of biologically solubilized nano rock phosphate measured by DLS technique.

Table 2. Comparison of rock phosphate and nano rock phosphate

	Rock phosphate	Nano rock phosphate
Particle size	1295.8 nm	450.9 nm
Polydispersity index	1.322	0.803
Elemental composition	Calcium phosphate, dolomite, aragonite, quartz, silicon dioxide, calcite, apatite, chloroapatite, Al_2O_3 and fluorapatite	Lime CaO, dolomite, aragonite, quartz, calcite, Al_2O_3, calcite, chloroapatite and fluoroapatite
Number of diffraction peaks	25	13
Transmittance peak	2161.81, 1428.03, 1037.52, 873.60, 790.67, 569.86 and 465.72 cm^{-1}	3277.43, 1643.05, 1532.17, 1099.23 and 613.25 cm^{-1}.

Fourier transform infrared spectroscopy (FTIR)

Functional groups of RP and biologically solubilized RP were characterized using FTIR. The results are shown in Fig. 3 and Fig. 4, respectively and a comparison between their transmission peaks is given in Table 2. An FTIR spectrum of RP has transmittance peaks at 2161.81, 1428.03, 1037.52, 873.60, 790.67, 569.86 and 465.72 cm^{-1}. The transmittance peak at 2161.81 cm^{-1} represents oxygenated C=O groups, 1428.03 cm^{-1} indicating strong absorption bands of carbonate, 1037.52 cm^{-1} indicating the absorption bands of phosphates, 873.60 cm^{-1} representing bending mode characteristic to the carbonate of calcite in the ore, 790.67 cm^{-1} attributed to 1,2,4 trisubstituted strong C-H bending, 569.86 cm^{-1} indicating bending of phosphate in the apatite spectrum and 465.72 cm^{-1} representing calcite bands these results were on par with the results of (9). An FTIR spectrum of biologically solubilized RP has transmittance peaks at 3277.43, 1643.05, 1532.17, 1099.23 and 613.25 cm^{-1}. 3277.43 cm^{-1} attributed to the strong, broad O-H stretching of alcohol, 1643.05 cm^{-1} representing C=C stretching of alkene, 1532.17 cm^{-1} indicated the strong N-O stretching of nitro compounds and 1099.23 cm^{-1} attributed to HPO_4^{2-} and PO_4^{3-} antisymmetric stretching which was correlated with the findings of another study (10). Moreover, there was some variation in the band sites and intensities following the solubilization process.

X-ray diffraction

The crystalline structure and phase of RP and biologically solubilized RP were examined using XRD, with results presented in Fig. 5 and Fig. 6, respectively. A comparison of their elemental compositions is provided in Table 2. The highest intensity peak of apatite is located at about 31.9° and it is closely followed by

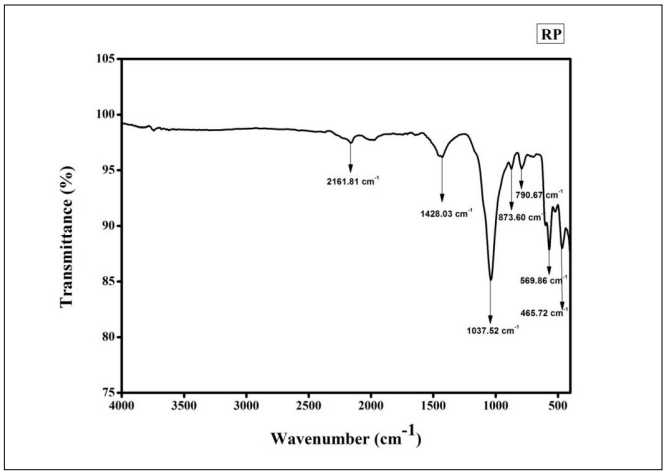

Fig. 3. FTIR spectra of rock phosphate.

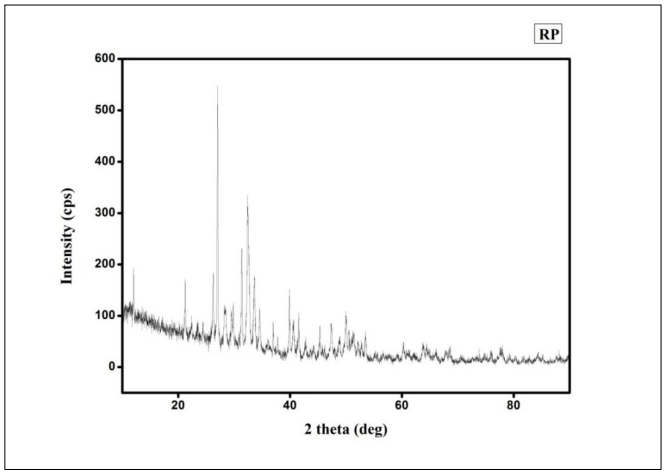

Fig. 5. XRD spectra of rock phosphate.

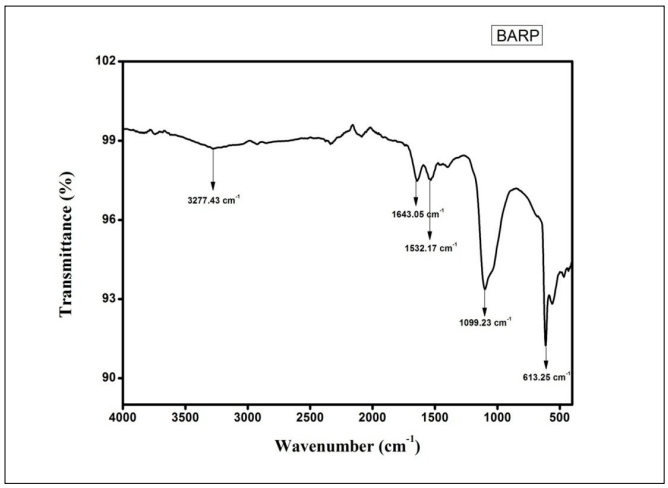

Fig. 4. FTIR spectra of biologically solubilized rock phosphate.

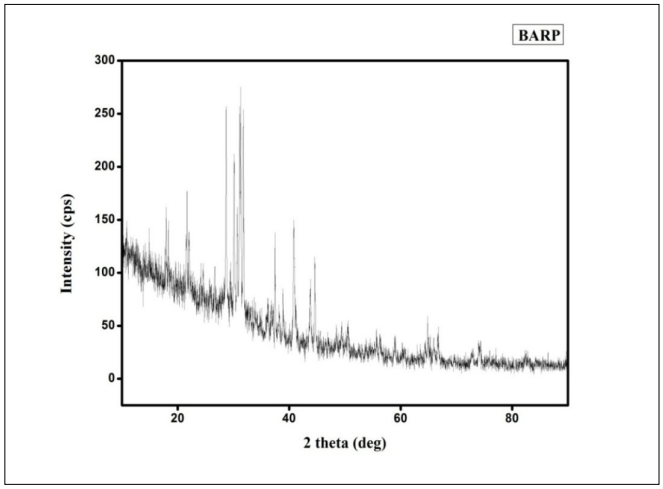

Fig. 6. XRD spectra of biologically solubilized rock phosphate.

three other high-intensity peaks between 32° and 34°. Additionally, apatite has diagnostic peaks with lesser intensities, roughly at 26°. Calcite is the primary component of phosphate ore and has a separate main peak located at 29.4° (9). The results were like the findings of one study (5) where the sample contained quartz SiO_2, as evidenced by the strongest peak seen at 2θ values of 28.04 on the lattice planes (101) and observed the peaks corresponding to calcium phosphate, lime CaO, dolomite and chloroapatite with the 2θ values of 11.82, 18.20, 22.28 and 35.96 respectively. XRD patterns of RP are like the findings of a previous experiment (2), indicating that they were composed of rich phosphate-containing minerals like apatite, calcite, etc. XRD pattern of RP has 25 peaks, whereas biologically solubilized RP has 13 peaks. The decrease in the number of peaks of biologically solubilized RP signifies a drop in the crystallinity of RP.

Scanning electron microscopy

The RP and biologically solubilized RP were analyzed for surface morphology using a scanning electron microscope (SEM) and the results were shown in Fig. 7. and Fig. 8. respectively. The SEM micrograph of RP illustrates the crystalline characteristics of the material, corroborated by XRD techniques. At the same time, the biologically solubilized RP exhibits less crystallinity and forms a coating over the RP.

Statistical analysis

The statistical analysis for ICP-MS results was carried out and it was found that the mean of RP was 20418.11 ppm and the standard deviation of RP was 49311.72 ppm. In contrast, the mean and standard deviation of ball-milled RP were 18057.722 ppm and 49114.65 pm, respectively. The statistical analysis of DLS measurement of RP was a mean of 1295.8 nm, mode 1279.1 nm and a standard deviation of 181.1 nm and the statistical analysis of biologically solubilized RP was a mean of 450.9 nm, mode 548.3 nm and standard deviation of 116.1 nm.

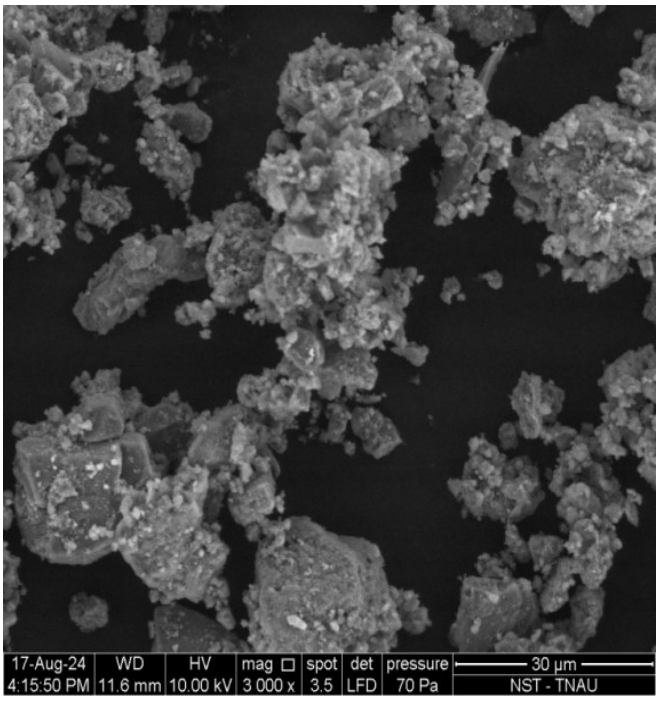

Fig. 7. SEM micrograph of rock phosphate.

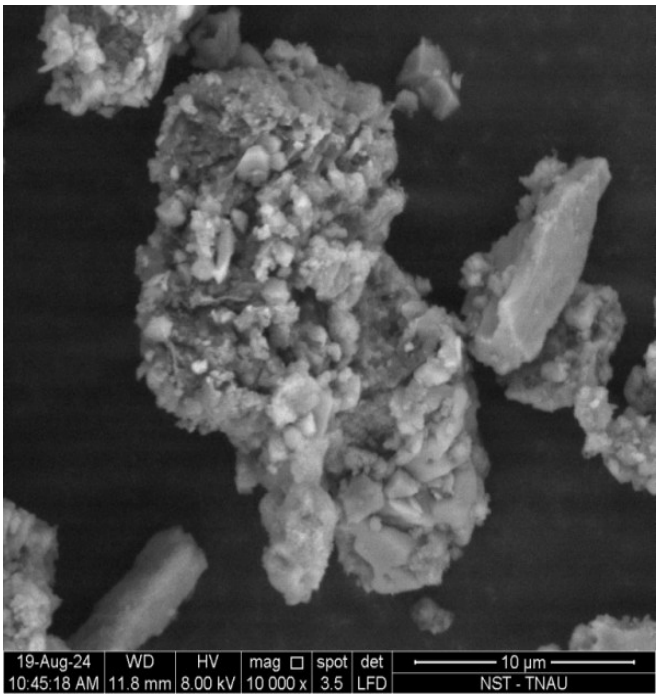

Fig. 8. SEM micrograph of biologically solubilized nano rock phosphate.

Conclusion

The nano phosphorus fertilizer was synthesized from RP utilizing *B. megaterium*. The synthesized nano RP exhibited a dimension of around 490 nm and a polydispersity index of 0.803. The XRD peaks show the presence of phosphate minerals and reduction of crystallinity of RP after biosolubilization, which was again confirmed with the scanning electron microscope images of nano RP. The functional groups of RP and nano RP were analyzed through FTIR and the results confirmed the presence of phosphate minerals. In this paper, the method of synthesis of nanophosphorus fertilizer is described. Further studies on the release kinetics of the developed nano phosphorus fertilizer and bio-efficacy studies have to be carried out for the potential outcome of this study, including the phosphorus release pattern and reduced environmental impacts.

Authors' contributions

CSR participated in topic conceptualization, methodology, and supervision. JJ conducted experiments, collected data, analyzed and wrote the original draft. MP, DB, NS and MR have done the overall monitoring.

Compliance with ethical standards

Conflict of interest: Authors do not have any conflict of interest to declare.

Ethical issues: None

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