INTERNATIONAL JOURNAL OF EARTH AND ATMOSPHERIC SCIENCE
Journal homepage: www.jakraya.com/journal/ijeas

ORIGINAL ARTICLE

Soil Properties Management and the Role of Nanoparticles of Elemental Sulphur

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Submitted: 30/04/2015

Revised: 04/06/2015

Accepted: 17/06/2015

Abstract

Improper use of fertilizers and less scientific agricultural practices caused deterioration of the soil cover on the earth surface. Excessive farming without adequate replenishment of soil chemical components has adversely affected the agricultural productivity of soils. Sulphur deficiency in agricultural soil is one of the major concerns affecting crop yield. Supplying elemental sulphur as a fertilizer is proven to be a solution for this problem. The elemental sulphur gets oxidised by microbial activity to a form that can be assimilated by the plants, provided it is in the form of sufficiently small sized particles. Submicron to nano sized elemental sulphur particles embedded with other fertilizers is expected to improve crop yield considerably. A procedure to prepare a fertilizer containing nanoparticles of elemental sulphur is introduced in this paper. Monoammonium phosphate or diammonium phosphate, elemental sulphur and KOH are used to prepare an NPKS fertilizer composition with the elemental sulphur as particles of size < 5 μm. The method converts ~68 % of the elemental sulphur into submicron to nano sized particles. Nanoparticles of elemental sulphur will be oxidized by the aide of soil microbes over time and subsequently absorbed by plants, which makes the fertilizer a sustainable source of sulphur nutrient.

Keywords: Soil sustainability, Nutrient supplementation, Nanosulphur, NPKS.

1. Introduction

With the current rate of population growth, the world population is expected to hit 9.1 billion by 2050, which necessitates an increase in agricultural production by ~70 % (Jaggard *et al.*, 2010). However, the considerable imbalance between soil erosion and soil production limits the availability of agricultural lands (Montgomery, 2007; Suresh *et al.*, 2013; 2014a). Urbanization and industrialization also limits the availability of agricultural lands (Kaarstad, 1997; Baruah and Dutta, 2009). Agronomic research in the last few decades is hence concentrated in increasing the crop yield (Jamal *et al.*, 2010 and references therein). Application of chemical fertilizers has largely helped improving the yield in countries like China and India, being the largest consumers of fertilizers in the world. Currently India consumes more than 25 million Tons of fertilizers. In terms of nitrogen (N), phosphorus (P) and potassium (K) the consumption is about 15 %, 19 % and 14 % of the global consumption, respectively (Jaga and Patel, 2012). The deficiency in P has seriously affected the agricultural productivity in the Developing World. The scarcity of high grade phosphate reserves constrains the availability of P as a fertilizer product, and hence an increase in the production of monoammonium phosphate (MAP) in comparison to diammonium phosphate (DAP) is predicted (Blair, 2009). The advantage of MAP over DAP is that the former can be made using raw materials with less purity. Similar to P, deficiency of S in soil has been affecting crop production. Owing to the practices of sulphur (S) free fuels and reduction of emission from biofuels, the availability of S as oxides in gaseous form in the atmosphere has been reduced. Agricultural practices without S-containing fertilizers have caused excessive consumption of S from soil, creating a need of sulphur supplementation (WO 2014/009326 A1). Sulphur supply to agricultural soil is generally done by applying sulphate fertilizers (e. g. ammonium sulphate). The advantage of sulphate is that plants can directly assimilate it, as it is soluble in water. However, the high solubility makes the sulphates easily leachable, reducing its longevity in the soil. An alternative method is to apply elemental sulphur to the soil which then will get oxidised to plant-assimilable sulphate form by microbial activity. The oxidation of elemental sulphur also depends on field conditions like temperature, moisture, pH etc. (Chapman, 1989). Since elemental sulphur is insoluble in water, it will be available for the plants for a longer period of time when compared to sulphates. Blair (2009) compared the loss of S from soil, when applied as elemental sulphur and as gypsum to see the complete loss of S from gypsum in a year against the loss of only ~50 % of the elemental S.

Considerable numbers of patents have been obtained by industrial and academic organization on preparation of elemental sulphur containing fertilizers (e.g. U.S. Pat. No. 2013/0167604 A1; U.S. Pat.No. 2012/0128981; U.S. Pat.No. 2012/0128981 A1; WO 2001087803 A1; U.S. Pat.No. 5571303; U.S. Pat.No. 3333939; U.S. Pat.No. 5653782). Generally, elemental sulphur in the form of prills or cakes is milled to mix with other fertilizers or molten sulphur is used to coat other fertilizers. However, the uniform distribution and subsequent absorption of sulphur will be adversely affected by the larger grain sizes, non-uniform coating thickness and non-uniform size distribution of the 'other fertilizer' on which sulphur is coated. The oxidation rate of elemental sulphur largely depends on particle size distribution (Hu *et al.,* 2002). Significant increase in the rate of oxidation of sulphur fertilizer is noted with decrease in particle size and increase in applied amount (Hu *et al.,* 2002), which shows the need of micronising elemental sulphur for fertilizer applications. Also, Massilimov *et al.* (2012) observed a hindrance in plant growth caused by coarser (fine ground) particles of elemental sulphur. They studied the effect of application of submicron to nano-sized particles and reported up to 125% enhancement in plant growth, when applied with a proper wetting agent for sulphur. Their results re-iterate the need of sub-micronizing elemental sulphur to use it as a fertilizer.

Here we discuss the influence of addition of elemental sulphur to the soil. A new method to embed sub-micron to nano sized elemental sulphur on monoammonium phosphate or di-ammonium phosphate to produce S-MAP (sulphur embedded MAP) and S-DAP (sulphur embedded DAP) is introduced in detail. As an additional benefit, potassium is also included in the fertilizer product to get an NPKS combination of fertilizer. The benefits and agricultural advantages of the soil obtained by the addition of nanosulphur particles are discussed.

2. Materials and Methods

Pure elemental sulphur is used in the experiments reported here. Commercially available mono ammonium phosphate (MAP) and diammonium phosphate (DAP) fertilizers are procured from GSFC Limited, Vadodara. All other chemicals used are of LR Grade. De-ionized Milli-Pore water is used for all the experiments and analysis.

Massilimov *et al.* (2008) describes the precipitation of elemental sulphur particles of size ~1 μm or less when a solution of polysulphide of an alkali or alkaline earth metal is diluted up to 50 times. They have demonstrated precipitation of sub-micron sized particles using solutions of polysulphide of Na, K, Ba, Ca and Sr. Instead of a large volume dilution, addition of mineral or organic acid (HCl, HNO_3, HCOOH etc.) also causes precipitation of elemental sulphur. Polysulphide of K can be prepared as described in Massilimov *et al*. (2008). To a boiling solution of KOH, pulverized elemental sulphur can be added as slurry in water to produce potassium polysulphide, as per the following reaction:

$$8\,S + 6\,KOH = 2\,K_2S_3 + K_2S_2O_3 + 3\,H_2O$$

On acidification, two S atoms will be released from the K_2S_3 molecule. The released S will form a precipitate of particles of size ~1 μm. These particles can then be separated from the solution by filtration.

The monoammonium phosphate has a pH of 4.5 in a saturated solution and it can be used to liberate elemental S from K_2S_3. Stoichiometrically calculated amount of KOH solution is brought to boiling on a hotplate, to which pulverized sulphur slurry is added slowly to produce K_2S_3 solution of cherry colour. The solution is then left boiling for ~30 minutes for completion of the reaction; after which it is allowed to cool down to room temperature. The density of the solution is ~1.2 g/cm^3. To this solution, the anionic surfactant sodium lauryl sulphate is added. This will keep the elemental sulphur particle from conglomeration, when precipitated. When the solution of MAP in water, which has a pH of ~4.4, is added drop by drop to the K_2S_3 solution with continuous stirring, elemental sulphur submicron particles are precipitated. Release of some amount of H_2S also is noted at this stage.

The solution containing dispersed micronized elemental sulphur and MAP is then dried at~70 °C temperature so as to obtain sulphur embedded MAP in the form of a soft cake. This cake is then crushed to powder form. The final product contains potassium as well, which is an essential plant nutrient. Hence the final product of this process is essentially an NPKS combination.

The pH of the saturated solution of DAP is close to neutral (pH ~6.5). Addition of the DAP solution to the K_2S_3 solution also causes precipitation of elemental sulphur. On drying this solution, sulphur embedded DAP containing potassium is obtained.

The procedure has been repeated to test the reproducibility. Standard analytical procedures were employed to analyze the products. Kjeldahl method is used to determine the nitrogen content, where as the P_2O_5 content is determined using colorimetric technique using a spectrophotometer. Replicate analyses showed <5 % variability for both these methods. Elemental sulphur concentration is determined by separating it out by filtration and then weighing. Flame photometric technique is applied for estimation of the concentration of potassium. In house standard solutions of K are used for calibration of the instrument. Thiosulphate concentrations are estimated by iodometric titration which reproduced the results of replication within 1.7 %.

3. Results and Discussion

The concentration of nitrogen in the S-MAP is ~6.5%, where as that of P_2O_5 is ~39.5%. Concentration of potassium varies between 10 and 15%. The concentration of sulphur in elemental form is ~9%, and that in the form of thiosulphate varies between 3.3 and 5.5%. The concentration of nitrogen in the product S-DAP is 30.9% with a concentration of elemental sulphur of 11%. The analytical results are shown in Table 1. A recovery of ~68% of elemental sulphur as precipitated particles is observed during the process (Fig 1).

Size of the elemental sulphur particles has been estimated using a microscope. Individual particles are of the size <5 µm (Fig 2). The UV absorption by the particles infer a peak at 280 nm wavelength (Fig 3), indicating their nanometre size range (Chaudhury *et al*., 2009).

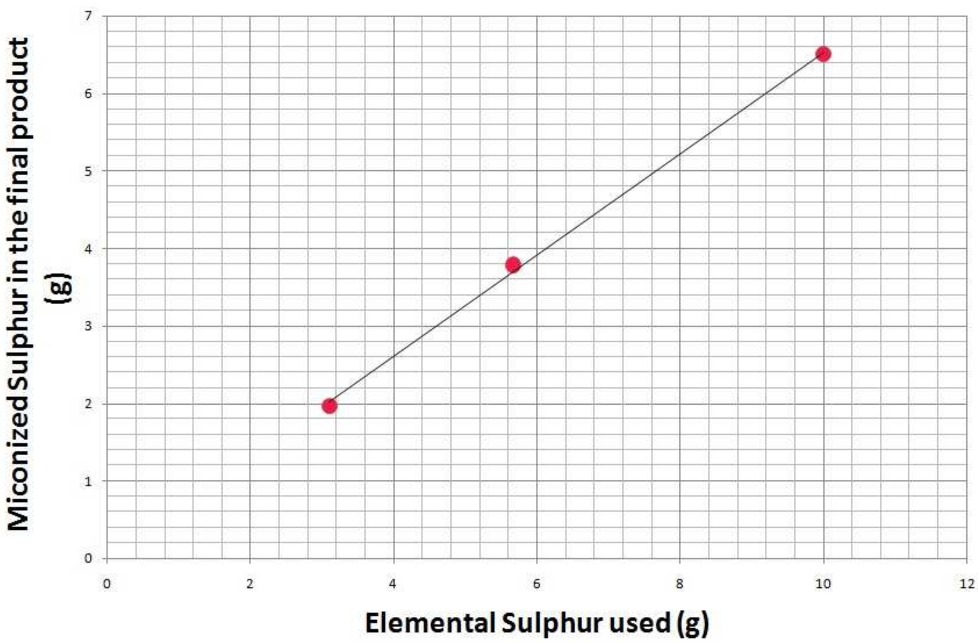

Fig 1: The amount of submicron sized elemental sulphur produced vs. the amount of elemental sulphur prills used as a raw material. The linear curve fitted shows a recovery of ~68 % of sulphur in the submicron form.

Table 1: Details of raw materials used and the composition of the final product obtained in the process of preparing sulphur containing fertilizer

Raw Materials (g)				Products			
Experiment Number	S	KOH	MAP	P_2O_5 (%)	N (%)	K (%)	S elemental (%)
1	4.4	8.5	33.1	40.2	6.9	10.0	8.0
2	100.0	154.7	583.8	40.6	6.7	15.2	9.5
3	50.0	77.4	291.9	40.5	7.4	11.1	8.5
4	5.0	8.8	29.1	39.4	6.9	11.1	7.3

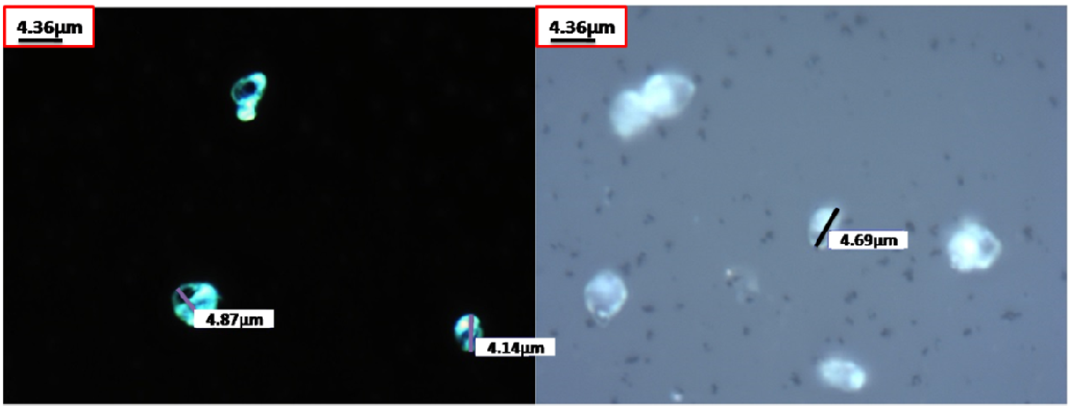

Fig 2: Microscope images of the nanoparticles of sulphur separated from the solution. The largest particles are marked with their sizes. The two images are from two separate experiments, showing the reproducibility of particle size.

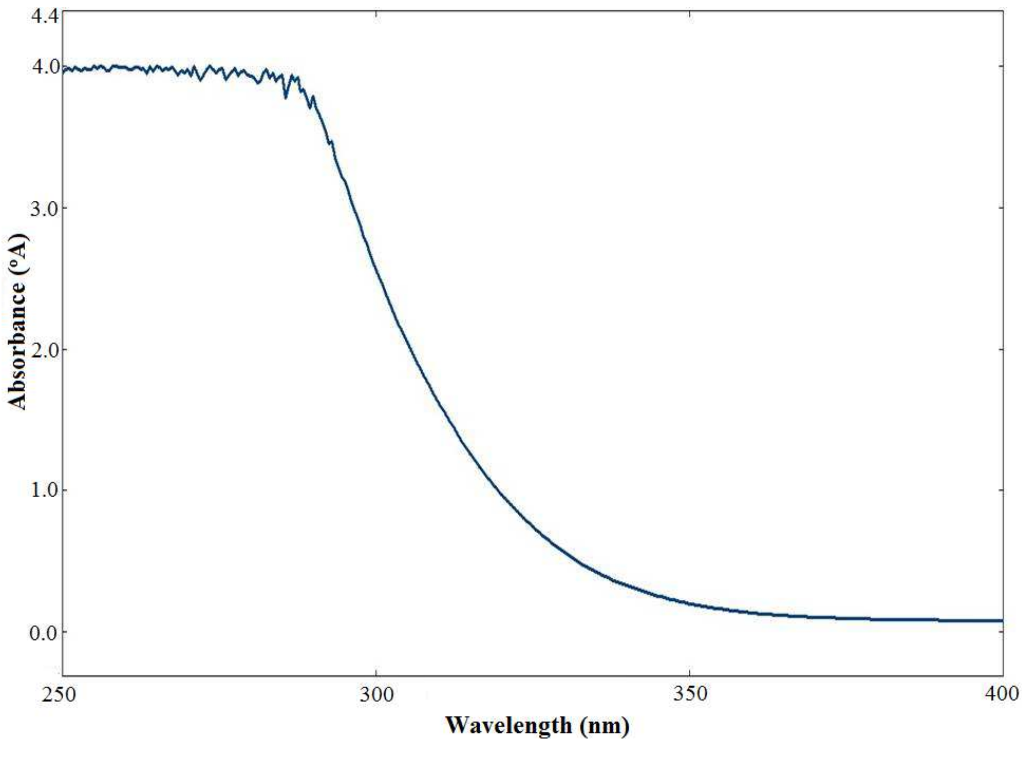

Fig 3: UV Absorption spectrum of the nanoparticles of sulphur. Methanol is used as wetting agent for recording spectrum

Many field trials have been conducted to study the effect of S in grain yield (e.g. Ludecke, 1965). More than 10% increase in yield of tomato and rice after applying S Enhanced Fertilizers (SEF) has been noted by Shell Thiogro research. A 100% increase in the yield of clover has been reported by Flavel *et al.* (2010) when monoammonium phosphate (MAP) mixed with granules of elemental sulphur was used for fertilization, when compared with the application of only MAP. The new product developed by the procedure discussed here is expected to be superior in performance, as it contains nanoparticles of elemental sulphur, instead of granules. In locations of high potential of leaching, the sulphate fertilizers were completely removed in 2 weeks; whereas the micronized elemental sulphur remained in the field for longer period (Flavel *et al.*, 2010). They reported that the production of harvestable dry matter continued for longer period when micronized sulphur enhanced MAP is used in place of only MAP. An enhanced utilization of P by plants is also reported when micronized S is present in the fertilizer. The interaction of N and S in the fertilizers when applied to soil has been extensively studied by Jamal *et al.* (2010) to report an increased N uptake when applied with S. Reduced mineralization of S from fertilizers in the soil when applied with N has been reported earlier by Kowalenko and Lowe (1975). The presence of nanoparticles of elemental sulphur with N, P, and K in the new product developed is expected to have advantages of improved utilization of all nutrients, hence increasing the agricultural output. Thiosulphate ions are known to act as a nitrification inhibitor and as a urease formation inhibitor (Goose, 1984). The thiosulphate ions present in the current product will have the added advantages of increasing the availability of N. Presence of K and S in the fertilizer is known to increase the uptake rate of Zn micronutrient and increases the microbial oxidation of S in the soil (Malvi, 2011). The new product developed here containing submicron to nano sized particles of elemental sulphur with N, P and K as plant nutrients is expected to have all the advantages discussed so far.

The interrelationship with soil organic carbon content and elemental sulphur content in soil has been noted by Forster *et al.* (2012). Soils in India have variable soil organic carbon content (Suresh, 2014b). The influence of soil organic carbon content on the fate of nanoparticles of elemental sulphur and other fertilizers may need further studies to understand the cycling of carbon in soils.

Environmental impacts caused by leaching, evaporation, and photolytic, hydrolytic and microbial degradation of S can be minimized by using smaller particles. The application of nanoparticles of S with minimal environmental impact has been pointed by Kumar *et al.* (2011). Chaudhury *et al.* (2009) also reported fungicidal activity of nanoparticles of S. When the nanosulphur particles in the NPKS fertilizer is applied to the soil, the particles in the soil may act as a pesticide. The product developed by the new process discussed here has potential of improving the soil quality for agriculture by enhancing nutrient absorption by plants, and acting as an agent of protection from fungus. Rigorous field trials are to be conducted for revealing further advantages and influences of the product on soil quality and sustainability.

4. Conclusion

A method to prepare plant nutrient combination containing N, P, K and submicron sized S to be used as a fertilizer has been devised in the laboratory. Particles of elemental sulphur were precipitated by adding solutions of MAP or DAP into potassium polysulphide solution. On drying and crushing the product, a fertilizer containing uniformly distributed submicron (< 5 µm) sized S particles is yielded. When considered with reported field studies using micronized elemental sulphur containing fertilizers, the application of the new product is expected to multiply crop yield. The sulphur particles may also act as pesticide and fungicide, as the particles are expected to have longevity in soil. Extensive field trials may provide better results of the product as a fertilizer.

Acknowledgements

We are grateful to Dr. N. Mishra, Dr. D. H. Garg, Mr. B. N. Butala and the management and research advisory committee of GSFC Limited, Vadodara for supporting this research. We express our thanks to the editor and the reviewers for their comments and suggestions. Mr. P. N. Patel, Mr. M. C. Solanki and Mr. Bhavit Patel are thanked for their laboratory support.

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