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The use of the laser granulometry technique for measuring the size of sulphur particles containing triple superphosphate fertilizer

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***ABSTRACT**: Fertilizer industries are trying to develop many new products containing a small amount of sulphur in the fertilizer, in order to have a specific action to enrich the soil and the plant with what they need of organic matter and other elements. Recently, one of the most important things is the production of phosphate fertilizers containing a considerable percentage of sulphur element.*

The laser granulometry technique is used to characterize the size of sulphur particles incorporated in the triple superphosphate fertilizer. An entire experimental process is introduced to separate sulphur particles from the other components of the fertilizer. This process is based on the solubilization of phosphate fertilizer in organic or in inorganic acid. For this reason, we studied the conditions, that ensure its perfect solubilization while maintaining the size of sulphur particles, such as: stirring time, stirring speed and temperature. Also, we evaluated the effect of three acids used as extractants such as: citric acid, sulfuric acid and acetic acid. The first one (citric acid) proved its performance for the solubilization of phosphate fertilizer without significant influence on the size of sulphur particles. However, the second one (sulfuric acid), decreased the solubility of triple superphosphate fertilizer and maintained the size of sulphur particles. Nevertheless, the third one (acetic acid) had no impact on the solubility but reduced the size of sulphur particles. The others parameters related to stirring time, speed and temperature demonstrated a varying effect with regard to the solubility of the phosphate fertilizer and also to the size of sulphur particles.

***KEYWORDS**: Sulphur particles, Fertilizer, Solubilization, Laser granulometry, Experimental design.*

I. INTRODUCTION

Phosphate fertilizers provide great benefits for soil fertility and for a normal growth of many agricultural products. That because, phosphorus element (P) plays an indispensable role in improving the productivity of yields [1][2][3][4].

Multiple researchers [5][6][7] reported the techniques of manufacturing phosphate fertilizers. The input of new amelioration to the process of these fertilizers manufacturing has also been reported [7] to achieve several objectives such as: decreasing energy consumption, increase the production with reduced specific reactive consumption, respect the environment…etc.

Phosphate fertilizer becomes more and more efficient if it is enriched, in small quantities, with other nutrients like as: sulphur, calcium, magnesium, sodium…etc. In this paper, triple superphosphate fertilizer (TSP) enriched with elemental sulphur (S^0) constitute our interest.

Many agronomic researchers [8][9][10][11] show the benefit of S-containing fertilizers to the promotion and enhancement of cultures. Furthermore, the phenomenon of elemental sulphur dispersion in fertilizers has been studied repeatedly using different approach. For this purpose, we mention the use of new stirring device technology [12][13] or the inclusion of surfactant additives [14][15][16] for obtaining a fine dispersion and a homogenous distribution of S^0 particles in the fertilizer matrix. Furthermore, it was pointed out that the size of sulphur particles in fertilizers greatly impacts the effectiveness of fortified fertilizers.

In general, there are several methods to determine the size of the particles. However, the performance of each method depends on the morphological conditions of these particles [17][18]. Additionally, granulometric analysis techniques are extensive: laser diffraction, settling, sieving… etc; each technique has its domain of application and its limitations [19]. Nevertheless, we focused especially in this work to the laser granulometry technique for measuring the size of sulphur particles within TSP fertilizer.

Laser granulometry is one of the best methods used for measuring and estimating the particle size distribution. This technique has attracted the interest of several researchers, especially in soil and sediment science [20][21][22][23][24]; that due to the adoption of this technique physical models (Mie and Fraunhofer theory) for examining particle size distribution [18].

The usual method consists of analyzing the size of sulphur particles in the TSP fertilizer using a microscope. However, the aim of this study is to examine the possibility of using the laser granulometry as an alternative technique for this analysis. For this purpose, elemental sulphur particles were extracted from the phosphate fertilizer matrix without affecting their size.

II. EXPERIMENTAL PROCEDURES

2.1 PREPARATION OF SULPHUR CONTAINING TRIPLE SUPERPHOSPHATE FERTILIZER

The method used in this work to prepare sulphur-containing triple superphosphate fertilizer (TSP-S), consistes in incorporating elemental sulphur (10% w/w) in the fertilizer matrix. An anionic surfactant (0,5% w/w) is used for the dispersion of liquid sulphur in the phosphoric acid. This prepared mixture, is added to the phosphate rock through moderate stirring. Fig. 1, shows the appearance of the dried processed product.

Fig. 1: Imagery of the prepared TSP-S fertilizer sludge obtained with a stereo-microscope camera

2.2 SOLUBILIZATION OF PHOSPHATE FERTILIZER AND EXTRACTION OF ELEMENTAL SULPHUR FOR LASER GRANULOMETRY CHARACTERIZATION

The solubility of phosphate fertilizers constitutes a big issue in the fertigation field. Agronomic researchers are interested in the solubility of mineral fertilizers, for the phosphorus (P) management and the reduction of P loss in the soil, thereby a good exploitation of this nutriment by plants [25][26][27]. Other researchers are interested in phosphate-solubilizing microorganisms in order to increase fertilizer efficiency and also for a sustainable agriculture [28][29]. However, we interested in this article to analyze sulphur particles in TSP fertilizer by the laser granulometry technique. For this purpose, the solubilization of TSP fertilizer must be performed for the isolation of S^0 particles.

Some previous works have reported the appropriate conditions for the solubility of phosphate fertilizers, such as: type of chemical extractants, temperature, stirring speed and solubilization time [30][31][32]. Nevertheless, we determine in this study the effect of six parameters on TSP fertilizer solubility; these parameters are: stirring time, stirring speed, temperature and as extractants; citric acid, sulfuric acid and acetic

acid. To examine the effect of each parameter in an accurat and economical way, a design of experiment has been used. Table 1 summarized the levels tested, in a screening design, of each parameter.

The steps carried out for phosphate fertilizer solubilization are as the following:

- Solubilization of a representative sample of 45 g of TSP-S fertilizer (prepared before) in 1500 ml of the extractant shown above and in the appropriate conditions of each experimental test. Table 2 presents the Plackett-Burman matrix of this study.
- A centrifugation method is performed to separate the solid residue from the solvent at 25°C for 15 min at 2000 tr/min. Fig. 2 shows the centrifuge tubes after separation into the centrifuge machine.
- The solid residue is then washed with water under a 63 µm sieve until the sulphur particles are completely isolated.
- The isolated elemental sulphur particles are then dried and characterized by the laser granulometry technique.

Table 1: Experimental conditions for the solubilization of TSP fertilizer

Parameter	Stirring time (min)	Stirring speed (tr/min)	Temperature (°C)	Citric acid (%)	Sulfuric acid (%)	Acetic acid (%)
Low level (-1)	60	300	50	0	0	0
High level (+1)	120	500	80	2	2	2

Fig. 2: Centrifuge tubes after the separation of solid residue from the solvent

III. RESULTS AND DISCUSSION

3.1 THE SOLUBILITY RATE OF TSP FERTILIZER

Two significant issues were studied in this work: the solubility of TSP fertilizer and the characterization of isolated elemental sulphur particles using the laser granulometry technique. For this purpose, we investigated under different experimental conditions, as summarized in table 2, two responses which are: the solubility rate of TSP fertilizer and the size of sulphur particles in which 90% of the sample is below this dimension.

Table 2: Experimental design of TSP fertilizer solubility and elemental sulphur granulometry

Test N°	Stirring time (min)	Stirring speed (tr/min)	Temperature (°C)	Citric acid (%)	Acetic acid (%)	Sulfuric acid (%)	Y1: Solubility rate (%)	Y2: D (0.90) (µm)

1	120	500	80	0	2	0	81.64	377.21
2	60	500	80	2	0	2	77.36	386.10
3	60	300	80	2	2	0	76.60	387.21
4	120	300	50	2	2	2	91.31	395.92
5	60	500	50	0	2	2	38.31	405.32
6	120	300	80	0	0	2	56.36	413.07
7	120	500	50	2	0	0	86.44	397.75
8	60	300	50	0	0	0	77.73	400.51

The study of numerous parameters using the screening design methodology allows the experimenter to save time and obtain convincing information on eatch parameter [33]. By the way, using the Placket-Burman design for the six parameters studied provides eight experiments as it is shown in table 2. This combination of experiments allowed us to find the most significant factors among the six factors tested. Fig. 3 is an illustration of the data analysis presented in table 2. This graphical representation shows the effects of the factors on the response (a) and the statistical Pareto approach (b).

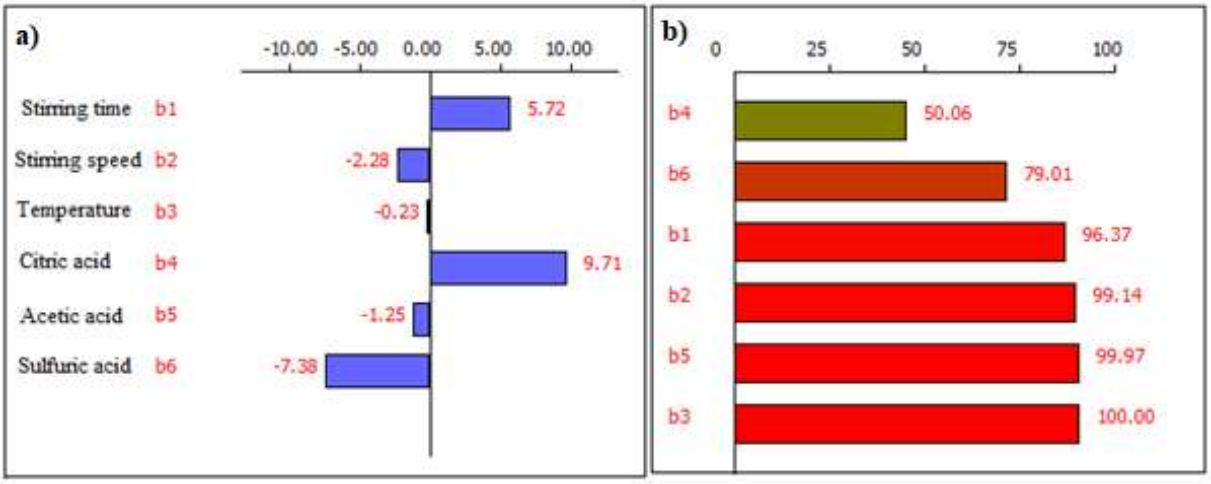

Fig. 3: a) Effects plot of TSP fertilizer solubility and b) its cumulative Pareto approach

The analysis of fig. 3 above, reveals that the solubility of TSP fertilizer is diversified. That because this response is highly influenced by the citric acid used as chemical extracting agent, to increase the solubility of TSP fertilizer, which is compatible with the bibliography [31][32]. According to the Pareto graph, it is claear that two factors are active on the solubility of TSP fertilizer. These are citric acid and sulfuric acid, which constitute 79% of the response. In addition, according to a previous study [34], commercial fertilizers are not completely soluble. Generally, 85 to 90 % of the total P of these fertilizers is dissolved in water and the balance is soluble in citrate.

The effect plot presentation, shows that citric acid has a positive effect, however the extraction with sulfuric acid has a negative effect on the response. Furthermore, stirring time parameter promotes the solubilization. As the extraction time is longer, the TSP fertilizer solubility is better. The other remaining

parameters: Acetic acid extracting agent, temperature and stirring speed have no significant effect on the response.

3.2 ANALYSIS OF SULPHUR PARTICLES BY LASER GRANULOMETRY TECHNIQUE

The analysis of elemental sulphur particles by laser granulometry technique requires a whole extraction process, which depends of several parameters. These parametres are the same as those discussed before. In this work, we investigated the conditions that allow an approximate determination of elemental sulphur particle size containing in the slurry of TSP fertilizer, by laser granulometry method. Furthermore, it is known that this technique allow the measurement of particle size characteristics and among them: D (0.90), which is our interest. The data treatments in table 2 still produce the results shown in fig. 4.

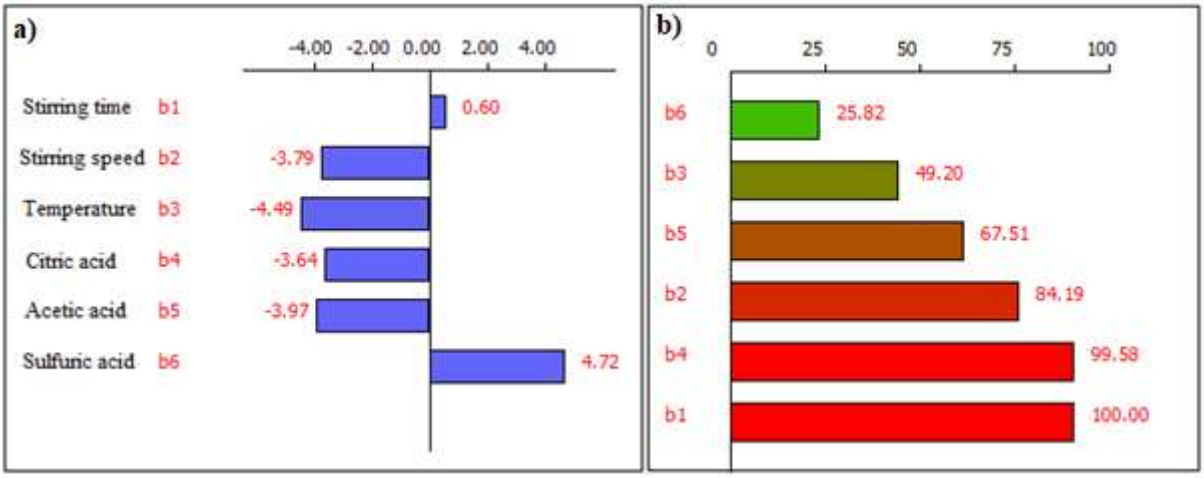

Fig. 4: a) Effects plot of sulphur particles analysis by laser granulometry technique and b) its cumulative pareto approach.

The cumulative Pareto approach presented in fig. 4 (b), shows that the size of elemental sulphur particles resulting from the present process, is influenced by four parameters. These parameters are: sulfuric acid extractant agent, temperature, acetic acid extractant agent and stirring speed. They constitute 84,19 % of the experimental response. Otherwise, the analysis of the effect plot (fig. 4, a) gives us further information on the impact of eatch parameter on the response as follows:

Sulfuric acid extractant agent influences positively the size of sulphur particles. In other words, the extraction of S^0 particles using this solvent has no impact on the size of sulphur particles. Consequently, this result explains the negative influence of this parameter on the solubility response.

The temperature, acetic acid extracting agent and stirring speed influence negatively the size of sulphur particles. The solubilization temperature experienced in this work indicates that its increase damaged the size of sulphur particles. Additionally, the extraction with acetic acid at high speed reduces the particle size of S^0 .

Finally, the stirring time and the extraction with citric acid have no significant influence on the analysis of sulphur particles by the laser granulometry technique.

IV. CONCLUSION

This work provided an overview of the analysis of sulphur particles, extracted from TSP fertilizer, by laser granulometry technique. The extraction of S^0 particles requires a long solubilization process in which some parameters have been evaluated. Moreover, screening design methodology has been adopted with eight experiments for the six parameters tested. The responses desired are the solubility rate of TSP fertilizer and the size of S^0 represented by D (0.90).

It is concluded that the favorable conditions for sulphur extraction could affect the characterization of this element by the laser granulometry technique. As a highlight, it is confirmed that citric acid is a relevant extracting agent for the solubilization of TSP fertilizer and restricts the size of sulphur particles.

This article demonstrated that laser granulometry technique is a useful tool to identify the size of elemental sulphur particles extracted from TSP fertilizer. The appropriate conditions for a better solubilization of TSP fertilizer are well determined. However, sulphur particles size extracted under the solubilization method proposed herein, are critical and is likely to open new pathways for phosphate fertilizer solubilization.

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REFERENCES

[1] A. Ehmann, I. Bach, J. Bilbao, I. Lewandowski, and T. Müller, "Phosphates recycled from semi-liquid manure and digestate are suitable alternative fertilizers for ornamentals," *Sci. Hortic. (Amsterdam).*, vol. 243, pp. 440–450, 2019.

[2] K. Oufdou, N. Bechtaoui, E. A. A, L. Benidire, K. Daoui, and M. Göttfert, "Symbiotic Rhizobacteria for Improving of the Agronomic Effectiveness of Phosphate Fertilizers," *Procedia Eng.*, vol. 138, pp. 325–331, 2016.

[3] J. F. L. Filho, J. S. da S. Carneiro, C. F. Barbosa, K. P. de Lima, A. do A. Leite, and L. C. A. Melo, "Aging of biochar-based fertilizers in soil: effects on phosphorus pools and availability to Urochloa brizantha grass," *Sci. Total Environ.*, vol. 709, p. 136028, 2020.

[4] S. Fertahi *et al.*, "New generation of controlled release phosphorus fertilizers based on biological macromolecules: Effect of formulation properties on phosphorus release," *Int. J. Biol. Macromol.*, vol. 143, pp. 153–162, 2020.

[5] J. F. Wilson, "Manufacture Of Triple Superphosphate; 2913330," 1959.

[6] A. Hakam, M. Khouloud, and Y. Zeroual, "Manufacturing of superphosphates SSP & TSP from down stream phosphates," *Procedia Eng.*, vol. 46, pp. 154–158, 2012.

[7] A. Fourati *et al.*, "Process For Producing Triple Superphosphate (TSP) And Complex Fertilizers Which Are Granulated, With Reaction Devices, For Granulation-Drying, For Packaging The Product And For Treating The Waste; WO 2016/043673 A1," 2016.

[8] F. Degryse, B. Ajiboye, R. Baird, R. C. da Silva, and M. J. Mclaughlin, "Oxidation of Elemental Sulfur in Granular Fertilizers Depends on the Soil-Exposed Surface Area," *Soil Sci. Soc. Am. J*, vol. 80, pp. 294–305, 2016.

[9] C. Zhao, F. Degryse, V. Gupta, and M. J. Mclaughlin, "Low Effective Surface Area Explains Slow Oxidation of Co-Granulated Elemental Sulfur," *Soil Sci. Soc. Am. J*, vol. 80, pp. 911–918, 2016.

[10] F. Degryse, C. Rodrigo, R. Baird, T. Beyrer, F. Below, and M. J. Mclaughlin, "Uptake of elemental or sulfate-S from fall- or spring-applied co-granulated fertilizer by corn — A stable isotope and modeling study," *F. Crop. Res.*, vol. 221, pp. 322–332, 2018.

[11] C. C. Boswell and D. K. Friesen, "Elemental sulfur fertilizers and their use on crops and pastures," *Fertil. Reserach*, vol. 35, pp. 127–149, 1993.

[12] M. R. A. Garcia and K. J. Hutter, "Process for preparing an elemental sulphur-containing fertilizer; WO 2010/058038." Shell Int Research, 2010.

[13] K. J. Hutter, I. C. James, and M. R. A. Garcia, "Process for the manufacture of sulphur-containing compositions and sulphur-containing fertilizer compositions. WO 2013/098404 A1." Shell Int Research, 2013.

[14] A. El Agri, A. Hafnaoui, M. Khouloud, M. S. Lakehal, M. El Asri, and A. Meliani, "The use of experimental design methodology in the formulation of a new additive for the dispersion of elemental sulfur in triple superphosphate fertilizer," *Mediterr. J. Chem.*, vol. 10, pp. 595–607, 2020.

[15] C.P. Allais, K.J. Hutter, and R.A. Garcia Martinez, "Process for preparing an emulsion of elemental sulphur particles. WO 2014/009326 A1," 2014.

[16] J. B. M. Antens, A. Sunil, G. M. R. Alberto, R. Lambert, J. T. O'BRIEN, and J. R. Marinus, "Sulphur Containing Fertilizers And Process For The Preparation Thereof; WO 2010/086395 A1." Shell Int

Research, 2010.
[17] A. D. Switzer, "Measuring and Analyzing Particle Size in a Geomorphic Context," *Treatise Geomorphol.*, vol. 14, pp. 224–242, 2013.
[18] J. Dodds, "Techniques to analyse particle size of food powders," *Handbook of food powders*. pp. 309–338, 2013.
[19] G. l. Lopez, "Grain Size Analysis," *Encyclopedia of Geoarchaeology*. pp. 341–348, 2017.
[20] S. J. Blott, D. J. Croft, K. Pye, S. E. Saye, and H. E. Wilson, "Particle size analysis by laser diffraction," *Geol. Soc.*, vol. 232, pp. 63–73, 2012.
[21] A. Erktan, C. Legout, S. De Danieli, N. Daumergue, and L. Cécillon, "Comparison of infrared spectroscopy and laser granulometry as alternative methods to estimate soil aggregate stability in Mediterranean badlands," *Geoderma*, vol. 271, pp. 225–233, 2016.
[22] G. Varga, F. Gresina, G. Újvári, J. Kovács, and Z. Szalai, "On the reliability and comparability of laser diffraction grain size measurements of paleosols in loess records," *Sediment. Geol.*, vol. 389, pp. 42–53, 2019.
[23] A. Bieganowski *et al.*, "Laser Diffractometry in the Measurements of Soil and Sediment Particle Size Distribution," *Adv. Agron.*, vol. 151, pp. 1–65, 2018.
[24] S. J. Blott and K. Pye, "Particle size distribution analysis of sand-sized particles by laser diffraction : an experimental investigation of instrument sensitivity and the effects of particle shape," *Sedimentology*, vol. 53, pp. 671–685, 2006.
[25] J. F. L. Ferreira, C. F. Barbosa, J. Santana da silva carneiro, and L. C. A. Melo, "Diffusion and phosphorus solubility of biochar-based fertilizer : Visualization, chemical assessment and availability to plants," *Soil Tillage Res.*, vol. 194, p. 104298, 2019.
[26] S. Kant and U. Kafkafi, "Fertigation," *Encyclopedia of Soils in the Environment*. pp. 1–9, 2005.
[27] X. Wang, J. Xiong, and Z. He, "Activated dolomite phosphate rock fertilizers to reduce leaching of phosphorus and trace metals as compared to superphosphate," *J. Environ. Manage.*, vol. 255, p. 109872, 2020.
[28] M. M. Alzoubi and M. Gaibore, "The Effect of phosphate solubilizing bacteria and organic fertilization on availability of syrian rock phosphate and increase of triple superphosphate efficiency," *World J. Agric. Sci.*, vol. 8, pp. 473–478, 2012.
[29] M. M. Rafi, M. S. Krishnaveni, and P. B. B. N. Charyulu, "Phosphate-solubilizing microorganisms and their emerging role in sustainable agriculture," in *Recent Developments in Applied Microbiology and Biochemistry*, 2019, pp. 223–233.
[30] A. C. Braithwaite, A. C. Eaton, and P. S. Groom, "Some factors associated with the use of the extractants 2 % citric acid and 2 % formic acid as estimators of available phosphorus in fertiliser products," *Fertil. Reserach*, vol. 19, pp. 175–181, 1989.
[31] A. C. Braithwaite, A. C. Eaton, and P. S. Groom, "Factors affecting the solubility of phosphate rock residues in 2 % citric acid and 2 % formic acid," *Fertil. Reserach*, vol. 23, pp. 37–42, 1990.
[32] A. C. Braithwaite, "The use of chemical solubility tests in comparing phosphate fertilisers," *Fertil. Reserach*, vol. 12, pp. 185–192, 1987.
[33] S. Benkaddour *et al.*, "Removal of Basic Yellow 28 by biosorption onto watermelon seeds, Part I : The principal factors influencing by Plackett-Burman screening design," *Surfaces and Interfaces*, p. 100732, 2020.
[34] S. H. Chien, L. I. Prochnow, S. Tu, and C. S. Snyder, "Agronomic and environmental aspects of phosphate fertilizers varying in source and solubility : An update review," *Nutr Cycl Agroecosyst*, vol. 89, pp. 229–255, 2010.