Journal of Agricultural Chemistry and Environment, 2021, 10, 213-221
https://www.scirp.org/journal/jacen
ISSN Online: 2325-744X
ISSN Print: 2325-7458

Agrotechnical Assessment of Struvite Application

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How to cite this paper: Peeva, G., Yemendzhiev, H., Koleva, R. and Nenov, V. (2021) Agrotechnical Assessment of Struvite Application. *Journal of Agricultural Chemistry and Environment*, **10**, 213-221.
https://doi.org/10.4236/jacen.2021.102014

Received: April 14, 2021
Accepted: May 24, 2021
Published: May 27, 2021

Abstract

Agrotechnical assessment of struvite produced by a lab-scale sedimentation unit is performed. As a source of phosphates and ammonia, liquor obtained through dewatering of Municipal wastewater treatment plant sludge was in use. The range of phosphates and ammonia was in the range of 130 - 250 and 380 - 560 mg/L, respectively. Seawater brine with a magnesium concentration of around 60 g Mg^{2+}/L was applied as a source of magnesium. The agrotechnical characteristics of struvite obtained were compared to ammonium nitrate and carbamide in regards to the productivity effects on maize hybrid P9241. The results show that the effectiveness of struvite and some commercial fertilizers is quite close. The highest yield in the experiment was achieved with the application of carbamide plus ammonium nitrate (56.64 kg/ha), while in applying struvite solely it is 54.60 kg/ha. The highest protein content of maize (9.7%) was observed in the case of struvite/ammonium nitrate application.

Keywords

Phosphorus, Struvite, Fertilizer, Wastewater Treatment

1. Introduction

The reduction of the consumption of the natural resources on the Earth to the minimum has been one of the biggest challenges before scientists all over the world during the past few years. Phosphorus (P) is an essential element for all forms of life. It is necessary for metabolic processes (ADP/ATP) and is an integral part of the DNA molecule as well as the cell membrane. For those reasons, P in the form of phosphate is applied as an agricultural fertilizer to maximize plant growth. Currently, organic (e.g., manure, compost, biogas, and others) and inorganic phosphate rock-based fertilizers are employed in agriculture. Due to the finite availability of phosphate rock resources and unstable phosphate rock prices, sewage sludge has become an interesting secondary phosphate resource. To improve the P uptake of plants during fertilization, knowledge about the availability of P to plants when fertilizer is added is necessary. Previous experiments with novel secondary P-fertilizers from wastewater treatment demonstrated very low P plant-availability of such fertilizers [1].

European countries have critical reserves of phosphorus and nitrogen. Industrial, domestic wastewater, and those from stock-breeding are the alternative. It is considered that one resident generates around 2.5 gP/d of urban wastewater [2].

Wastewaters and manures can be also applied as sources of phosphorus and nitrogen, for the acquisition of magnesium ammonium phosphate hexahydrate (MAP) or struvite. MAP, $MgNH_4PO_4 \cdot 6H_2O$, is a crystal substance containing magnesium, ammonium, and a phosphate ion, in equal molar ratios. Crystals are formed in an alkaline environment, under the following reaction, as precipitated product can be also applied in agriculture as bio slow-releasing fertilizers [3]:

$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O = MgNH_4PO_4 + 6H_2O + 2H^+$$

Animal fertilizers are a valuable source of nutritional substances for plants and they can improve soil productivity. Wastewaters, manure, and deposits from stock-farming contain high levels of nutrients, nitrogen, phosphorus, calcium. The USA, Canada, China, and Belgium have developed industries for the producing of struvite from wastewaters and sludge. The obtained product can be applied in agriculture as phosphorus fertilizer or in specific industries [4].

Struvite has the feature of being a slow-released fertilizer of nutrients (nitrogen, phosphorus, magnesium) in the soil. MAP is used for fertilizing grass, tree seedlings, decorative plants, vegetables, flowers, and grass gardens [5]. There is data for fertilization of Chinese cabbage with struvite obtained from the wastewaters of the semiconductor industry. The fertilization effect from the application of struvite is equal to one of the conventional fertilizers. The results from laboratory tests clearly show how the growth of Chinese cabbage accelerates better with the use of struvite instead of organic fertilizers and compost [6]. The content of magnesium in struvite makes it an alternative fertilizer for some plants, like beetroot [7]. Another advantage of the slow release of nutritional substances in the soil is that roots are not burned this way. Slow-release fertilizers are appropriate for areas with less frequent fertilization (less than once a year or every few years) (like pastures and woods). There is data demonstrating that adding fertilizers characterized with slow P release (such as struvite) increases the green and dry weight of legumes. The ameliorative effect in the use of struvite depends on the reactions of different sources of inorganic compounds (N, P, and Mg) in the formation of stable complexes with different solubility [8].

Several inorganic products can be used as a plant P source: liquid and solid fraction of processed fertilizer, organic residual streams, wastewater deposits, which combine these products in an optimal N/P/K ratio. However, while using struvite, it is still unclear how much P shall be released from these fertilizing products in a form assimilable by plants. It has been observed that only a small part of P (15% - 20%) is directly absorbed by the crop, while the other part becomes a component of soil reserves in regard to P. Yet, in soils with deficit P the reaction of absorption and growth of cultures depends on the form of the P compounds and on the speed of releasing P to the soil and plant environment [9].

According to Lindsay [10], struvite is significantly more soluble than calcium phosphates at alkaline pH. Consequently, it is a potential phosphorus fertilizer for limestone soils. It was found that MAP is very effective in moderately sour and moderately alkaline soils. Plants fertilized with struvite in semi-deserted areas also absorbed the phosphorus to a great extent [11].

Heavy metal concentrations (As, Cr, Ni, Fe, Zn and Hg) in precipitated struvite was studied. When the molar ratio of Mg:N:P was 1.5:1:1, with pH 9.0, concentrations of As, Cr, and Ni in the struvite were under the measurement limit and concentrations of Hg and Zn were under the respective standard. The analyses of heavy metals show that material obtained from the precipitation can be used as agricultural fertilizer [12]. It has also been found that the use of struvite as a fertilizer leads to the lowest accumulation of copper (Cu), without detection of cadmium (Cd), arsenic (As), lead (Pb), or nickel (Ni) in Chinese cabbage, with the use of an optimal dose of struvite for growing Chinese cabbage −1.6 g struvite/kg of soil. As a result of this finding, it has been concluded that accumulated precipitations of struvite obtained from wastewaters of semiconductor industry are effective as a complex fertilizer in cultivating Chinese cabbage [6].

Struvite as fertilizer could be a beneficial investment in the field of agriculture. It was found that a kilogram of MAP can be deposited by 100 m^3 of wastewater per day, and 1 kg struvite/d is sufficient for the fertilization of 2.6 hectares of arable land [13]. It is supposed that one wastewater treatment plant (WWTP) can recover a kilogram of struvite out of 100 m^3 of wastewater, as well as 0.63 million tonnes of phosphorus per year, like P_2O_5, if 50% of the population in the world are connected to wastewater treatment plants [14].

Actually, the formation of struvite in wastewater treatment plants can lead to scaling and thus operational problems reducing the treatment efficiency. However, struvite has significant commercial value as an agricultural fertilizer. Therefore, controlled struvite formation in wastewater treatment plants not only presents an opportunity to recover nutrients but also corresponds to the valorisation of wastes [12]. Struvite provides potential efficiency savings and environmental benefits over conventional fertilizers due to its low solubility. Conventional mineral P fertilizers are readily soluble and can cause high P concentrations in land runoff when rain falls soon after fertilizer application, with an increased risk of eutrophication of receiving water bodies. When incorporated into the soil, highly water-soluble P fertilizers also lead to high soil solution P concentrations for early crop growth. This solution P quickly becomes adsorbed and immobilised onto soil particle surfaces. This results in a much more limited P supply to crops in the later stages of growth when crop P demand is high. Struvite, as a less soluble "slow release" fertilizer, could provide a longer-term source of P for crop growth than readily soluble forms of P, thus more closely matching the plant's demand for P later in the growing season and increasing its efficiency of use. The slower dissolution of struvite could also reduce the amount of fertilizer P that becomes adsorbed onto soil particles, or released to land runoff. These benefits could therefore potentially be used to either increase crop yields, or allow reduced application rates of P whilst maintaining or increasing yields with minimum environmental impact: all of which would be economically advantageous to the agricultural industry as it moves towards sustainable intensification in the future [15].

However, a number of experimental studies and laboratory tests carried out in recent years regarding the elimination and recovery of nutrients such as NH_4^+ or PO_4^{3-} as struvite, show that there is still a significant gap connected to investigation of economics of this process, particularly for full-scale applications. Filling this gap is a prerequisite for a effective planning of project infrastructure for large-scale applications and for developing an up-to-date database on subject [16].

The study aims to present agrotechnical characteristics of the struvite using fugate obtained through dewatering of sludge liquor in WWTP. The scope is to compare fertilizers used in practice, considering the yield, and quantitative and qualitative indexes of maize.

2. Material and Methods

2.1. Struvite Precipitation Techniques and Measurements

Struvite crystallization process was achieved using fugate obtained through dewatering of sludge liquor in Municipal wastewater treatment plant (MWWTP), Burgas city, Bulgaria. The precipitation process was carried out on lab scale by mixing of pre-alkalized fugate (pH = 9) and sea concentrate (brine) as magnesium source aiming 2 mol Mg:1 mol P. The sea brine was contained 60 g Mg^{2+}/L and it was collected from the solar salt production area close to Pomorie city, Bulgaria.

Analytical measurement of chemical oxygen demand (COD, mgO_2/L), concentrations of NH_4-N (mg/L) and PO_4^{3-} (mg/L) were determined by Spectrophotometer (HACH LANGE DR 3900) using cuvette tests. The solution pH was measured by Multi-Parameter Meter (HQ40d Portable). Scanning electron microscopy (SEM) was applied to be characterized struvite particles (type, size of crystals) by scanning the surface with a focused beam of electrons under vacuum.

2.2. Agrotechnical Experiments and Analysis

The experiment was conducted during six-month period (April-September, 2020) at the training and experimental field (TEF) of the Department of Horticulture at the Technical University of Varna, Bulgaria. The experiment was started with maize hybrid P9241 (selection from Corteva Agriscience Farm) with two repetitions, on April 2020, with the surface area of the crop lot −6.3 m^2.

Struvite product was applied in two options. In the first option, there was only one fertilization before sowing, recalculated for 0.5 kg/ha P_2O_5, while in the second one—apart from Struvite before sowing, two applications of ammonium nitrate were conducted during the maize vegetation (phase 6 - 8 leaf and in the tasselling phase) −0.8 kg/ha N both (a total of 1.6 kg/ha N). The other options of aimed attempted comparison included widely used fertilizing products (ammonium nitrate, carbamide), which were applied three times—First, immediately before sowing; Second, in phase 6 - 8 maize leaf (June 2020); and third, in the tasselling phase of maize (July 2020). A fertilizer dosage based on the necessary amount of an active substance for a surface area of 0.1 ha was specified, recalculated in a physical weight for the respective fertilizer for a surface area of 6.3 m^2. The nitrogen fertilizer dosage is equally shared during the three fertilization processes as the total reached 2.4 kg/ha of active substance. The dose during sowing, used by experimental lots, is around 70 cm, with an inter-row distance of 20 cm.

The following fertilizer mixtures were applied:

1) Control—without fertilizer addition;

2) Addition of ammonium nitrate (triple application);

3) Addition of carbamide (applied before sowing) + ammonium nitrate (two applications during vegetation);

4) Addition of struvite (applied before sowing);

5) Addition of struvite (applied before sowing) + Ammonium nitrate (two applications during vegetation).

The productivity of the maize plants was determined separately for each of the two replicates of the specific variant of the experiment, the results being recalculated in kg/ha. The mass of 1000 seeds (absolute weight) is determined in the Agroecological Laboratory of Technical University (Varna) by Seed Counter (Model: Contador, Manufacturer: Pfeuffer GmbH Germany) by variants and repetitions. The indicators that directly testify to the quality of the corn grain and are subjected to express analyses are moisture, protein, fat and starch. The biochemical analysis of the corn grain was per-formed in the Agroecological Laboratory of the Technical University—Varna. For this purpose, a NIR-analyser was used (Model: DA7200 NIR, Manufacturer: Perten Instruments AB, Sweden), and three grain samples were analysed of the specific fertilizer variant.

3. Results and Discussion

3.1. Maize Growth Conditions

The experimental study was carried out during 6 month-period (April-September, 2020). The maize growth was influenced by the air temperature and the precipitation amount in the period.

The values of the minimum air temperature were the lowest in June (8.6˚C) and August (14.6˚C). The highest maximum values of temperature in June and August, respectively 36.1˚C and 37˚C were reported. During the temperature-critical phenophases, sweeping and flowering reached values above 35˚C, which adversely affects maize plants, resulting in reduced pollen viability and less pollination, which ultimately affects productivity.

During the experiments, the precipitations were 203.75 L/m^2, as the distribution by months is presented in **Figure 1**. The uneven monthly distribution of precipitation is very impressive. In the first two months (April and May) precipitation is extremely limited as a factor for the development of maize plants, while in

June the highest amount of precipitation was reported (130.25 L/m^2). It should be noted that during the extremely important for the formation of the final productivity of the crop—August (the formation ends, the pouring and ripening of the grain), the precipitation has the lowest values (only 3.75 L/m^2), which is one of the reasons why maize plants do not reach their high productivity potential.

3.2. Agrotechnical Assessment of the Struvite

Depending on the sampling period from WWTP, elemental content of wastewater was different and in a wide diapason. The concentrations of phosphates, ammonias, magnesium ions, calcium ions, and COD were in range of 130 - 250 mg/L, 380 - 560 mg/l, 102 mg/L, 108 mg/L and 1250 - 2500 mgO$_2$/L, respectively.

The precipitated struvite powder product was observed using SEM technique. Typical orthorhombic pyramidal structures, with crystal size of 12 - 15 μm (**Figure 2**) were reported. Size of crystals is an important characteristic in fertilization. Large struvite particles (more than 350 μm) induce soil retention effect of nutrients [17]. Some studies reported fine crystal size of 13 - 15 μm which corresponding with our results [18].

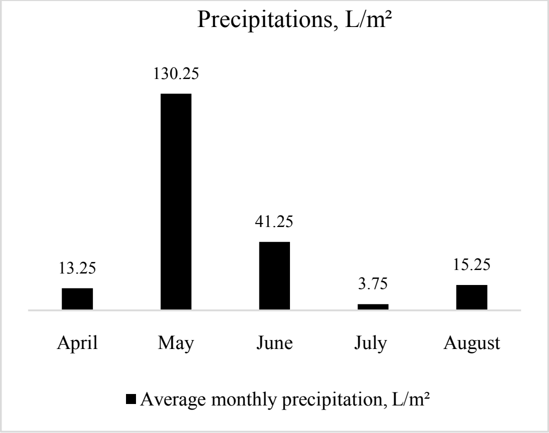

Figure 1. Average monthly precipitations (L/m^2) during the experiment.

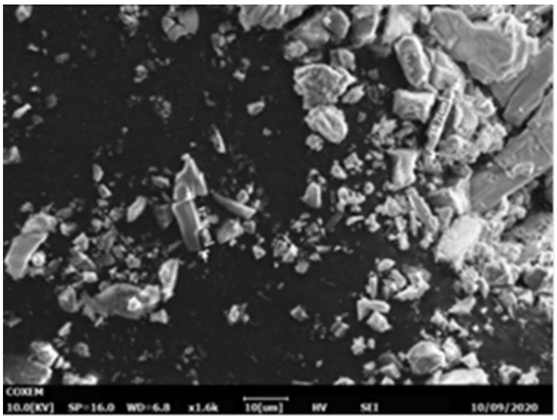

Figure 2. Orthorhombic struvite crystals (observed by SEM) with size of 12 - 15 μm.

Table 1. Productivity of maize hybrid P9241 applying different fertilizers.

Fertilizer	Yield, kg/ha	M_{1000}, g
Control sample	51.43	238.92
Ammonium nitrate	55.87	246.40
Carbamide + Ammonium nitrate	56.64	249.20
Struvite	54.60	245.27
Struvite + ammonium nitrate	55.11	246.36

Table 2. Qualitative indexes of maize hybrid P9241 while using different fertilization options.

Fertilizer	Wet, %	Proteins, %	Fats, %	Starch, %
Control sample	14.1	8.8	3.4	58.9
Ammonium nitrate	14.2	9.5	3.3	59.0
Carbamide + Ammonium nitrate	14.1	9.5	3.2	58.5
Struvite	14.0	8.8	3.2	58.2
Struvite + ammonium nitrate	14.1	9.7	3.2	57.5

The results from the productivity of maize hybrid P9241 followed by fertilization with traditional widely used fertilizers and Struvite are shown in **Table 1**.

The results obtained regarding productivity show higher yields while using traditional granulated fertilization products compared to Struvite and Struvite + ammonium nitrate, as the close values among fertilization options and the lack of statistically proved differences are noticeable. The highest yield in the experiment was achieved with the application of carbamide + ammonium nitrate (56.64 kg/ha) and ammonium nitrate (55.87 kg/ha). The results of both options with Struvite are very close (55.11 kg/ha, with combined application of Struvite and ammonium nitrate, and 54.60 kg/ha with the application of Struvite only). The values of the absolute weight (a mass of 1000 seed) show the same tendencies as the ones showed for the production. The highest mass is for the lots with applied carbamide + ammonium nitrate (249.20 g) and ammonium nitrate (246.40 g). The options with Struvite are close and have statistically not proven lower values.

The qualitative indexes of maize production are presented in **Table 2**. The contents of humidity are 14% and the indicator is within the admissible one. The highest protein content is with the Struvite + ammonium nitrate (9.7%) option, while the lowest is with the use of Struvite only, and with the non-fertilized control lot (8.8% both). Different fertilization options do not have a significant difference in the content of fats in the corn (3.2% both); the value is slightly higher with the ammonium nitrate (3.3%), as the control one is 3.4%. The last two options of the experiment have the highest content of starch (ammonium nitrate—59.0% and the control—58.9%), while Struvite + ammonium nitrate has the lowest values (57.5%).

4. Conclusion

The exhaustion of non-renewable resources of phosphorus (phosphate rocks) leads to increased demand for alternative sources. Wastewaters, sludge, and manures produced from wastewater treatment plants and livestock farms contain a high concentration of phosphates and ammonia. Struvite crystallization is an approach to the effluents to be utilized. On one hand, struvite crystallization from wastewaters provides a high-quality, slow-release fertilizer; on the other hand, the ecological risk of water and soil pollution with high levels of phosphorus and nitrogen is reduced. The advantage of magnesium ammonium phosphate is that it is an inexpensive product, which qualities are similar to conventional fertilizers. Furthermore, struvite could be used as an alternative and inexhaustible resource of phosphorus and nitrogen in the precipitation process. The struvite is the fertilizer of the future that will replace conventional products.

The study presents the fertilizer ability of struvite produced from fugate obtained through dewatering of sludge liquor in MWWTP. The agrotechnical characteristics of the product were compared to ammonium nitrate and carbamide in regards to the productivity effects on maize. The effectiveness of struvite and commercial fertilizers is quite close. The highest yield in the experiment was achieved with the application of carbamide plus ammonium nitrate (56.64 kg/ha), while in applying struvite solely it is 54.60 kg/ha.

Acknowledgements

This work was supported by the Bulgarian Ministry of Education and Science—National Science Fund under project DN 17-14. Also supported by Project BG05M2OP001-1.002-0019: Clean technologies for a sustainable environment—water, waste and energy for circular economy (Clean & Circle), Centre of Competence.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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