

# Sustainable Production of Struvite

## Using Wastewater for Sustainable Agricultural Activities

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### ABSTRACT

The production of struvite in several countries is investigated in the study as well as the economical and environmental benefit as a result of its mass production. The aim of the study is to propose a valuable agricultural sustainable fertilizer or fertilizer additive in the agricultural countries lacking resources for fertilizer production, like Turkey.

Fertilizer industry has significant contribution to the agricultural sector by raising the fruitfulness of agricultural products by 50% and the efficiency on the vegetal production. The researches show that the expenses for fertilizer result in 10.5 times more profit at harvest.

The main reason for fertilizer application is to supply elementary needs of agricultural plants during their growth, for instance nitrogen, phosphorus, potassium, calcium, magnesium, sulphur. Therefore the selection of an appropriate fertilizer should be based on the soil type and composition. The most commonly applied fertilizer is composed of nitrogen and phosphorus in addition to other minor elements in Turkey similar to the rest of the world. Since, the soil in Turkey lacks nitrogen and phosphorus, the fertilizer usage is necessary in agricultural growth. The use of fertilizer is 85kg/hectar in Turkey, which is much below the average usage in other countries, such as Japan (321kg/hectar), France (240kg/hectar), England (283kg/hectar), Greece (115kg/hectar), Spain (155kg/hectar). The world average of fertilizer usage is 116kg/hectar. There has been no investment on fertilizer sector in Turkey in the last 20 years and importing has increased significantly as a result.

In 1990, the fertilizer consumption was 5 million ton and 28% of the need was made by using imported fertilizer. However, in 2000, approximately the half of the consumption (46%) was responded by import [1].

Around the world there is an augmentation on production of fertilizers containing phosphate with an increasing demand for phosphate rock by 1.5% each year [2]. About 85% of the phosphate is used for the production of fertilizer and there are 7 billion tons of phosphate rocks as  $P_2O_5$  remaining in reserves. Considering 40 million tons of P as  $P_2O_5$  consumption each year, the available resources of P are expected to be exhausted in 100/250 years [3]. In Turkey, there are three regions, which have good reserves of phosphate. Eti Holding Güneydoğu Anadolu Fosfatları İşletmesi was established in Mardin, Mazıdağı in 1987. It had a capacity of production of phosphate concentrate 557, 300 tons per year meeting  $\frac{1}{4}$  of the need of Turkey. However, the establishment was closed in 1994 because of the high cost and the location of the fertilizer producing plants being away from the mining area [4]. There is currently no reserve used to extract phosphate for the fertilizer industry of Turkey. Therefore, finding a cheap method to obtain phosphate is very critical for the country. Considering the importance of fertilizer usage and existence of limited resources for its production, especially P with no substitute in nature, a technology developed for the recovery of the materials from waste can provide a break through solution. One of the recent innovations is production and recovery of struvite ( $MgNH_4PO_4 \cdot 6H_2O$ ) from the waste. If the formation of struvite is controlled, then it can be beneficiary since its precipitation removes  $NH_4^+$ -N and  $PO_4^{3-}$ -P from the water and the precipitate has the potential use as a fertilizer [5].

The recovery of struvite has been accomplished using the wastewater as the resource for  $\text{NH}_4^+$ -N and  $\text{PO}_4^{3-}$ -P mainly for the following reasons:

- To prevent uncontrolled precipitation of struvite to keep the hydraulic performance of the plants at least the same,
- To meet the regulation limits set for the nutrients (N and P) to prevent the eutrophication of the receiving water body,
- To recycle the wastewater rich in N and P content (effluent from the anaerobic digesters, animal waste treatment, coke plant wastewater, etc.) to be used in the industrial process or irrigation,
- To reduce the cost associated with the struvite production,
- To conserve limited phosphorus rock reserves.

Struvite can be produced from industrial wastewater, which is rich in nitrogen(N) and phosphorus (P). Since struvite is a problematic deposit formed especially in anaerobic digesters, in which mineralization of organics to  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  takes place, the major part of the research has been on the effluent from anaerobic digesters to take advantage of the enriched wastewater regarding the components of struvite. It should be noted that this approach does not solve the problems encountered in the digester regarding struvite formation. In recent years, the domestic and industrial wastewater treatment industry seeks for technologies to reduce P and N concentration to minimal levels so that wastewater can be reused and one of the approaches adopted is the removal of P and N by the precipitation of struvite. Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) yields one of the most nutritive fertilizers because it consists of Mg, N and P, which are the main elements to increase the agricultural yield, and it is a concentrated, granular, non-sludgy, non-odorous, and slow-release fertilizer and fairly valuable by-product. Struvite can be effectively used as a slow-release fertilizer at high application rate without a risk of damaging plants. Suggested uses are diverse and include ornamental plants, young trees in forestry, grass, orchards and potted plants. If high recovery efficiency can be achieved in wastewater treatment plants, then recovered products can be used as a substitute of existing fertilizer products. There are also fertilizer companies using struvite as an additive and they mix it with other inorganic and organic materials to adjust the amount of nitrogen, phosphoric acid and potassium.

Struvite or MAP is a white crystalline solid substance consisting of magnesium, ammonium, and phosphorus in equal molar concentrations. Struvite forms according to chemical reaction below:



A sample from struvite formed from the synthetically prepared wastewater in this study is shown in Figure 1.



Figure 1. A sample from struvite formed from the synthetically prepared wastewater in this study

Struvite precipitation is achieved by either pH changes or concentration changes or both. Typically, magnesium addition and pH adjustment of 8.1 to 8.9 is used to cause precipitation. In precipitating struvite for domestic and industrial reuse of wastewater, magnesium and pH are controlled to derive the reactions so that struvite precipitates while leaving the water with minimal P and N [6].

Different Mg:N:P ratios have been studied in the literature for the different wastewaters used as the resource for  $\text{NH}_4^+\text{-N}$  and  $\text{PO}_4^{3-}\text{-P}$ . The molar ratio of Mg:N:P is 1:1:1 for struvite formation, but there is always a need to search the optimum conditions for struvite formation and recovery in bench scale at the laboratory because of varying composition and different components of wastewaters.

There are a few successful examples illustrating the mass production of struvite from waste in the world, such as in Japan (Unitika, Hiagari Sewage Treatment Plant), Australia (Oxley Creek Wastewater Treatment Plant, Brisbane), USA (Sacramento Regional Wastewater Treatment Plant), Italy (Treviso Wastewater Treatment Plant). In all of this this plants, the effluent from the anaerobic digesters operating in sewage sludge treatment is used as the raw material for struvite production with some differences in their operations, for instance the chemical used to promote struvite crystallization, to adjust the pH and the technique adopted to collect precipitate. Although the cost of producing struvite and its selling price may differ from one country to another from one wastewater type to another, it has been shown that the recovery is technically and economically feasible [7]. In the same study the payback period of a struvite plant processing 55000m<sup>3</sup>/day wastewater is calculated as less than five years. Currently there is no production of struvite from waste in Turkey and the value of struvite as a P containing fertilizer is still to be recognized.

The process flow sheet for the production and distribution of di-ammonium phosphate fertilizer, triple super phosphate, recovered struvite and enhanced struvite (processing struvite with phosphoric acid, to produce a fertilizer containing two parts slowly soluble dimagnesium phosphate ( $\text{MgHPO}_4$ ) to one part highly soluble di-ammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ), referred to as “enhanced struvite”) are compared with the aim of establishing an approximate comparison between the three.

Table 1. Total average cost, at the farm (\$ per tone  $\text{P}_2\text{O}_5$ )

triple super phosphate	358.49-377.35
di-ammonium phosphate	428.3-449.05
phosphate mineral rock	354.28-367.92
recovered struvite	275.47-2254.71
recovered "enhanced struvite"	409.43-1632.07

For struvite recovery, it is assumed that Mg will have to be added at the sewage works to bring concentrations up to the stoichiometry with phosphorus necessary for struvite precipitation. Capital costs, which are a significant element of the recovery cost, are calculated using 6%/year discount rate. Because of the high level capital costs compared to recovery operating costs, the economics of recovery will be very dependent on the struvite recovery rate (% of the sewage works inflow phosphate recovered), and rates from 13%-80% are considered. Costs and environmental impacts take into account estimates, based on crop areas at average distances, of transport requirements to move fertilizers from import arrival ports to the field, and to move struvite from sewage works to the (via regional processing centers indicates of “enhanced struvite”). The costs and environmental impact related to the use of recovered struvite therefore depend on the supply/demand ratio: if supply is significantly lower than demand (struvite only replaces existing fertilizers a small part of the potential markets) then transport distances will be lower and thus so will costs an environmental impact. Total production and distribution costs for struvite and “enhanced struvite” thus compared to at-the-farm prices (market prices plus delivery) for existing fertilizers as follows: The highest price range for recovered struvite “enhanced struvite” assumes a very low efficiency in the sewage works (13%), application in small to medium sewage works (50000 pe) and a high supply/demand ratio (longer transport distances). The lowest price range assumes 80% recovery efficiency in 250000pe sewage works and the lower supply/demand ratio.

If high recovery efficiencies can be achieved in sewage works and recovered products can be used substitute existing fertilizer products and to meet regional demand, then struvite based products could be cost effective. In particular, the substitution of struvite for di-ammonium phosphate fertilizer looks especially attractive economically provided that these conditions are met [8].

There are some studies trying to point out the possibilities of recovering struvite from different wastewaters and its usage in agricultural activities. In addition to domestic wastewaters there are many other alternatives to be used as raw material for struvite, such as, cheese whey, animal manure, poultry wastewaters or effluents from the anaerobic digestion of these type of wastes.

To demonstrate the formation of struvite from wastewater, a small scale experimentation is carried out in the scope of study. The wastewater produced from dairy industry is chosen to determine the potential of struvite formation in cheese whey.

The biggest part of pollution in dairy industry is the cheese whey. To produce 10 kg cheese 100 kg milk is used and the residual 90 kg is cheese whey. In Turkey, the cheese production is 40000t/y, so 360000t/y cheese whey has arised. Therefore, there is big nutrient loss and the arised cheese whey causes environmental pollution if there is no recycling units.

Cheese whey is a protein and lactose rich by-product of the cheese industry and its cost-effective utilization or disposal has become increasingly important due to more stringent legislative requirements for effluent quality [9]. Cheese whey is typically a high strength wastewater [10] making aerobic treatment unfeasible because of high rates of oxygen requirement. Since the dairy effluents are warm and strong, the use of anaerobic treatment technology is recommended [11].

Having high concentrations of nitrogen and phosphorus, cheese whey makes a good practicing area of struvite precipitation and formation from the view point of both the treatment and recovery. Moreover, yielding a high pH effluent, which favors struvite precipitation, anaerobic digestion of the cheese whey makes probably one of the best pre-treatment techniques for cheese whey to be used for the struvite precipitation.

In this study, struvite formation potential and  $\text{NH}_4^+$ -N removal in anaerobic digester effluent of cheese whey was investigated. Depending on the struvite formation potential of the effluent from the anaerobic digester, ionic molar concentrations of  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$ -P providing the maximum removal of  $\text{NH}_4^+$ -N were determined. A pH range that favors struvite formation and precipitation was also investigated under the conditions where the molar ratio of Mg:N:P kept at the stoichiometric level (1:1:1). Cheese whey was obtained from Atatürk Orman Çiftliği (A.O.Ç.) cheese factory located in Ankara, Turkey and kept in the refrigerator approximately at 0°C during the work. Characterization of the raw cheese whey is given in Table 2.

Table 2. Characterization of the anaerobically treated cheese whey

	Raw Cheese Whey	Digested Effluent (settled)
Soluble COD (mg/l)	58371	2225
SS (mg/l)	9773	180
VSS (mg/l)	8947	40
TS (mg/l)	60438	8044
NH4(mg/l)	185	570
PO4 (mg/l)	1265	125
Mg <sup>2+</sup> (mg/L)	-	36.7
pH	5.92	8.12

Each struvite reactor contained 100 mL of screened anaerobic digestion effluent and was continuously mixed using a magnetic stirrer. Then the required stock solutions were added. In the first set, although no pH adjustment was made, the pH of the solution was monitored until steady-state conditions prevailed in the reactor, which was determined by observing a fixed pH with a variation of  $\pm 0.01$  pH units. In the non-pH adjusted experiments, pH level was observed varying in a range of 6.93-7.40. For each experiment, after the steady-state conditions were reached, stirring was stopped and the samples were left 1 hour for the precipitation before the  $\text{NH}_4^+$ -N and  $\text{PO}_4^{3-}$ -P analyses were made.

Although struvite may be formed in trace amounts whenever the  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  ions are present, it has to be saturated in the solution for the precipitation to be observed. According to the characterization given before, the ion product of the digested effluent was calculated as;  $\text{IP} = 6.55 \times 10^{-8}$  and the conditional solubility product,  $\text{K}_{\text{so}} = 9.95 \times 10^{-7}$ . Since the IP of the solution was smaller than the  $\text{K}_{\text{so}}$ , no struvite precipitation could be observed initially and therefore its formation is decided to be promoted by adding the inadequate ions,  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$ -P in this case.

It is clear that IP increases as the molar concentration of the ions increase. Therefore, one way to initiate the struvite formation is to increase the molar concentration of the ions. Another way to observe the struvite formation is to increase the pH of the solution, since the  $\text{K}_{\text{so}}$  decreases with increasing pH. Under the light of this theoretical information, the experiments were conducted in two sets: one set with different molar ratios of the ions and no pH adjustment, molar ratios of Mg:N and P:N between the range of 1:1 to 4:1 and other with different pH values (7.0-10.0) at fixed molar ratio of Mg:N:P equal to 1:1:1 to be able to find out the specific optimum conditions for the maximum removal of  $\text{NH}_4^+$ -N. Major results obtained from the experiments indicated that:

- The struvite formation and precipitation can be induced by the addition of  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  ions into the supernatant of the anaerobic reactor decomposing cheese whey to obtain 68% removal of  $\text{NH}_4^+$ -N at Mg:N:P ratio of 1:1:2 around pH 7.0.
- The change in the initial concentrations of the struvite forming ions did not affect the  $\text{NH}_4^+$ -N removal performance of the method considerably due to the pH of the system being around neutral.
- For the Mg:N:P molar ratio of 1:1:1, the percent  $\text{NH}_4^+$  removal increased from 44 to 68% by increasing the initial pH from 7 to 10. This indicated that if initial pH control was adopted for the Mg:N:P molar ratio of 1:1:2,  $\text{NH}_4^+$  removals more than 68% would be achieved.
- The removal of  $\text{PO}_4^{3-}$  also increased with the increasing pH due to the availability of the  $\text{PO}_4^{3-}$  ion to form struvite or other minerals like althausite.

It is clear that the application of struvite formed from wastewater increases the sustainability of the agricultural activities by slowing down the depletion rate of the P reserves left while reducing the N and P loads of the wastewater. Recovery of N and P by any means is very significant for ecologically sustainable future and there should be more research done on this subject regarding its mass production techniques and application.

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