



## Extraction of Struvite from Wastewater

M. Kamal Nath, G. Karthik, S. Muhaideen Kani, S. Anu Prathap

Department of Civil Engineering, G.K.M. College of  
Engineering and Technology, Chennai, Tamil Nadu, India

### ABSTRACT

The increase in human population need for food production is also increasing day by day. In order to produce healthy organic food depends on the natural fertilizer, so the availability of source for the natural fertilizer production has been decreased. In order to solve the problem without affecting the environment, an eco-friendly and cost-effective fertilizer is in need to be produced. In our project the natural fertilizer can be precipitated from wastewater. Nitrogen and Phosphorous in wastewaters are a burning environmental issue of the present world. Wastewater which contains a high amount of phosphorous and nitrogen would be a good source for production of fertilizer. Our project deals with the production of natural fertilizer called Struvite (Magnesium, Ammonium, Phosphorous). Addition of a source of Mg is essential to maintain the favourable condition of  $PO_4$  and Mg crystallization. Struvite is a phosphate-based fertilizer although it contains a significant amount of magnesium and nitrogen, and it is an effective alternative source of rock phosphate to maintain the agricultural food production system. This project deals with the extraction of struvite from the wastewater by Electrolysis. Also it consumes less energy and produce considerable amount of struvite which will be helpful in the production of phosphate fertilizer and also reduces the problems dealt with struvite in wastewater treatment plants pipes. The slower nutrient leaching loss and its fertilizer quality make struvite an eco-friendly fertilizer. It is possible to overcome the acute shortage of rock phosphate if all the municipal and livestock wastewaters are connected with the wastewater treatment plants.

**Keywords:** Wastewater, Phosphate recovery, Magnesium Ammonium Phosphorous (MAP), Electrolysis, Struvite fertilize.

### I. INTRODUCTION

Phosphate fertilizer used for the agricultural purposes has been increasing for the past few years, similarly the availability of phosphorous rock which is used to produce phosphate fertilizer has been decreasing over the years due to increase in population and usage of fertilizer. The cost of phosphate fertilizer also increased considerably, this problem has to be properly identified in the future in order to meet the agricultural requirements. In order to overcome the problem research has been made on alternate resource for Phosphate it is found that wastewater and biogas plant effluents contains considerable amount of Phosphorous that can be effectively used as alternate resources for producing Phosphorous fertilizer. Wastewater contains considerable amount of phosphorous that can be precipitated using various methods. Here we carry out electrolysis method to extract the Phosphorous fertilizer from the wastewater called Struvite which is also called as MAP (Magnesium, Ammonium, Phosphorous) ( $MgNH_4PO_4 \cdot 6H_2O$ ). The extracted struvite sample therefore taken into further tests like SEM and XRD which will produce information about the morphology of the crystal and various properties of struvite. The extracted struvite crystal can directly used as fertilizer without any addition of chemicals, it is also an Eco-friendly fertilizer. This method can be cost efficient considering the other methods and electrolysis consume less power. Struvite which is present in the wastewater creates problem in wastewater treatment plants. It occupies the pumps and pipelines and affect the flow of flow of water and also reduce the efficiency of treatment plants considerably. So, extracting struvite from the wastewater will be an added advantage where treatment plants work as efficient as they are. This process also carried as a

primary treatment method in large treatment plants removes the struvite before the treatment of wastewater.

## II. RELATED WORKS

Few researches has been made on Struvite precipitation from fertilizer industries by Sh.Ei.Rafie and AndrzejMatynia. Both of the researchers have been done using crystallization principle with the help of crystallizers, they had used liquid bittern as source of Magnesium. The effluents from the fertilizer industries contains high amount of Ammonium Nitrogen and additionally they added the Phosphorus and Magnesium for the precipitation of struvite. The process will require various samples in large amount and the cost of crystallizers is high. It will take so much time for the struvite to settle down also the precipitation process will take more time. They had done the SEM and XRD analysis to study about the morphology of the struvite crystal.

Similarly, Ngo zongning and Azmi aris carried out coagulation process on struvite which is precipitated from leachate. Struvite precipitated from the leachate contains high amount of finer particles which do not settle hence they went for the coagulation process which enhance the struvite precipitation. They had used leachate from the landfills and applied for the coagulants. Struvite here precipitated using  $MgCl_2$  and  $H_3PO_4$  which are the sources of magnesium and phosphorous respectively. Here jar test apparatus used for the coagulation process and XRF X ray fluorescence is carried out to find the purity of struvite before and after the coagulation process.

## III. EXPERIMENTAL

In our project we had extracted the struvite from the sewage wastewater by using the electrolysis method. The electrolysis process is initiated with required data collected from the previous experimental methods. By analysing the specifications of the previous experimental studies, the suitable criteria for extraction of struvite from sewage are revised. The properties of wastewater are known and analysed.

### 1. Specification

#### a. Electrodes

An electrode is an electrical conductor used to make contact with a non-metallic part of a circuit. It is referred to as either an anode or a cathode. The anode

at which the electrons leave the cell and oxidation occurs. The cathode at which the electrons enter the cell and reduction occurs. In this process we are using the Magnesium as anode and Copper as a cathode cell.

**b. Magnesium Anode:** The magnesium ribbon is used as anode in electrolytic extraction. When certain electricity is induced in the anode, Magnesium ions ( $Mg^{2+}$ ) get dissolved with the electrolyte (sample wastewater) initiates electrolysis process.

**c. Copper Cathode:** Any conductive pure metal can be placed as cathode. Cathode completes the electric cycle. Hydroxyl ions ( $OH^-$ ) get disassociated from water molecules and settles over the cathode. Copper rod or wire is preferred as common cathode or any pure metal can be adopted.

#### d. Electrolyte



**Figure 1: Electrolysis Process on Waste Water**

Mixed stream of sewage acts as the electrolyte. Electricity passing the anode commences oxidation and reduction balancing the equilibrium of the process. The pH of electrolyte is well balanced to preferred value with adequate buffer. Magnesium present in the sample as hardened and it is electrically reactive and precipitates with Ammonia-Nitrogen ( $NH_3-N$ ) and phosphate ( $PO_4$ ) forming precipitate layers of MAP.

#### e. Electricity source

A Battery (or) AC source can be used as power generator. The current flow is limited to specified current intensity in terms of milliampere hour. A voltage regulator (or) resistor can be adapted for controlling current flow. The minimum power

required for struvite synthesis from a sample of quantity  $100\text{m}^3$  is about 70 watt-hour.



**Figure 2: Electrolysis Setup**



**Figure 3: Etching of a Magnesium Ribbon**

- Magnesium dosing by electron dissolution was used for struvite precipitation.
  - Impact of substrates concentration, pH and electric current on the process was assessed.
  - High Phosphorous removal rates of  $4.0 \text{ mg PO}_4\text{-P cm}^2\text{h}^{-1}$  at electric current density of  $45\text{Am}^{-2}$ .
  - This electrolysis process could potentially be used to make wastewater treatment plants more resource efficient and further research is warranted.
  - The electric current was used to generate hydrogen gas at the cathode with  $96\pm 6\%$  efficiency.
- Magnesium ribbon and copper wire respectively as anode and cathode can be etched using either concentrated Sulphuric acid or Picric acid. Picric acid is preferred as the best etching agent for magnesium.
  - Impurities like carbides, oxides and other bad conductors get dissolved with the acid by directly reacting the element with the agent

#### b. Process

The electrolytic cell which forms the centre piece of the test installation and through which the wastewater is directed contains a sacrificial magnesium anode and a metallic cathode. For the current production to the electrolysis process is taken from the battery though which will be easy and conventional.

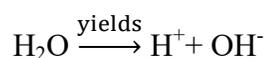
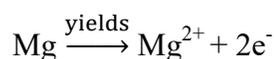
#### c. Synthesis of struvite

The Electrolysis circuit consists of a Beaker, Power source, Ammeter, Rheostat and connecting series.

An electric lead acid battery is fixed as the power source as they provide a continuous direct current flow without voltage fluctuation. Thus, a stable current flows within the circuit enabling oxidation and reduction.

The pH of the cell is maintained within limit. A current density of  $2\text{mA/cm}^2$  is sufficient and added intensity can also favour for struvite nucleation.

#### d. Oxidation



## 2. Extraction

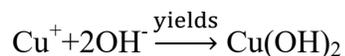
Extraction of phosphorous in the form of MAP also referred as phosphate recovery is achieved by many suitable methods available in the industry. Among the possible recovery methods electrolytic extraction is one of efficient methods adopted.

### a. Chemical etching of electrodes

- Etching is a process of chemical removal of the impurities associated with impure metal to which may result in pure metal form.
- In chemical etching concentrated acids can be a better etching agent. Example of etching agents are Sulphuric acid ( $\text{H}_2\text{SO}_4$ ), Hydrochloric acid (HCl), Nitric acid ( $\text{HNO}_3$ ), Picric acid, etc.,

Hydrogen dioxide molecules disassociates into Hydrogen atoms and Hydroxyl ions.

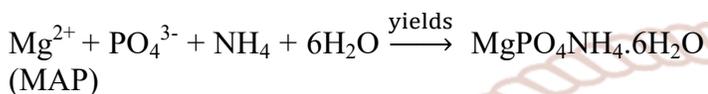
#### e. Reduction



The dissolved Hydroxyl ions associates with copper ions forming Cupric Hydroxide.

#### f. Overall Chemical Equation

pH level maintains the equilibrium (i.e.,) molar concentration of cell leading to precipitation.



Magnesium metal is highly reactive to electrical conductivity forming the nucleus of the compound.

The precipitate gets settled at the bottom of the cell. The colour of the precipitate is analysed with formed data.

Soon the optical property of the water sample changes from opaque to semi-transparent and the suspended solution gets dissolved.

The current flows through the circuit for about 2 hours to enable complete nucleation of struvite.

#### g. Preservation of sample

The sample is either filtered or not and oven dried. Appropriate temperature is maintained for crystal growth and moisture tight. Sample from different effluents are collected in separate containers and subjected to experimental testing Scanning Electron Microscopy and X-Ray Diffraction.

## IV. RESULTS AND DISCUSSIONS

The final result made on the struvite sample after the precipitation from the wastewater. To assess the quality of struvite created through precipitation SEM and XRD analysis has been done on it. Also, to know about the struvite crystal structure and its characteristics.

### SEM Analysis on Struvite Fertilizer Sample

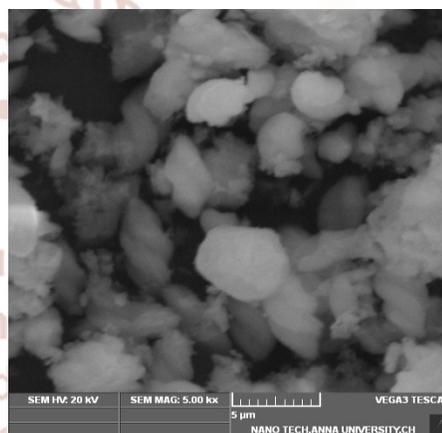


Figure 1: SEM image of struvite (5µm, 5000x)

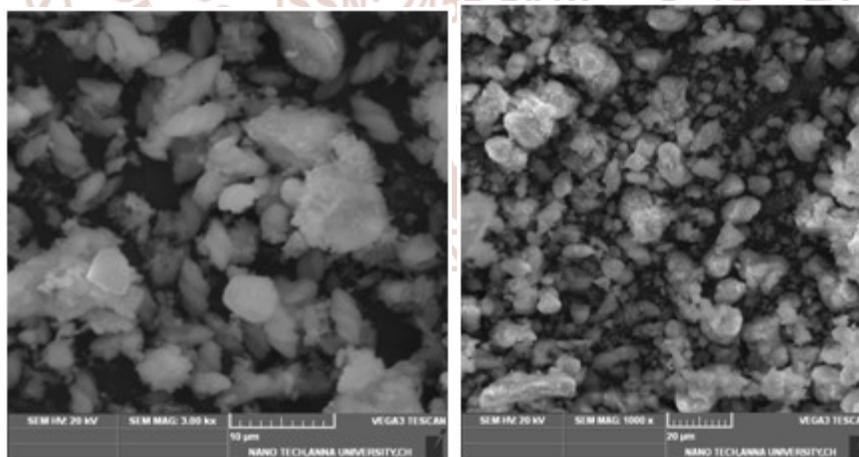


Figure 2: SEM images of struvite (10µm,20µm)

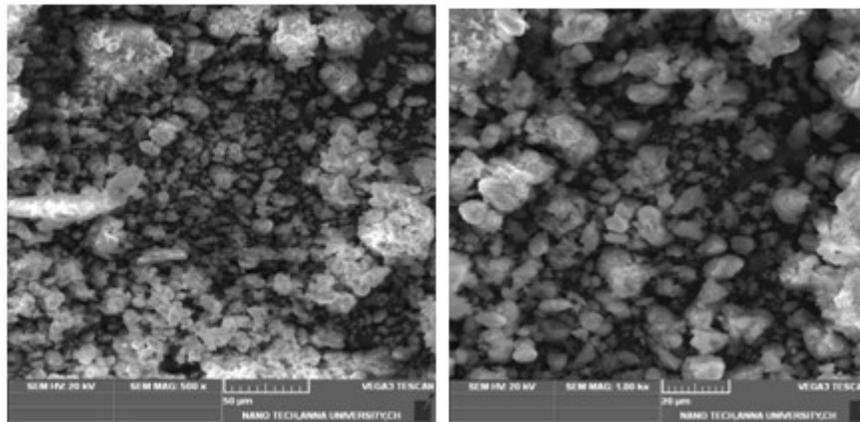


Figure 3: SEM images of struvite (10µm, 20µm, 50µm)

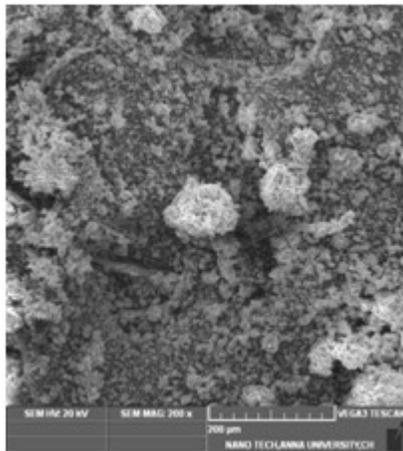


Figure 4: SEM image of struvite (200µm)

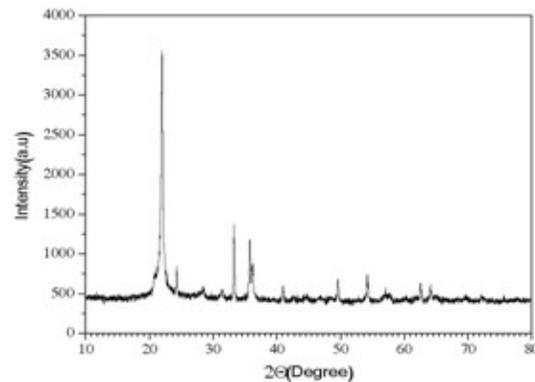


Figure 5: XRD Graph of Struvite fertilizer

Scanning electron microscope images of the exemplary product crystals are presented in the above. Diverse sizes within struvite crystals are clearly visible. Also, other particles can be identified, co-precipitated from wastewater in the common process conditions applied.

Struvite is precipitated from the wastewater containing ammonium and phosphorous with the additive of magnesium in it. It can be seen that the clear crystal shape of the struvite in the SEM images.

The irregular bounded shaped crystal precipitated with the length varies from 10µm, 20µm, 50µm, 200µm respectively.

#### XRD Analysis on Struvite Fertilizer Sample

##### Lyric WCC-XRD:

Although XRD methods have been used for struvite phase identification, the use has been limited to qualitative confirmation of the presence of phosphate phases in precipitates. However, quantitative phase analysis using XRD data can further be approached with Rietveld refinements.

The precipitate is cleaned and dried at 55° for 24hours. Power X-ray diffraction (XRD) data were collected by standard X-ray diffraction using monochromatized Cu-Kα radiation from 2θ=10° to 80° XRD analysis was used to qualify the phase compositions of the samples using the Rietveld refinement method by fitting the full profile experimental XRD data with a calculated diffraction pattern.

The Le Ball refinement were performed using RIETICA program. Peak profiles were modeled using a pseudo voigt peak shape. Experimental parameters refined were the instrument zero, scale factor, the lattice parameters  $u$ ,  $v$ ,  $w$ ,  $\gamma_0$ ,  $\gamma_1$

Molar ratio and pH is one of the parameters in Struvite crystallization. When the pH is raised, pH did not show significant changes in the XRD spectra.

## V. CONCLUSIONS

Struvite crystallization process is an effective eco-friendly process that removes and recovers P and N from wastewaters. The hazardous elements in wastewaters mainly Ammonia and Phosphorus might be converted to a valuable resource through the extraction of struvite fertilizer. Struvite would be the principal P fertilizer after exhaustion of all mined P rock in near future. It is a slow-release valuable fertilizer that reduces the cost of production of agriculture. So, it is necessary to develop the optimum conditions for small-scale and commercial production of struvite.

## FUTURE PROSPECTS

- i. Production of struvite from wastewaters will reduce the hazard of eutrophication in the water bodies by removing N and P
- ii. Struvite will be the most effective alternative source of P that will help to continue agricultural and animal production after exhaustion of all mined phosphate rock.
- iii. Small-scale and commercial struvite production plant will be established at the wastewater production site throughout the world.
- iv. Production of struvite from wastewater and its utilization as fertilizer would partially help to reduce global warming and thus, it would be an effective eco-friendly fertilizer.

## REFERENCES

1. Matynia, A., Wierzbowska, B., Hutnik, N., Mazienczuk, A., Kozik, A. and Piotrowski, K., 2013. Separation of struvite from mineral fertilizer industry wastewater. *Procedia Environmental Sciences*, 18, pp.766-775.
2. Rahman, M.M., Salleh, M.A.M., Rashid, U., Ahsan, A., Hossain, M.M. and Ra, C.S., 2014. Production of slow release crystal fertilizer from wastewaters through struvite crystallization—A review. *Arabian journal of chemistry*, 7(1), pp.139-155.
3. Camargo, C.C., Guimarães, J.R. and Tonetti, A.L., 2014. Treatment of landfill leachate: removal of ammonia by struvite formation. *Water SA*, 40(3), pp.491-494.
4. Dhakal, S., 2008. A laboratory study of struvite precipitation for phosphorus removal from concentrated animal feeding operation wastewater.
5. Cusick, R.D., Ullery, M.L., Dempsey, B.A. and Logan, B.E., 2014. Electrochemical struvite precipitation from digestate with a fluidized bed cathode microbial electrolysis cell. *water research*, 54, pp.297-306.
6. Lee, M.R., 2013. *Treatment of landfill leachate in coagulation-flocculation method by using micro zeolite and micro sand*(Doctoral dissertation, Universiti Tun Hussein Onn Malaysia).
7. Li, X.Z. and Zhao, Q.L., 2003. Recovery of ammonium-nitrogen from landfill leachate as a multi-nutrient fertilizer. *Ecological Engineering*, 20(2), pp.171-181.
8. El Rafie, S., Hawash, S. and Shalaby, M.S., 2013. Evaluation of struvite precipitated from chemical fertilizer industrial effluents. *Adv. Appl. Sci. Res*, 4(1), pp.113-123