Production of Slow-Release Fertilizer from Wastewater Through Struvite Crystallization

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Abstract
Struvite crystallization is a methodology to remove phosphorus from wastewater and reuse as struvite (fertilizer) to ease both the scarcity of phosphorous rock resources and water eutrophication. Wastewater treatment plants, especially those employing secondary treatment and anaerobic sludge digestion, have historically encountered phosphate precipitates, most commonly being Struvite. In certain cities, the intensive livestock farming produces massive livestock wastewater with high concentration of phosphorous. Discharge of these compounds to surface water not only causes water eutrophication but also wastes phosphorus resources which is essential for the plant growth. Therefore, it is necessary to remove the phosphorous from livestock wastewater with its recovery and reuse as fertilizer. As a valuable slow-release mineral fertilizer, struvite crystallization has become a focus in phosphorus recovery. The reaction factors including molar ratio of magnesium and phosphate, solution pH, co-existing substances and seeding assist of struvite crystallization are summarized. In conclusion, struvite crystallization is a promising tool for recovering phosphorous from livestock wastewater. The blade agitator reactor which shall be setup and used is one of the promising solutions for removing more than 80% of phosphorous and recovering as struvite. Struvite precipitation occurs in an equimolecular concentration of Mg2+: NH4+: PO4 3- at slightly alkaline conditions. The raw wastewater type shall be the domestic wastewater & shall be collected from the Sewage Treatment Plant nearer to the locality. Initially Jar test shall be performed for 1L each to derive the optimum dosage of Mg source, A reactor shall be fabricated for up to 7.5litres of capacity.
The fertilizers extracted from the wastewater using the Mg sources as reagents shall be used to grow the Ragi plants (Finger millet) and the observations shall be made at 7th, 12th, and 18th day. Five pots shall be used, where 1st is for conventional (absence of fertilizer), chemical fertilizer (urea) shall be used in 2nd, fertilizer such as MgCO3, MgCl2 and MgSO4 shall be used in 3rd, 4th, and 5th pots respectively. A Comparison is to be made for the use of MgCO3 (struvite fertilizer) & MgCl2 and MgSO4 and similar results compared to chemical fertilizer (urea) used in the plant growth, thus using struvite crystals as fertilizers shows the faster growth rate. After the struvite crystallization process in the supernatant, Phosphate and Nitrate removal from the wastewater sample is also planned to be assessed

Index Terms: struvite, waste water, nitrate, phosphate, BOD removal, Fertilizer, Eutrophication

INTRODUCTION
Water is an important resource for all the living organisms to survive, but it is getting polluted day by day because of our illegal activities for our personal growth. Most of the water bodies are at dangerous level as the domestic wastewater and industrial effluents releasing into them. These wastewaters are generally rich in phosphorous (P) and nitrogen (N) and as discharging it without eliminating the phosphorous (P) and nitrogen (N), increases the eutrophication in the water bodies. The algal growth will increase in the water surface which reduces the penetration of sunlight into the water and reduces absorption of atmospheric oxygen and hence decreases the self- purification of water. As the wastewater is very much rich in phosphorous and nitrogen, it is a key factor for the environmental issues in the present world. Hence removing nitrogen and phosphorous

from the wastewater through struvite crystallization process, reduces the P and N level in wastewater, resulting in prevention of eutrophication. The phosphorous and nitrogen in the wastewater are the best essential organic nutrients for the animal and plant growth. A large amount of nitrogen of nitrogenous and phosphate fertilizers is applied in the soil every year to increase the fertility of the soil. The present consumption of rock phosphorous (P) is over one million tons yearly as fertilizer and nitrogen (N) fertilizer consumption might be their fold of this.

Besides crop production, P in one of the vital elements needed for animal growth, milk and egg production as well. The daily nutritional requirements for dairy cattle and beef cattle have been stated as 86-95 g/day and 35-40 g/day respectively. Animal cannot utilize the whole amount and are excreted through manure or urine that exists in the wastewater. (Suzuki, et al.,) Only 14% of corn P and 31% of soya bean meal can be digested by swine. A large percentage of phosphorous is unavailable, and most of it is excreted into the environment through manure and urine. The excreted phosphorous is dissolved into the water and transported to the nearby water bodies or infiltrate into the ground water. The livestock waste stream is therefore, very rich in phosphorous. A significant amount of nitrogen comes out through excreta as a residue of protein supplement as well as dead animals. Improper management of livestock waste creates a nuisance and obnoxious environment which also greatly affects public health. A lot of currency is expended for imparting rock phosphate to fulfill the national demand but proper recovery of phosphate from waste water can be reduced with the important or rock phosphate.

Great efforts have been done by researchers for the removal of nitrogen from waste water through biological nitrification and de-nitrification, ammonia-stripping, electrochemical conversion, ion exchange, microwave irradiation and struvite precipitation. Struvite precipitate is one of the innovative physio-chemical processes which can majorly contribute for the removal of ammonia and phosphorous forming complex under required conditions. It is also an ecologically sound technique which is not only cost effective, but also sustainable in terms of possible recovery of recyclable constituents from industrial effluents and domestic effluents which are rich in nutrients. Phosphorous in wastewater is of three forms, Phosphate (Ortho phosphate), (O4P3-), polyphosphate (PO4) and organically bound phosphorous. Controlled reaction between phosphate, magnesium and ammonium ions provides sparingly soluble product called struvite (MgNH4PO4.6H2O) which can be utilize directly in agriculture as mineral fertilizer. The required dosage of Mg2+ salts (MgCl2, MgSO4, and MgOH2) etc... The most common forms of nitrogen in waste waters and ammonia (NH3), ammonium ion (NH4+), nitrate (NO3) and organic nitrogen. It is also an ecologically sound technique which is not only cost effective, but also sustainable in terms of possible recovery of recyclable constituents from industrial effluents and domestic effluents which are rich in nutrients.

MATERIALS AND METHODOLOGY

Materials

Domestic wastewater sample

Figure 1: Domestic sewage water collected from STP.

- **Magnesium sources (magnesium salts or powder), sodium hydroxide (NaOH), Hydrochloric acid (HCl) and reactor.**

Figure 2: Magnesium salts for Struvite crystallization

DESIGN OF REACTOR FOR CRYSTALLIZATION PROCESS

The reactor was designed and fabricated to carry out the experiment to produce the struvite fertilizer in larger quantity. The type of the reactor is blade agitator reactor consisting of two blades of 103mm length (total length) attached to stainless steel rod of depth 150mm and thickness of 5mm. The blades are attached using welding at the end of the stainless steel rod.

This stainless steel rod is attached to the aluminum shaft of length 80mm, diameter of 120mm and hollow in nature. The stainless steel rod is attached to the aluminium shaft through allen holes made at the bottom and threads formed inside the shaft. The aluminium shaft is connected to the motor fixed on the plate of the reactor through the allen holes made at the top of the shaft and the threads within it.Thus by this way the blades, stainless steel rod and aluminium shaft were fixed to the motor.

The motor is fixed on the top of the plate using araldite (a standard epoxy adhesive gum), so that the motor wouldn't come out from the plate when the reactor is run. The motor weighs half kilograms. The whole reactor can resist this weight, as the reactor is made of Acrylic glass material (also known as Plexiglass) which can easily resist this weight.

The stainless steel weighs more than aluminium. If the total weight of all the blades, rod and shaft reaches above the weight of an motor fixed to the reactor, results in shaking the reactor and may also damages the whole reactor. Thus the total weight of whole blades, rod and shaft should be minimum or less compared to the weight of the motor. Hence, to reduce the weight under the motor, aluminium is used to make the shaft and it is hollow in nature.

The same aluminium is not used to make the rod, because lesser the weight used to rotate the blades and mix the wastewater of 5 liters with the magnesium source of 25g, will make the rod bend accordingly. This results in initial loss within the reactor, while bent rod won't mix the wastewater with magnesium sources properly. Meanwhile, the weight of the whole blades, rod and shaft has not exceeded the single weight of the motor.

The motor gets heated when the reactor is continuously run. But it has no effect on the plate or the reactor, as the melting point of the acrylic material which has been used to make the reactor is 160°C. This material can easily bear the heat produced by the motor.

The motor which has been used in this project to rotate the blades is initially a motor of an exhaust fan. The motor has an voltage of 220V – 250V and has a capacity of 30W power. Initially the motor can also easily rotates to a speed of above 1500rpm without any shaft or blades attached to it. As the motor carries the weight of all rod, shaft and blades, the speed of that motor is still above 500rpm. While mixing the 5 liters of wastewater with 25g of magnesium sources, the speed of the motor still reaches above 200rpm.

A dome shape of 90mm depth is provided at the bottom of the reactor to hold or to carry the settled precipitate formed from in the wastewater. Initially the dome shaped piece provided at the bottom of the reactor can hold the water up to 1 liter, i.e., it is of 1litre capacity. All the sediments and suspended particles will be settled on the dome shaped piece. Any shaped piece can be provided at the bottom of the reactor, but it is not so economical as dome shaped piece. The precipitate can be easily removed from the using this shaped piece and it also easy to clean and maintain.

A tap is provided above the dome shaped piece to a height of 95mm from the bottom of the reactor to ease the work of letting out supernatant from the reactor so that all the supernatant water getting out, it is now easy to collect the precipitate manually.

The reactor is of depth 250mm, diameter of 180mm and is in cylindrical shape in nature, which has a capacity of 7.5 liters and made of acrylic material. Electric current is must and should for running the reactor. The

reactor is fully known as blade agitator reactor as mentioned previously. Acrylic glass material is used for making the reactor because of its transparent characteristics and it's minimal weight.
As the reactor can't stand alone because of the dome shaped piece provided at its bottom, it is fixed to a stand. This stand is also of acrylic material and in circular shape. It is an extra piece attached to the bottom of the reactor to make the reactor stand firm while running and while not running.
The figure below shows the pictorial representation of the reactor which was designed and setup, and the table below shows the dimensions and the speculations of each material used in reactor for the purpose of struvite crystallization process.

Table 1: Table showing the dimensions and speculations of the reactor and its materials

Capacity	7.5Lit
Speed of motor	200rpm
Material	Acrylic
Shaft depth	150mm
Motor power	30W & 220 – 250V
Diameter of the reactor	180 mm
Height of Reactor	250 mm
Height of Round bottom	50 mm
Radius of Round bottom	90 m

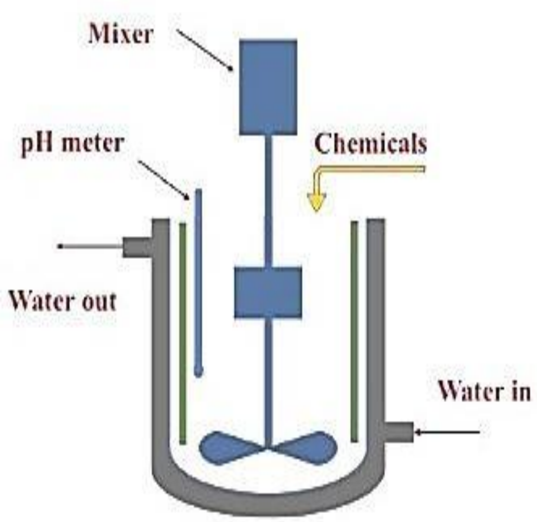
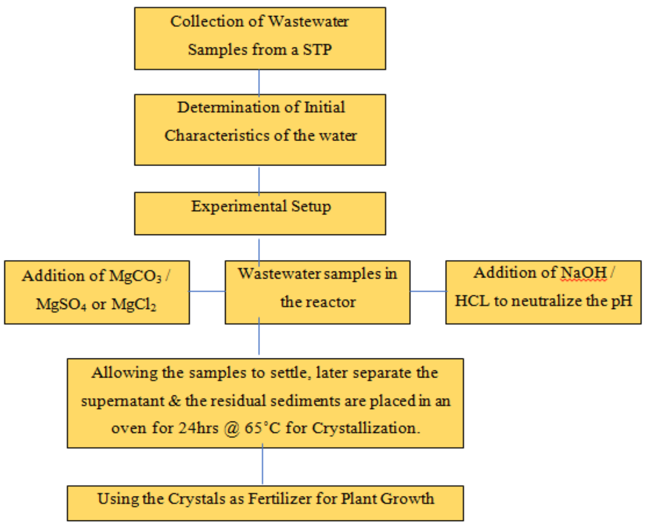


Figure 3: Blade agitator reactor used for struvite crystallization process

Methodology

- The Domestic wastewater should be collected before the treatment itself because the precipitate will not be forming if it is collected after the treatment and used.
- The domestic wastewater should be collected after screening so that the unwanted particles for struvite crystallization process can be removed.
- Initially the various physico-chemical characteristics of the collected wastewater sample such as pH, turbidity, BOD, phosphate, nitrite, etc., should be determined.
- The reactor should be designed and setup in the place where the experiment is going to be conducted.
- Collected wastewater sample of known quantity (liters) should poured into the reactor.
- pH should be measured to know whether the wastewater is in acidic or in alkaline condition. Anyhow, the pH of the wastewater should be neutralized.
- If the wastewater is in alkaline condition add required amount of HCl to it, so that the pH of that wastewater is neutralized.

- If the wastewater is in acidic condition add required amount of NaOH, so that the pH of that wastewater is neutralized.
- Anyhow, to carry the struvite crystallization process the pH of the collected wastewater sample be within 8.3 to 9.3.
- If it is less than that, the required precipitate in the struvite crystallization process might not form.
- Now the magnesium source should be weighed and added into the reactor.
- The magnesium source can be one among the magnesium chloride (MgCl2), magnesium sulphate (MgSO4), magnesium carbonate (MgCO3), etc.
- After all the necessary preparations has done to run the reactor, the reactor will be working to a minimum duration of 20minutes.
- In these 20 minutes of duration, the wastewater will be mixed with the one of the suitable magnesium sources to form the precipitate.
- The magnesium source added into the wastewater acts as +ve ion and the wastes or unwanted particles present in the wastewater acts as –ve ion.
- These +ve ion attracts the –ve ion in the reactor, thus leads to form struvite embryoids.
- Further reaction and ion attraction will result in forming the struvite precipitate in the reactor containing wastewater and magnesium source.
- After the reaction process in the reactor, the particles are allowed for sedimentation to a duration of 20 to 30 minutes. So that the formed precipitate will be settled at the bottom of the reactor.
- Now, collect the supernatant to determine the same various physico-chemical characteristics which were carried out for raw water.
- Collect the settled precipitate, filter it using the Whatmann filter paper or using pure white cotton cloth and pour it into the crucibles.
- Keep that crucibles in the oven for 24 hours at 65o C so that the precipitate dries and loses the moisture content in it.
- If the temperature gets above 65o C, then ammonia will be evaporated from the precipitate resulting in absence of nitrogen in the precipitate formed.
- If less is the temperature, duration for the oven should be more resulting in time consuming for precipitate to dry.
- After drying the precipitate, it should be cooled under standard room temperature or using desiccator and then weighed using digital weighing balance.
- This is the fertilizer obtained from the wastewater through struvite crystallization process using magnesium sources as metal salts.



INITIAL CHARACTERISTICS OF WASTEWATER SAMPLE

Table 2: Table showing the initial characteristics of wastewater sample

Characteristics	Trial 1	Trial 2	Trial 3	Average value
pH	8.6	9.0	9.2	8.9
Alkalinity	152.6	158.3	157.5	156.1
Acidity	10	11	9	10
Dissolved Oxygen (DO)	10.4	10.6	10.8	10.6
Turbidity	347	338	335	340
Biochemical Oxygen Demand (BOD)	380	370	390	380
Nitrite	11.4	11.6	11.0	11.0
Phosphate	23.8	23.6	24.6	24

EXPERIMENTAL SEQUEMCE TO BE FOLLOWED

After determining the Initial characteristics of the waste water sample, measured volume of up to 5 liters of raw wastewater shall be poured into the reactor using volumetric flask Using digital weighing balance, A weighed amount of 25g of $MgCO_3$ (5g/L) will be added into the reactor containing 5 liters of raw wastewater. As the measured quantity of domestic wastewater and $MgCO_3$ will be added into the reactor, an electric motor is used to rotate the blades with the speed of above 200 RPM. Here both domestic wastewater and $MgCO_3$ mixes vigorously and continuously. The duration for this reaction purpose is fixed for about 20 minutes. The magnesium source added into the wastewater acts as +ve ion and the wastes or unwanted particles present in the wastewater acts as –ve ion. These +ve ion attracts the –ve ion in the reactor, thus leads to form struvite embryoids. Further reaction and ion attraction will result in forming the struvite precipitate in the reactor containing wastewater and magnesium source Then allowing the particles in the reactor for settlement of about 20-30 minutes. The precipitate will be settled at the bottom of the reactor. Through the tap provided, the supernatant would be collected to determine the same various physico-chemical characteristics which was determined for raw wastewater. Then the precipitate shall be collected, filtered through Whatmann filter paper and poured into crucibles. The obtained precipitate after filtering and pouring into the crucibles shall be kept in the oven at 65oC for 24 hours (one day). After drying the precipitate, it will be cooled under room temperature (25°C). This is the precipitate obtained from the domestic wastewater collected from sewage treatment plant through struvite crystallization process. And this precipitate shall be used as a fertilizer for the plant's growth. Similarly, other sources of Magnesium salts like $MgCl_2$ and MgS04 Shall be used and then the precipitate formed by the struvite crystallization process shall be used as a fertilizer for the plant's growth & comparison shall be made using Urea or any other conventional fertilizer to determine which is the best fertilizer. Impact of struvite precipitation on Turbidity / BOD/ Phosphate / Nitrite removal shall also be studied

RESULTS AND DISCUSSION

Impact of Struvite Precipitation on Turbidity

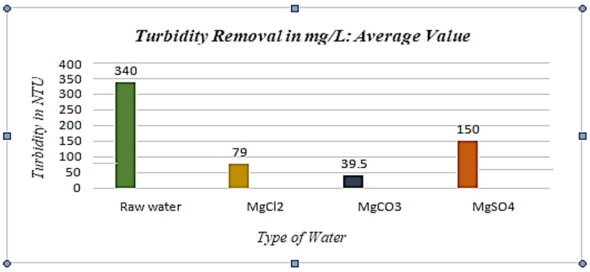


Figure-4: Results showing the turbidity removal from wastewater sample in NTU (Avg value).

The average results of the Turbidity tests are shown in the graph. The mean turbidity present in the raw wastewater was found to be 340 NTU. The mean turbidity in the wastewater with MgCl2 after the struvite crystallization was found to be 79 NTU. The mean turbidity in the wastewater with MgCO3 after the struvite crystallization was found to be 39.5 NTU. The mean turbidity in the wastewater with MgSO4 after the struvite crystallization was found to be 150 NTU. The maximum mean turbidity removed when MgCO3 used as Mg source comparing with other two salts.

Impact of Struvite Precipitation on BOD Removal

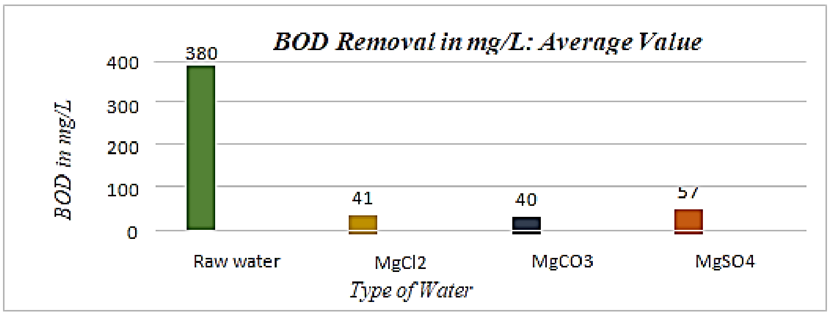


Figure 5: Results showing the BOD removal from wastewater sample in mg/L for Average value

The average results of the BOD tests are shown in the graph. The mean BOD present in the raw wastewater was found to be 380 mg/L. The mean BOD in the wastewater with MgCl2 after the struvite crystallization was found to be 41 mg/L. The mean BOD in the wastewater with MgCO3 after the struvite crystallization was found to be 40 mg/L. The mean BOD in the wastewater with MgSO4 after the struvite crystallization was found to be 57 mg/L. The maximum mean BOD removed when MgCO3 used as Mg source comparing with other two salts.

Impact of Struvite Precipitation on Phosphate Removal

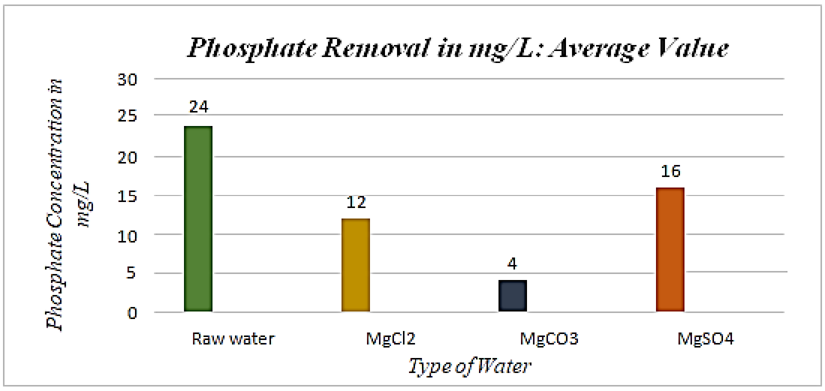


Figure6: Results showing the Phosphorous removal from wastewater sample in mg/L (Average value)

The average results of the Phosphate tests are shown in the graph. The mean Phosphorous present in the raw wastewater was found to be 24 mg/L. The mean Phosphorous in the wastewater with MgCl2 after the struvite crystallization was found to be 12 mg/L. The mean Phosphorous in the wastewater with MgCO3 after the struvite crystallization was found to be 4 mg/L. The mean Phosphorous in the wastewater with MgSO4 after the struvite crystallization was found to be 16 mg/L. The maximum mean Phosphorous removed when MgCO3 used as a Mg source comparing with other two salts.

Impact of Struvite Precipitation on BOD Removal

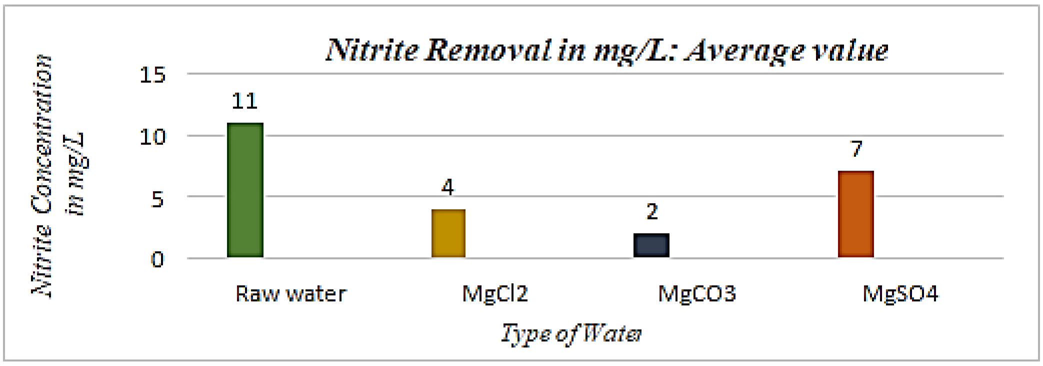


Figure 4.16: Results showing the Nitrogen removal from wastewater sample in mg/L for Average value

The average results of the Nitrite tests are shown in the graph. The mean Nitrogen present in the raw wastewater was found to be 11 mg/L. The mean Nitrogen in the wastewater with MgCl2 after the struvite crystallization was found to be 4 mg/L. The mean Nitrogen in the wastewater with MgCO3 after the struvite crystallization was found to be 2 mg/L. The mean Nitrogen in the wastewater with MgSO4 after the struvite crystallization was found to be 7 mg/L. The maximum mean Nitrogen removed when MgCO3 used as a Mg source comparing with other two salts.

Particulars	Conventional plant growth in CM without any fertilizer	Plant growth in CM with chemical fertilizer (Urea)	Plant growth in CM with MgCO3 fertilizer	Plant growth in CM with MgSO4 fertilizer	Plant growth in CM with MgCl2 fertilizer
5th day	1.4-1.6	1.4-1.7	1.3-1.6	1.4-1.5	1.2-1.5
7th day	2.3-2.5	2.7-3	2.5-2.8	2.4-2.6	2.5-2.6
12th day	4.6-4.8	5.5-5.9	2.3-5.6	4.8-4.9	4.7-5.1
17th day	5.2-5.3	6.4-6.6	6.1-6.3	5.2-5.5	5.3-5.4

The obtained struvite precipitate was used as a fertilizer for the growth of Ragi (Finger millet) the Table shows the results of Ragi plant growth (finger millet) using urea as chemical fertilizer and using struvite fertilizer extracted from domestic wastewater. The fertilizer obtained from the MgCO3 which was used as magnesium source in the struvite crystallization process shows the similar plant growth as compared to the Chemical fertilizer (urea) and shows higher growth rate compared to MgSO4, MgCl2 and conventional (only Ragi seeds and soil, with absence of any fertilizer).

CONCLUSION

Struvite crystallization process is highly effective in removing nitrogen and phosphorus from wastewater via crystallization process. It is particularly well suited for nutrient-rich wastewater. The hazardous elements in wastewaters (mainly NH4 and PO4) might be converted to a valuable resource through this process. Water bodies are polluted because of discharging domestic wastewater and industrial effluents into them. This waste water is very much rich in Phosphorous and Nitrogen which causes eutrophication in the water bodies. Thus, production of struvite from wastewater will reduce the hazard of eutrophication in the water bodies by removing P and N and produces successful slow – release fertilizer.

Also, struvite will be the most effective alternative source of Phosphorous that will help to continue agricultural production after exhaustion of all mined phosphate rock. The crystals formed in the Struvite Crystallization process is Magnesium Ammonium Phosphate (MAP) which is the good nutrient for the plant and animal growth, hence MAP is used as fertilizer for plants. In the meantime, thus reducing the consumption of Rock Phosphorous which is costlier than Struvite Crystal fertilizer and the cost of production in agricultural can also be reduced. This project indicated significant mass production of struvite and proved that struvite technology is an economic efficient technique to avoid harmful effects of eutrophication with successful production of slow-release fertilizer rich in ammonia and phosphorous. Following points shall be considered for the future scope of work:

- Struvite crystals can be generated by using the various Magnesium salts to find out the production rate and growth rate of the plant.
- Propose the Struvite Crystallization Reactor for the sewage treatment plant at TKEC campus, the same can be utilized for the plantation purpose for the entire college campus.
- The supernatant obtained in the reactor can be analyzed and proposed for the future treatment or reuse.
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