Precipitation of struvite by sustainable waste materials and use as slow release fertilizer – A circular economy approach

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Abstract: The increased concern on the quantity of wastewater generation subsequent degradation in the quality of surface water sources, especially through eutrophication has urged many researchers to find sustainable ways to recover the nutrients and reuse as a natural fertilizer. Precipitation and simultaneous removal of struvite, otherwise called as magnesium ammonium phosphate hexahydrate (MgNH₄PO₄·6H₂O), from the wastewater using natural coagulants will be a better alternative. In the present study, the wastewater rich in ammonia was treated using sustainable modus operandi and nutrient-rich struvite was recovered. The objective of the research was to (i) optimize the quantity and struvite precipitation rate and study the effect of pH and (ii) germinate the seed (cereals) with optimal struvite dosage. Initially, the wastewater obtained from the hostel was characterized and subsequently coagulated using natural coagulants like pumpkin seeds and fish bones to precipitate the struvite. The raw wastewater found to have a pH of 6.64±0.32, the turbidity 304±28 NTU, ammoniacal nitrogen 32±3.9 mg/L, total solids 2240±72 mg/L and total alkalinity as 950±25 mg/L. The struvite with varied dosages in the order of 0.25 to 1.5 grams per 500 grams of soil was used for seed germination. At an optimal dosage of 0.5 grams per 500 grams of soil showed an effective plant growth and increased yield. Additionally, the wastewater after recovering struvite can be treated with a reed-bed system providing a circular economical solution for the modern agriculture industry.

Keywords: Struvite, Coagulation, Reedbed, Reuse, Seed germination

1. Introduction:
The livelihood of the people in India and world are mainly dependent on three main factors such as water, food and shelter securities. At present, India is experiencing a major problem i.e. water shortages in the river basins. Due to this water shortage there are simultaneous effects on agriculture growth, urbanization and industrialization. To eradicate the problem of water shortage water should be used efficiently and wastewater should be treated efficiently. The wastewater is defined as that water that is discharged after the human use. It is also referred as an effluent that comes from household, commercial establishments and institutions, hospitals, industries and so on [1, 2, 3]. It also consists of storm water and urban runoff, agriculture and aquaculture effluent. Managing the wastewater is one of the major problems that are being faced all over the world especially in developing countries like India. It creates a great impact on both fundamental integrity of our life support systems and biological diversity of aquatic systems. More than 80% of the water is getting wasted due to the lack of
knowledge in reusing the wastewater. It leads to water shortage in some places which affects the people livelihood [4, 5].

In general wastewater contains higher fraction of organic matter, solids, faecal contaminants, emerging pollutants, micro, and macro nutrients [6]. The reason for the eutrophication of many water bodies are due to the macro nutrients. The presence of macronutrients like nitrogen, and phosphorus in the wastewater are the biggest threat to environment if the wastewater not properly treated [7] leading to eutrophication. The presence of nutrients also leads to scale formation and corroding the piping’s (Figure 1). The nitrogen and phosphorus are essential nutrients for the plants and are optimally used for the growth and yield [8], furthermore the nutrients were applied artificially in the soil every year to increase the soil fertility. The country spends huge amount in the purchase and processing of synthetic nutrients, hence to have sustainable growth the use of naturally available nutrients is sensible. Struvite is one such natural slow release fertilizer that has 5.7% of nitrogen, 9.9% of magnesium, and 12.6% of phosphorus [9]. Struvite is a compound that can be precipitated from the wastewater by the following equation,

\[
\text{Mg}^{2+} + \text{NH}_4^+ + \text{HPO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4.6\text{H}_2\text{O} \downarrow + \text{H}^+
\]

Precipitation of struvite often occurs in wastewater when ammonium, phosphate, and magnesium ions exceed the struvite solubility limit. In the wastewater, the concentrations of ammoniacal nitrogen is lesser compared to the dissolved phosphorus, hence blending of digested sludge or cattle manure are better options [10]. Additionally, the magnesium ion is a limiting constituent in the wastewater, hence externally needs to be substituted by magnesium salts like MgCl\(_2\), MgSO\(_4\), MgO, and Mg(OH)\(_2\) [9, 11]. There are many nutrients recovery techniques were researched all over the world such as biological processes, chemical processes, electrolysis, adsorption, and crystallization [12, 13, 14]. The above techniques have both advantages and disadvantages, with more emphasis were given for the chemical based recovery of struvite.

The chemical precipitation using coagulants are investigated by many researchers and found to be good option for agglomeration of struvite particles [15, 16]. The cost analysis showed that requirement of chemical coagulants for precipitating the struvite was too much and requires a sustainable solution. Therefore, the natural coagulants like pumpkin seeds and fish bones that are rich in magnesium and phosphorus content respectively were investigated for struvite precipitation.

In the present study, the wastewater rich in ammonia was treated using natural coagulants to recover the struvite and further applied for seed germination. The objective of the study was to (i) characterize the wastewater from the hostel, (ii) effect of pH and natural coagulants dosages on the rate of struvite precipitation and (iii) optimal usage of struvite for rapid growth and higher yield of cereal seeds. In the second phase, the supernatant wastewater was treated using a reed-bed system for the recovery of non-potable water.
Fig. 1 The photographic view of scale formation in the sewage piping’s

2. Materials and Methods

2.1. Wastewater source
The wastewater was collected from the sewage treatment plant inside the SASTRA University, Thanjavur, Tamil Nadu, India campus at three different days. The university was spread over area of 230 acres with a student population of more than 10,000 contributing nearly 0.4 MLD of wastewater generated from hostels, canteens, and academic zones. The wastewater treatment plant receives all the generated water through gravity passing through several screens to a circular sump acts as an equalization tank. Then water was pumped at a constant rate to an extended aeration system, subsequently water was allowed to settle in the secondary clarifier. The clarified water was filtered through activated carbon and pressure sand filter, and then treated water was used for gardening. The bio-sludge were dried in the solar ponds and mixed with cow dung and used as manure for plants inside the campus. Initially, the wastewater was collected as a grab sample at 10.00 AM and found that it predominantly contains the greywater (Results not shown). Subsequently the composite samples were collected and analysed for various parameters like pH, turbidity, dissolved oxygen, total hardness, total alkalinity, total solids, suspended solids, fixed solids, ammoniacal nitrogen and total phosphate. The wastewater was blended with equal portion of cow dung to increase the pH and ammoniacal nitrogen concentration. The physico-chemical parameters for the wastewater samples were analyzed as prescribed in the standard procedure for water and wastewater analysis [17].
2.2. Experimental setup
The wastewater samples were coagulated with coagulants like pumpkin seeds and fish bones powder at varied dosages. The dosages of the coagulants were varied from 5, 10, 20, 25, 30, 35, 40, 45, and 50 g per 500 mL of the wastewater. It was found that the 25g of fish bone and 35g of pumpkin seed powder provided an optimal turbidity removal (Results not shown). The coagulation was performed in the jar apparatus, where the wastewater samples were kept in a 600 mL beaker with a working volume of 500 mL. After the coagulants were added, the rapid mixing for 1 minute and slow mixing for 20 minutes were performed. The detailed schematic methodology is shown in Figure 2. Finally, the mixture was off and contents were allowed to settle for 30 minutes. The supernatant was collected in a storage can for further processing. The precipitate was collected and dried in oven at 105°C for 1 hour to remove the moisture. The contents were ball milled and stored for seed germination test.

![Fig. 2 Schematic representation of overall methodology](image)

2.3. Seed germination test
The obtained struvite from the blended wastewater was used for the seed germination test. The cereals were used in the experiments for germination test. The seeds are put into different pots with the varying amount of struvite. Struvite is added by varying its dosage in the order of 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 5.0, 7.0, and 9.0 per 500 grams of soil. Firstly struvite is added with the dosage of 5.0g, 7.0g, and 9.0 g per 500grams of soil respectively for 7 days. But, the there were no signs in the growth of plant. Later plants are planted with the dosage of 0.5g, 1.0g, 1.5g, and 2.0 g per 500g of soil.

3. Results and Discussion

3.1. Wastewater characteristics
The wastewater characteristics are shown in Table 1. It was found that the wastewater is not appropriate for the precipitation of struvite. The most vital parameters leading to effective struvite precipitations are the necessity of higher concentrations of ammoniacal nitrogen and pH. The literature evident shows that pH above 8.5 and ammoniacal nitrogen above 150 mg/L is highly effective for struvite precipitation [2, 9]. The photographs of the wastewater and the blended wastewater are shown in Figure 3.

| Sl. No | Parameters                      | Wastewater | Blended Wastewater |
|-------|---------------------------------|------------|--------------------|
| 1.    | pH                              | 6.64±0.32  | 8.72±0.88          |
| 2.    | Turbidity (NTU)                 | 304±28     | 7000               |
| 3.    | Dissolved Oxygen (mg/L)         | 3.87±1.22  | 0.1±0.5            |
| 4.    | Total Hardness (mg/L)           | 420±10     | 3800±250           |
| 5.    | Total Alkalinity (mg/L)         | 950±25     | 5500±80            |
| 6.    | Total Solids (mg/L)             | 2240±72    | 15960±280          |
| 7.    | Suspended Solids (mg/L)         | 180±82     | 7560±105           |
| 8.    | Fixed Solids (mg/L)             | 620±40     | 9800±220           |
| 9.    | Ammoniacal Nitrogen (mg/L)      | 32±3.9     | 248±22             |
| 10.   | Total Phosphate (mg/L)          | 8.72±3.8   | 89.22±12.1         |

Hence, the wastewater was blended with the cow dung with an optimal ratio 1:1 to obtain a maximum struvite quantity. The characteristics of blended wastewater was shown in Table 1, and found that the values are in good agreement with the previous studies on struvite precipitation using a mixture of methods [2, 11, 18, 19].

3.2. Coagulation process:
The pumpkin seed and the fish bones are collected from the near-by market and were washed, dried and made powder using the ball mill. The different dosages of coagulants were tried and found that at an optimum dosage of 25g of fish bone and 35g of pumpkin seed the maximum precipitation was
obtained. The effect of pH was studied; the pH was varied from 2, 4, 6, 7, 8, 9, 10, and 12 by varying the addition of 0.1 M HCl (hydrochloric acid) solution and 0.1 M NaOH (Sodium hydroxide) solution (Figure 4). The obtained results were in good agreement with [2, 20, 21]. The change in pH was closely related to the release of ammonium and the pKa value is 9.2, and hence the maximum reduction of ammonium could be achieved at pH 9.0–10.0 due to ammonia gas formation [2, 22, 23].

![Fig. 4 The effect of pH in the coagulation process for struvite precipitation](image)

3.3. Seed Germination Test:
Seed germination is the process in which activation of the embryo takes place through morphological and physiological alterations. Before the seed germination the seed absorb water and then the elongation of seed embryo takes place. When the radical grows out through the cover layers of the seed process of seed germination is said to be completed [24]. In this study, cereals seeds were sowed into different pots having varying dosages of struvite (0.25-9.0 g per 500 gram of soil). It was observed that cereals were not growing properly in the higher dosages (5g, 7g and 9g) of struvite, due to the shortfall in the C/N ratio. The growth of cereals were found to be maximum in the lower dosages of struvite and found to have a higher yield at 0.5 gram of struvite in 500 gram of soil after 30 days of sowing (Figure 5). The above results were in good agreement with [25, 26]. It was said that the germination index increased from 20% to 80% after the proper ratio of struvite to soil [25].
4. Conclusion:
The study concludes that the fine struvite particles are often generated in the process of recovering phosphorous and reuse from waste water effluents. The optimum conditions that are to be maintained for the removal of maximum amount of phosphorous from an-aerobically digested waste water were found to be pH 9.0. The Struvite which is recovered through the above process was applied for the cultivation of seeds. The fertilizing capacity was tested by putting struvite in various pots. This is known to provide essential crop nutrients N, P, K, Ca and Mg. Specifically, more amounts of both P and Mg were observed. As a sustainability point of view, instead of using chemical for precipitation, there are alternative waste materials that have more amounts of magnesium and potassium. The pumpkin seed was found to be alternative materials that are rich in magnesium compound. The fish bones that are found to contain higher percentage of potassium content, hence these materials can be powdered and used as a sustainable alternative materials. Thereby, it was proved that struvite deposits recovered from an-aerobically digested waste water were effective as a fertilizer providing many nutrients in the cultivation process.

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