Phosphorus recovery as induced struvite from deep dewatered liquors using magnesium chloride as a magnesium source

H R Rashmi* and C P Devatha
Department of Civil Engineering,
National Institute of Technology Karnataka, Surathkal, Mangalore-575 025, India
E-mail: *rashusmile14@gmail.com

Abstract: The phosphorus recoveries in municipal wastewater treatment plants (WWTPs) are in much demand as the price of phosphate rock are increased from the last decade. Due to the increase in pollution levels of the sewage sludge, it is difficult to use sewage sludge directly as fertilizers in agricultural fields. The present study aimed to work on the recovery of phosphorus from the deep dewatered liquors in a laboratory, batch test mode. Experiments were conducted to identify the initial characteristics of sludge and for recovery analysis, by varying the phosphorus and Magnesium (Mg:P) molar ratio. Characterization studies were performed by SEM and FTIR for confirmation of struvite formation. Results obtained revealed that recovery is 94% of the incoming phosphorus.

Keywords: Struvite, Crystallizations, Phosphorus, sludge, recovery.

1. Introduction

1.1 General
One of the essential elements of all form of life is Phosphorus. Phosphorus is a part of enzymes, proteins, DNA, the energy carrier ATP. Phosphorus is present in the food we consume hence it acts as an important part in the production of food. In European countries, Phosphorus is been recovered from the past so many decades. Fertilizers used in the European countries are sewage sludge even now it has been practiced [1]. In 2030 the phosphorus rich fertilizers will be in much higher demand [2]. As the sludge contains high organic pollutants, pathogens, and heavy metals, from the last decade the use of sludge has been restricted to the farm lands as fertilizers.

Enhanced biological phosphorus removal (EBPR) and chemical phosphorus removal are the two main technologies used for the removal of phosphorus. From the past few decades, phosphorus removal technologies have been significantly advanced and been applied in and around the world. The main reason for removing phosphorus in WWTP is for the elimination of eutrophication, chemical phosphorus removal technology is one of the methods.

Crystallization is one method of chemical phosphorus removal, which is a very promising technology used in various full scale operations in treating high nutrient side streams. Crystallization is a method used for treating water and sludge from dewatered, anaerobic digester and phosphorus rich side streams. The phosphorous content is high in the sludge, therefore, the technology which is used for phosphorus recovery from the sludge has a very high potential [3]. A lot of interest has been shown for the phosphorus recovery from the sludge because the potential for the recovery of phosphorus is high from the sludge.

Struvite (MgNH4PO4.6H2O) precipitate is a mineral of phosphate and has a chemical name of magnesium ammonium phosphate hexahydrate. Crystallization process has been used for the recovery of nutrients from various sources such as swine wastewater [4], human urine[5], landfill leachate [6] and sludge supernatant[7]. As ammonium, magnesium, and phosphorus are released in the anaerobic digestion in WWTP, Struvite formation leads to serious operational problems. Due to the accumulation of Struvite in pumps, pipes and dewatering equipment, the systems clogs[8]. In EBPR
systems, phosphorus release is high hence struvite formation has been a challenge. Figure 1 shows the formation of Struvite in the anaerobic digester pipe.

Molar ratio, pH, Temperature and foreign ions are the factors which affect the Struvite formation [9]. For the crystal growth, the phosphorus rich side stream is led into the chamber along with the seed materials. The pH is controlled by using NaOH or by CO2 stripping. For crystallization of struvite, the addition of magnesium is very much is essential, as the magnesium concentration is very much low when compared to ammonium and phosphorus. The various forms of magnesium are used such as magnesium hydroxide, magnesium oxide, and magnesium chloride.

![Figure 1: formation of Struvite in the anaerobic digester pipe[10].](image)

The present study has been focused on investigating the use of MgCl2 as magnesium sources for recovery of phosphorus from dewatered sludge, the morphology and purity of the struvite obtained was characterized using various techniques in order to help us to evaluate the potential for using MgCl2 as magnesium sources.

2. Materials and methodology

The sludge sample was collected from the secondary sedimentation tank located in the NITK campus and studied the basic properties of sludge which is tabulated in Table no 1. Sludge was conditioned and dewatered. The dewatered sludge of 100mls taken in a conical flask for deep dewatering using coconut shell powder as skeleton material which is modified by ferric chloride. Deep dewatering is carried out by mixing the ferric chloride at 300RPM for 15min in a magnetic stirrer. The supernatant was collected and further studied for the recovery of phosphorus in a different molar ratio of Mg/P. The process was taken up for the following mg/ P molar ratio of 0.5:1, 1:1, 1.5:1 and 2:1. And also the recovery potential of phosphorus at different pH was also determined. The pH was increased for 7, 8, 9, 10 and 11 with the help of sodium hydroxide. The aeration was provided for the complete mixing of the liquor and also for the increase of pH also mixing as to be done for 20min. Precipitation takes place later the supernatant is collected and checked for the purity. In all the experiments, The mixture was then centrifuged at 5000 rpm for 10 min to separate the precipitates. The precipitates were dried overnight at 90°C for various characterization analyses. The supernatants were filtered through 0.45 µm pore size membrane filter before analysis the the remaining phosphate. All batch experiments were carried out at room temperature (25 ± 1°C).

| Parameter                        | Values |
|----------------------------------|--------|
| Temperature(°C)                  | 26     |
| pH                               | 7.31   |
| Specific gravity                 | 2.61   |
| Electrical conductivity (ms/cm)  | 3.314  |
| Moisture content (%)             | 96.4   |
Parameter | Values
--- | ---
Total solids, TS (mg/L) | 20,634
Alkalinity (mg/L) | 2300
Chemical oxygen demand, COD (mg/L) | 11,768

3. Results and Discussion

3.1 Deep dewatering of the sludge

The deep dewatering of dewatered sludge using a coconut shell modified with ferric chloride showed an acceptable dewatering performance. The moisture content of the dewatered sludge was 81% whereas the deep dewatered sludge moisture content was reduced to 62%. From the result, it is indicating that the coconut shell modified with ferric chloride is dehydrants and also satisfactory in the process of deep dewatering.

3.2 Effect of Mg/P molar ratio

Fig 2 represents the recovery efficiency of phosphate in different Mg/P molar ratio of 0.5:1, 1:1, 1.5:1 and 2:1 by adding MgCl2. The recovery was low in the beginning whereas at 1:1 molar ratio the recovery was more than 90% and further recovery efficiency remains the same.

![Figure 2. Effect of Mg/P molar ratio on the recovery rates of phosphate from deep dewatered liquors.](image)

3.3 Effect of pH

Fig 3 shows the effect of pH at an optimum Mg/P molar ratio of 1:1 for the recovery of phosphate. The pH range of 9.5 to 10.5 is supportive for the maximum recovery of phosphate. The same as been reported by [11], [9] and [12], the dewatered sludge used are in the pH more than 8.5 hence there is no much pH adjustment is required which is much beneficial in applications of engineering.

![Figure 3. Effect of pH on the recovery rates of phosphate from deep dewatered liquors (Mg/P molar ratio of 1:1).](image)
3.4 Characteristics of Struvite

3.4.1 Surface morphology.

The SEM image of the sludge dewatered sludge and struvite is depicted in fig 4(a), (b) and (c). The morphology of secondary sludge dense and the Deep dewatered sludge image shows the less pore space and the recovered struvite image reports that the formed particles are in palletform.

Figure 4: SEM images of crystallization processed struvite.

3.4.2 Surface analysis.

The FTIR spectra of dewatered sludge and crystallized struvite are represented in figure 5.1017–1163 cm$^{-1}$ is the band of intensities which are correlated with phosphate. It can be accepted that the precipitates obtained in the experiments were struvite crystals as the FT-IR spectra were matching.

Figure 5: FTIR images of crystallization processed struvite.

4. Conclusions

The experimental setup was designed for the recovery of phosphorus from the deep dewatered liquors.
Recovery potential (94%) was achieved and the presence of struvite is identified by SEM and FTIR. The results obtained can be further developed for the industrial application in the large scale for the recovery of phosphorus.

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