



RECOVERY OF NUTRIENTS FROM STRUVITE CRYSTALLIZATION PROCESS USING GOAT MANURE

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ABSTRACT

Wastes collected from goat farm are converted into manure by various processes for their application in agricultural fields in order to yield more production of crops. But unexpectedly the nutrient present in the manure is not completely utilized by the plants sometimes due to surface water runoff, floods and certain other aspects. The production of mineral fertilizers has a significant environmental impact, including depletion of fossil fuels and minerals. Therefore, the nutrients present in this manure comprise of minerals such as Magnesium, Ammonium and Phosphate which is otherwise called as struvite. This struvite can be precipitated separately and can be made as a substitute for manure since struvite is far rich in nutrients compared to manure and also it is considered as a slow releasing fertilizer which has less soluble in water. This thesis work shows the amount of MAP (Mg , NH_4 , and P) nutrients generated when goat manure is used as the influent to the fluidized bed reactor with addition of MgCl which acts as a precipitating agent and also the impact of struvite precipitation in the concentration of total solids, hardness, pH, BOD/COD from the goat waste manure is observed.

Keywords: Goat manure, struvite crystallization, nutrient recovery.

1. INTRODUCTION

Recognizing that wastewater is a “renewable resource”, this challenge will begin with the recovery of nutrients. It will provide needed research to identify the full range of nutrient extracting processes and how this resource can be commoditized. It will identify areas where new processes might still be developed; evaluate each of these processes for current and future potential; identify paths and barriers for process implementation, and develop a tool allowing subscribers easy access to the information collected and created by this effort so that they can readily decide whether the process of interest has a net value to their agency or company, or not. In recent years, struvite has emerged as the most promising compound for recovery of nutrient from goat waste. The precipitation of struvite is affected by several factors, namely the pH, the chemical composition of the waste (degree of saturation with respect to magnesium, ammonium and phosphate; presence of other ions, such as, calcium, ionic strength of the solution), and the temperature of the solution.

Struvite also gets crystallizes from aqueous solution at neutral to alkaline pH. Struvite has a very low solubility in water of around 160mg/L at pH 7 & at 25°C. Its color is brownish-white and its shape is pyramidal like crystals.

Struvite is formed as a scale or belt like lines in centrifugal pumps and also clogs system pipes in which wastewater flows. It is formed when there is a mole to mole to mole ratio (1:1:1) of MAP in wastewater. Struvite creates inefficiency due to clogging of pipes, pumps, etc. In this study, the precipitation of struvite is investigated with the purpose to reduce harmful effects on the environment and retrieve nutrients.

$\text{NH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ where M corresponds to a metal that can be either magnesium (Mg), cobalt (Co), potassium (K) or Nickel (Ni) [1]. Struvite or magnesium ammonium phosphate hexahydrate crystallizes as a white orthorhombic structure (*i.e.* Straight prisms with a rectangular base). Table 1 summarizes the main chemical and physical properties of struvite crystals [2]. Struvite precipitates in a 1:1:1 molar ratio following the general equation (with $n = 0, 1$ or 2):



The occurrence and development of struvite crystals follow two chemical stages: nucleation (crystal birth) and crystal growth (development of crystals until equilibrium) [3]. Predicting or controlling these mechanisms is complex as it is controlled by a combination of factors including the crystal state of initial

compounds, thermodynamic of liquid-solid equilibrium, phenomena of matter transfer between solid and liquid phases [3], and kinetics of reaction [4] as well as several physico-chemical parameters such as: pH of the solution from which struvite may precipitate [5] super-saturation [6], mixing energy [4], temperature and presence of

foreign ions [7]. Therefore the purpose of this thesis is to broaden the understanding of struvite crystallization principles in order to improve struvite recovery from wastewater effluents in terms of quantity of product generated and characteristics (size, shape and purity) of the crystals formed.

Table 1: Physical and Chemical properties of Struvite

Nature	Mineral Salt
Chemical name	Magnesium ammonium phosphate hexahydrate
Formula	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$
Aspect	White glowing crystal
Structure	Orthorhombic (space group $\text{Pmn}2_1$): regular PO_4^{3-} octahedral, Distorted $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ octahedral and NH_4 groups all held together by hydrogen bonding.
Molecular weight	245.43 g. Mol^{-1}
Specific gravity	1.711 g. Cm^{-3}
Solubility	Low in the water: $0.018\text{g.}100\text{ml}^{-1}$ at 25°C in water High in acids: $0.033\text{g.}100\text{ml}^{-1}$ at 25°C in 0.001 N HCL; $0.178\text{g.}100\text{ml}^{-1}$ at 25°C in 0.01 N HCL.
Solubility constant	$10^{-13.26}$

2. MATERIALS AND METHODS

Goat manure is collected from a nearby goat farm which is three to four months old. Determining the characteristics of the manure such as pH, chlorides, TS, TDS, Electric conductivity, Dry matter, Total hardness, Total kjeldhal nitrogen, BOD, COD etc., is to be analyzed in the laboratory using the consecutive procedures. Procedure in standard method was followed for sample collection, preservation and transportation. The following table shows the initial characteristics observed in the goat manure.

Table 2: characteristic of diluted goat manure

Parameter	Concentration
pH	8.24
Ammonia	2.07 mg/l
Phosphate	5.8 mg/l
TDS	46.5 mg/l
TS	68mg/l
BOD	5 mg/l
COD	84 mg/l
Total hardness	552 mg/l
Calcium hardness	410 mg/l
Chlorides	114mg/l
Magnesium hardness	224.5 mg/l

2.1. Design criteria for holding tank

The diameter of the upper pyramidal cylinder = 200 mm

The diameter of the inner cylindrical pipe = 50 mm

Height of cylindrical part of reactor = 1500 mm

A Struvite Fluidized Bed Reactor was designed with a capacity of 4 litres. The shape of the reactor was cylindrical with conical base. It was divided into two distinct parts; the upper part which was rectangular cubes and the lower part of the reactor was rectangular pyramid. The pyramidal part of reactor acts as settling zone. The bottom of the reactor contains tap for removal of sludge, crystals and wastewater. A peristaltic pump was provided for proper mixing of wastewater, Mg.Cl_2 solution and NaOH solution in the reactor. The reactor was operated at a pH of around 9.0. Insufficient dosing of magnesium reduced the MAP removal performance.

A cylindrical aeration tank was installed in the middle of the reactor for aeration of wastewater. The lower part of reactor acts as settling zone for struvite, and an outlet was provided for removal of sludge and crystals. Another outlet was provided at the upper part for removal of wastewater, if wastewater flowing continuously in the reactor. A mechanical operated mixer was installed in the middle of the reactor of capacity 50 RPM and it can be removed later from the reactor. Due to vibration, mixing was done as a first step.

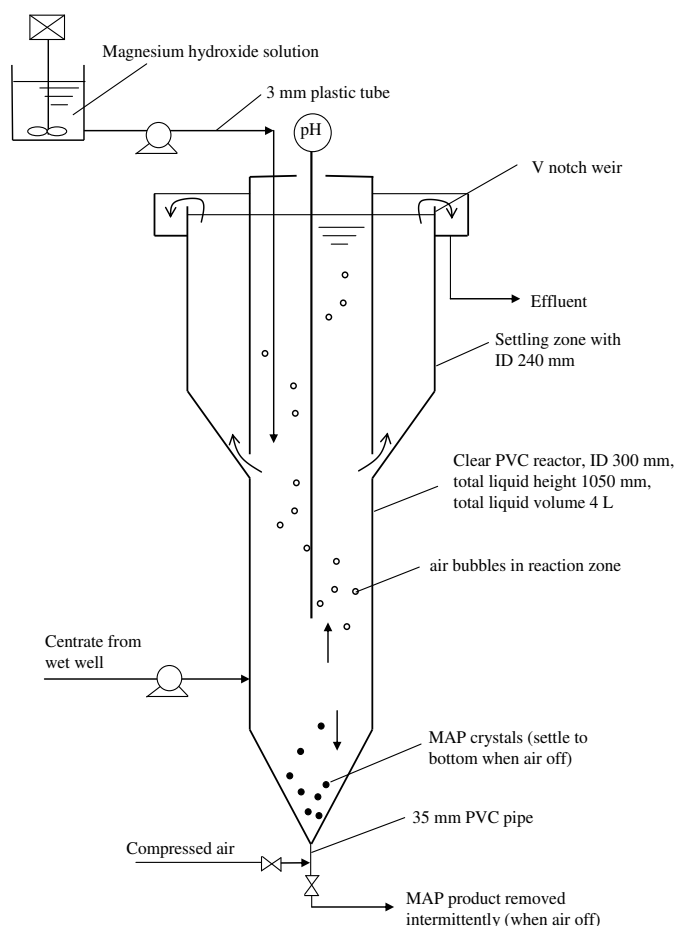


Fig. 1: Schematic sketch of Fluidized Bed Reactor

3. RESULTS AND DISCUSSIONS

3.1. The impact of struvite precipitation on pH

pH plays a vital role in struvite precipitation. The experiment was to identify the optimum pH for struvite formation. The pH of goat waste manure was found in the range 8.5 to 8.8 which was increased up to the pH 9.5 with the help of NaOH solution. After that magnesium chloride solution was mixed with wastewater and it was observed that when the precipitation started, the pH of the solution decreases in the range of 8.2 - 8.9 from its original pH 9.5. The optimum pH range for struvite formation is 8.5 - 9.5. The impact of precipitation on the pH was shown in Figure 2.

3.2. The impact of struvite precipitation on the concentration of phosphate

The concentration of phosphate in the goat waste manure was in the range of 20.1mg/L. After the precipitation of struvite, it was observed that the concentration of phosphate declined sharply in the range

of 17mg/L. About 98.2% of phosphate was recovered in the form of various compounds of phosphate along with struvite.

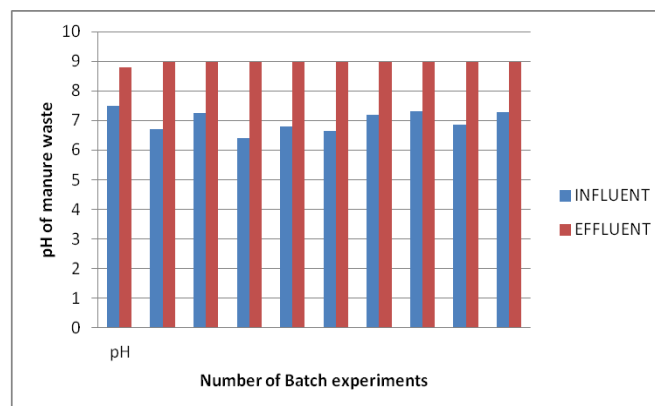


Fig. 2: Impact of Struvite Precipitation on pH

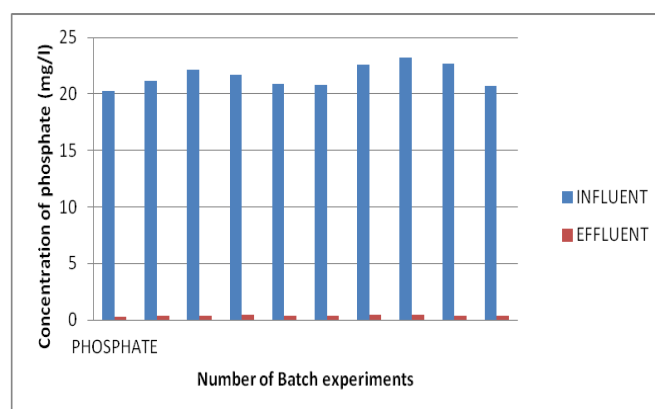


Fig. 3: Impact of Struvite Precipitation on phosphate

3.3. The impact of struvite precipitation on the concentration of ammonia

The concentration of ammonia was found to be in the range of 2.8mg/L in the goat manure. After the precipitation of struvite, it was observed that the concentration of ammonia declined sharply in the range of 0.6mg/l. About 84% of ammonia was recovered in the form of various compounds of phosphorus along with struvite.

3.4. Impact of Struvite Precipitation on Solids

In goat wastewater, the concentration of TDS and TS was found in the range of 15.1 mg/l and 64 mg/l respectively. After the addition of NaOH and magnesium chloride solution, it was observed that the concentration of TDS of the manure waste was sharply increased in the range of 22.92mg/l which result in increase of TS in the range of 78mg/l. This shows that

there was no 100% recovery of magnesium chloride. The maximum amount of magnesium was still in the solution and it affects the treatment facility of goat manure. The amount of TDS and TS was found within the permissible limit after the completion of treatment. The impact of precipitation on the TDS and TS of goat manure wastewater is shown in the fig. 5 & fig. 6.

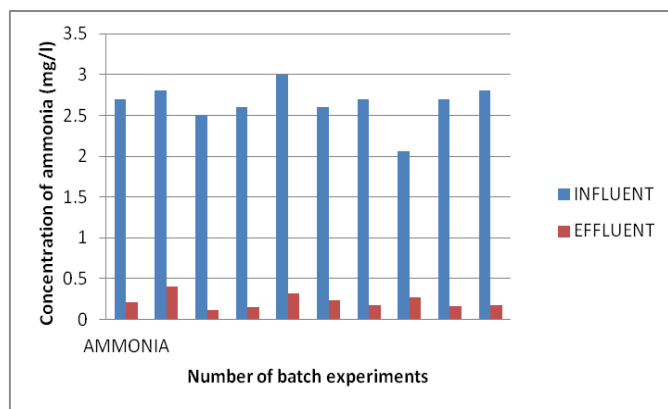


Fig. 4: Impact of Struvite Precipitation on Ammonia

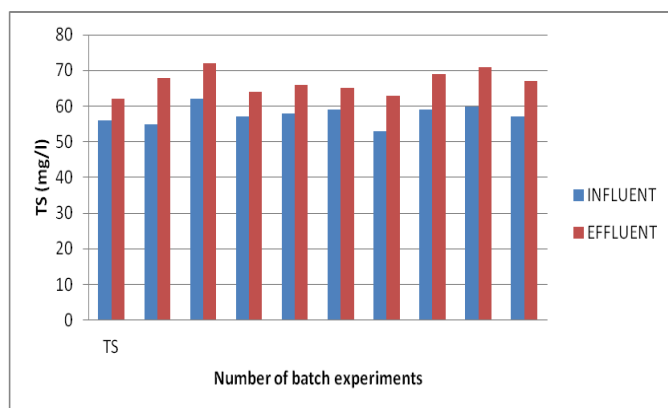


Fig. 5: Impact of Struvite Precipitation on TS

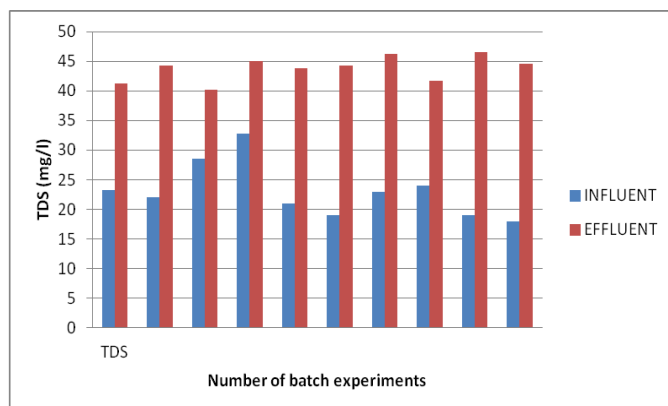


Fig. 6: Impact of Struvite Precipitation on TDS

3.5. The impact of struvite precipitation on the BOD and COD concentration

The BOD and COD of the goat manure wastewater were found in the range of 16mg/l and 404mg/l, respectively which was decreased sharply in the range of 0.5mg/l and 228mg/l after the struvite precipitation. The goat manure wastewater itself contains large numbers of microorganisms. They started consuming organic matter of the wastewater as food materials. Therefore a sharp decline was observed in BOD and COD concentration. As a result of decomposition the organically bound phosphate and ammonia was released into the solution and they were ready to participate in struvite precipitation.

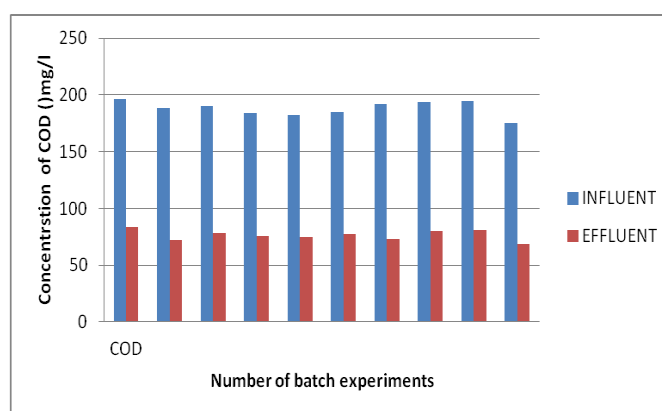


Fig.7: Impact of Struvite Precipitation on COD

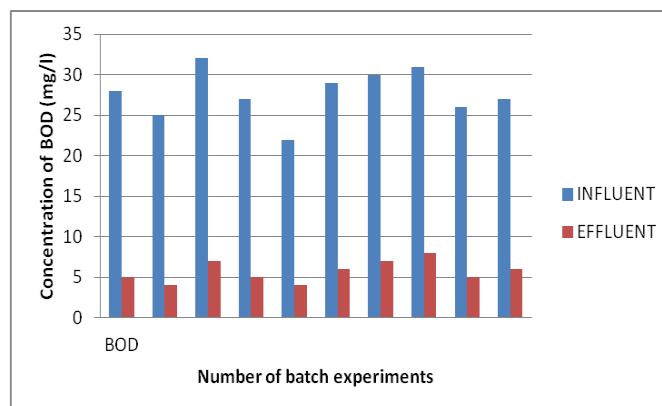


Fig. 8: Impact of Struvite Precipitation on BOD

3.6. Impact of Struvite Precipitation on the Hardness

The initial total hardness of the goat manure wastewater was found in the range of 462mg/l. After the struvite precipitation, the concentration of total hardness sharply increased. The total hardness was high because the magnesium was supplied from outside in the solution for struvite precipitation. After the precipitation of struvite,

the concentration of total hardness, increased and was found in the range of 768mg/l.

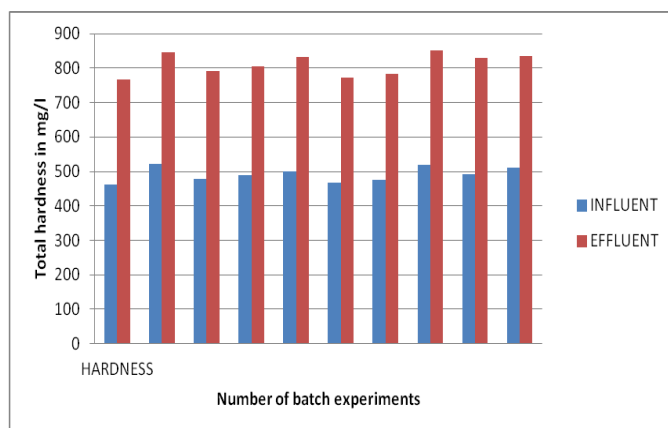


Fig. 9: Impact of Struvite Precipitation on Hardness



Fig. 10: Struvite obtained from goat manure

4. CONCLUSIONS

In this study, struvite precipitation is used to recover nutrients from goat wastewater. Four litres capacity of Fluidized Bed Reactor was designed to perform the experiment. The characteristic of goat manure wastewater was analyzed to assess the recovery potential of the method and percentage of reduction in pollutant concentration. As the result of this experiment the amount of struvite recovered was 98.28% of Magnesium, 84% of Ammonia and 98.2% of Phosphate. Application of struvite precipitation method will save the nutrients and reduce environmental pollution.

5. ACKNOWLEDGEMENT

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6. REFERENCES

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