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PRODUCTION OF SLOW RELEASE CRYSTAL FERTILIZER FROM WASTEWATER THROUGH STRUVITE CRYSTALLISATION- A REVIEW

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Abstract:- Struvite crystallization is a promising method to remove and recover phosphorus from wastewater to ease both the scarcity of phosphorus rock resources and water eutrophication worldwide. 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 phosphorus. Discharge of these compounds to surface water not only causes water eutrophication but also wastes phosphorus resources for plant growth. Therefore, it's necessary combining the removal of phosphorus 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. In this chapter, struvite crystallization mechanism, reaction factors, crystallizers, and the applications of struvite as fertilizer are discussed. Two steps of nucleation and crystal growth for struvite crystallization from generation to growth are introduced. The reaction factors, including molar ratio of magnesium and phosphate, solution pH, coexisting substances and seeding assist, of struvite crystallization are summarized. Several innovate types of crystallizer, which relate to the shape and size of harvest struvite to realize the phosphorus recycling, are demonstrated. Due to the influence of toxic or harmful impurities in struvite on its reuse as fertilizer, the environmental risk evaluation of struvite application is introduced. In conclusion, struvite crystallization is a promising tool for recovering phosphorus from livestock wastewater.

Keywords: Phosphorus, Nitrogen, struvite, livestock wastewater, Magnesium Chloride, fertilizer.

I. INTRODUCTION

The water is important resources for all the living organisms to survive. But the water which is present on the surface and below the surface is getting polluting day by day because of our illegal activities for our personal growth. The domestic wastewater and industrial effluent are releasing to water bodies, Hence most of the water bodies in our Bangalore are at endangerous level.

The waste water from the industry and domestic are generally rich in phosphorous (P) and nitrogen (N). If we release the wastewater into the water without eliminating the phosphorous(P) and nitrogen(N), which 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.

The waste water is rich in phosphorous and nitrogen which are burning the environmental issue of the present world. Hence if we remove the nitrogen and phosphorous from the waste water through struvite crystallization, we can reduces the P and level in waste water, thus water will not reach the eutrophication. The phosphorous and nitrogen in the waste water 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 there 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. 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 affect on 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 denitrification, ammonia-stripping, electrochemical conversion, ion exchange, microwave irradiation and struvite precipitation. Struvite precipitate is one of the innovative physio-chemical process 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 interms of possible recovery of recyclable constituents from industrial effluents and domestic effluents which are rich in nutrients.

Phosphorous in waste water is one of the three forms, Phosphate(ortho phosphate),(O_4P_3), polyphosphate(PO_4) and organically bound phosphorous. Controlled reaction between phosphate, magnesium and ammonium ions provides sparingly soluble product called struvite($MgNH_4PO_4.6H_2O$) which can be utilize directly in agriculture as mineral fertilizer. The required dosage of Mg^{2+} salts($MgCl_2$, $MgSO_4$, $Mg(OH)_2$ etc..). The most common forms of nitrogen in waste waters and ammonia(NH_3), ammonium ion(NH^{4+}), nitrate(NO_3) and organic nitrogen.

The crystals forms alkaline condition according to the reaction shown below.

$$Mg^{2+}+NH_4^{+}+H_2PO_4^{-}+6H_2O \Longrightarrow MgNH_4PO.6H_2O + 2H^{+}$$

Struvite yield one of the most nutrifine fertilizer because it consist of Mg, N, and P as micro and macro nutrients for soil fertilities in addition it is a concentrated, granular, non-sludgy, non-odours and slow-release fertilizers and fairly valuable by product. Struvite can be effectively used as a slow rate are fertilizer at high application rate without a risk of damaging plants.

II. LITERATURE REVIEW

1. "Recovery of Nutrients from Wastewater by Struvite Crystallization"

Ajit Kumar, Ashutosh Das, Mukesh Goel, K. Ravi Kumar, B. Subramanyam and J.S. Sudarshan, Department of Civil Engineering, SRMUniversity, Kattankulathur, Kanchipuram, T. N.,India

They collected the wastewater from STP of SRM University campus. All the physico-chemical characteristics were determined on the day of experiment except BOD and COD. They were designed a Mixed Suspension Mixed Product Removal Batch Reactor (MSMPRBR) of 12 liters volume, 30% of $MgCl_2$ solution was added into reactor at the rate of 7.5mL/minute. The pH of mixed wastewater was increased with the help of Boyu aquatic animal air pump (U-9900) at the rate of 5 L/minute till solution attains its investigated pH. Two litres of 30%magnesium chloride solution was added into reactor at the rate of 7.5mL/minute. The rate of magnesium chloride mixing may be varied according to the concentration of $PO4^+$ and NH^+ in the sample. Then solution was seeded with 1 g of previously generated pure struvite as parent crystal. After 24 hours. The precipitate was filtered by Whatman filter paper No. 42 and filtrate was kept in desiccator for drying with interfering air for 12 hours. Finally, filtrate was air dried at room temperature. The struvite cluster aggregate on parent seed material and grow with sludge.

2. "Phosphorous Recovery through Struvite Crystallization: testing of parameters which enhance the recovery of Phosphorous"

Anastasiia Buchyanska, Faculty of Environmental Science and Technology Department of Environmental sciences (IMV) Norwegian University of Life Sciences (NMBU) Ås, Norway August 2017

She carried out the experiment on Phosphorus recovery through struvite precipitation. During the laboratory experiment several reagents and solutions were used. The waste water containing NH4 and PO4-P was taken from Wastewater Treatment Plant in Hamar. For struvite precipitation was added magnesium chloride hexahydrate ($MgCl_2*6H_20$, Merck) to a mixture of the wastewater. To adjust pH sodium hydroxide (2M NaOH) and hydrogen chloride (1M HCl) were used. To measure phosphates 1 mg/L phosphate stock solution, 1 M ascorbic acid and, 1M ammonium molybdate were used. To define metals and non- metal elements ultra-pure nitric acid (HNO_3) and ultra-pure hydrogen chloride (HCl) were used. The jar test was done for the precipitation formation. Two sources of wastewater from HIAS sewage plant were used for the experiments. One source contained NH4 and other PO4-P. Ammonium wastewater sample was taken from the reject water after biological treatment. Phosphorus wastewater sample was taken from a sludge after biological treatment. Concentrations of wastewater were measured both at HIAS and laboratory at NMBU. The results of measurements showed that the concentrations of rejected water and sludge water were 2262 mg/l of NH4 -N and 189 mg/l of PO4 -P respectively. To compare the concentrations of the total nitrogen and phosphorus in average in normal wastewater (NH4 -N of 8 to 10 mg/L, PO 4- P of 1 to 3 mg/L) the concentrations of the experimental wastewater is very high.

She concluded that the test reaction time less than 20 min. If the precipitation of struvite for less than 20 min will give satisfactory results for phosphorus recovery, this would be advantageous for the treatment plant. The decrease in the time reduces energy consumption, therefore reduces the cost of running treatment plants and negative impact on the environment. Increase the sample volume to recover more struvite and to analyze the precipitate for microbial content. This should be done to confirm the safety of struvite as a fertilizer.

3. "Separation of struvite from mineral fertilizer industry wastewater"

Andrzej Matyniaa, Boguslawa Wierzbowskaa, Nina Hutnika, Agata Mazienczuka, Anna Kozika, Krzysztof Piotrowskib, et al,

The experimental data was concerning the recovery of phosphate ions from the phosphorus mineral fertilizers industry wastewater by continuous reaction crystallization of sparingly soluble salt: magnesium ammonium phosphate hexahydrate – struvite $MgNH_4PO_4.6H_2O$. The DTM (Draft Tube Magma) type continuous crystallizer was used in the experiment. Working volumes of jet pump DTM crystallizers used in the presented research were: Vw 1.2, 15 and 36 dm3. The wastewater collected from one of polish 3 phosphorous mineral fertilizer industry plants. Concentration of PO4 in the wastewater was 0.445 mass %. The pH was increased to 9 to 11 with 5 mass % of NaOH. The Magnesium Chloride hexahydrate- $MgCl_2.6H_2O$ and ammonium chloride NH_4Cl were introduced into the mixer and the continuous crystallization was done in 298K temperature under atmospheric pressure. Its effective in extracting the sparingly soluble Magnesium Ammonium Phosphate (MAP)- $MgNH_4PO_4.6H_2O$ with the crystal size of 26μm at pH 9 in 3600 seconds in Volume of 12 dm^3. Moreover, in the crystallizers of Vw 15 and 36 dm3 further, 2-time elongation of this time from 3600 to 7200 s caused increase in Lm by the next 10–12% (up to 29.6 μm-36.2μm). The size of the crystals were identified using Scanning Electron Microscope (SEM).

4. "Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by MAP precipitation as a slow release fertilizer"

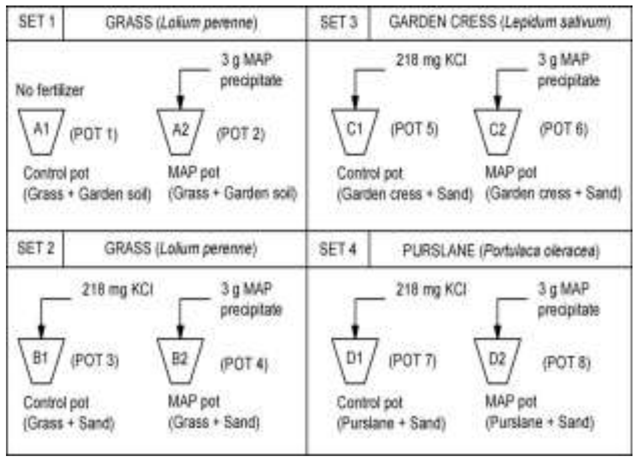
Kaan Yetilmezsoy, Zehra Sapci-Zengin , Department of Environmental Engineering, Yildiz Technical University, 34349 Yildiz, Besiktas, Istanbul, Turkey .

They investigated the Magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4·6H_2O$, MAP) precipitation on up- flow anaerobic sludge blanket (UASB) pretreated poultry manure wastewater in a lab-scale. All the physico-chemical tests were done for the UASB effluent, 400 ml of UASB sample was taken in 500 ml beaker and they added $MgCl_2$ and KH_2PO_4 and stirred for 15 minutes and kept it for 2 days for the crystal formation. The MAP precipitation help to remove 85.4% of NH_4^+–N from the UASB effluent, but also achieved.

In the final step, the fertility of the MAP precipitate as struvite was tested on the growth of three test plants including purslane (Portulaca oleracea), garden cress (Lepidum sativum) and grass (Lolium perenne). Results of agricultural experiments clearly indicated that the addition of struvite as a slow fertilizer significantly increased both fresh and dry weights of the test plants depending on their species and growing media in the ranges of 28–257% and 60–402%, respectively. Furthermore, rates of increase in fresh heights of test plants were found in the range of 18–156% for MAP sludge as compared with control.

5. "Production of nutrients from the Wastewater and used as Fertlizer" Munch and bar et al, 2008; Ryu et al,2008 carried out the experiment on production of MAP from wastewater from Bolivar wastewater treatment plant. The wastewater is of 40% industrial and 60% municipal 2+ maximum removal efficiencies of about 54% for total COD and about 50% for biologically recalcitrant color with the addition of $MgCl_2·6H_2O+KH_2PO_4$ at the stoichiometric ratio. With the proposed experimental conditions of the present investigation (pH = 9.0, $Mg^{2+}:NH^+_4-PO_4^{3-}$P=1:1:1

$MgCl_2.6H_2O$ + KH_2PO_4) the anaerobically pretreated effluent having an average NH_4^+–N concentration of 1318 mg/L was reduced to about 192mg/L by MAP precipitation.



wastewater which is rich in ammonium and less poor in Mg and PO_4^{3+}. Magnesium chloride solution was added as Mg source and 1N NaOH and 1N HCl were used to maintain pH from 8.5-9.2 and 1L flask , 1L beaker and glass stirring stick were used in the experiment. Within 40 minute of reaction time Ammonium – nitrogen and Phosphorous were removal efficiencies reached 92% and 75%. The size of the crystals were determined by X-ray Diffraction and Scanning Electron Microscope (SEM).

6. "Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant"

Nathan O. Nelson , Robert L. Mikkelsen, Dean L.

Hesterberg

They carried the experiment to remove the phosphorous from Anaerobic swine lagoon liquid collected from two active farms in North Carolina (designated LW, and RM). After collection, the effluent was stored at 4^{o} C for 24 h in a 30 L glass carboy, allowing any solids that were disturbed in the collection process to settle. Following the 24-h settling period, effluent was siphoned off the top of the container, transferred into 2.5-L glass containers, and stored at 4^{o} C until use. The Mg:P ratio was initially adjusted by adding the appropriate quantity of $MgCl_2.6H_2O$ to 2L of effluent and mixing for 10 min to dissolve.

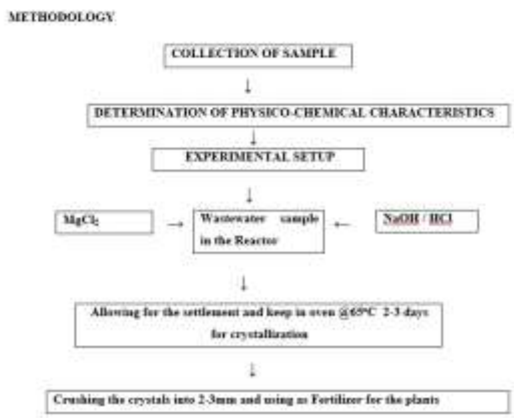
The effluent pH in each beaker was adjusted with 1.0 M NaOH,creat ing a pH range of 7.5–9.5 and 7.75–9.5 for the LW1 and RM effluents respectively. The beakers were covered with parafilm to reduce NH_3 volatilization. After a 24-h quiescent equilibration period at 25^{o} C, a 20-ml aliquot of effluent was pipetted from each beaker at 2 cm below the surface for PO_4^- -P and Mg_2^+ analysis.

Struvite formation reduced PO_4^- - P concentration of the two studied effluents by 91% and 96%, for LW and RM sample.

III. OBJECTIVES

- The main objective of the project is to recover the Phosphorous and Ammonium from the Wastewater which is the essential nutrient for the plant growth and animal growth and to reduce the consumption of Rock Phosphorous.
- To remove the Phosphorous and Ammonium from the Wastewater before it discharges into the waterbody and thus reducing algal bloom growth in waterbody which turns the water into eutrophication.
- To determine the optimum dosage of Magnesium Chloride in the struvite crystallization process.

IV. METHODOLOGY



V. MATERIALS

1. Waste Water / Effluent

The waste water sample (rejected water) will be collected from any of the Domestic Wastewater Treatment Plant after the screening and Industrial Wastewater Treatment Plant (any industries which is rich in Phosphorous and Ammonium content).

The sample Will be collected from the lake which is already in Eutrofication (Bellandur Lake, Bengaluru) and from the sewage water of arkavathi river (which flows near Kengeri).

2. Magnesium Chloride ($MgCl_2$)

Magnesium Chloride will be used as a source to recover the Phosphorous and Ammonium from the wastewater as Struvite Crystals.

$$Mg^{2+} + NH_4^{+} + H_2PO_4^{-} + 6H_2O \Longrightarrow MgNH_4PO.6H_2O + 2H^{+}$$

3. Sodium Hydroxide (NaOH)

Sodium Hydroxide will be used to increase the pH to the range 8.5 to 9.3

4. Hydrochloric Acid (HCL) or Sulphuric Acid (H_2SO_4) Hydrochloric Acid or Sulphuric Acid used to decrease the pH to the range of 8.5 to 9.3

5. Reactor for Crystallization

The reactor is required for the crystallization process. The required reactor with blades will be designed for the process.

6. pH Meter

pH meter will be kept in the reactor to maintain the pH in the range of 8.5 to 9.3

VI. JUSTIFICATION

Waterbodies in the urban areas like Bengaluru, Mumbai, Delhi, Chennai etc., are polluted because of discharging the domestic wastewater and industrial effluent to them. The wastewater is very much rich in Phosphorous and Nitrogen which causes eutrophication in the waterbodies. Hence that Phosphorous and Nitrogen should be removed from the effluent before it discharges into the waterbody. That can be done through the Struvite Crystallization. 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 mean time we can also reduce the consumption Rock Phosphorous which is costlier than Struvite Crystal fertilizer.

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