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A Review on Removal and Recovery of Phosphorus and Nitrogen from Domestic Wastewater by Struvite Crystallization

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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. The growth of uncontrolled Struvite increases pumping and maintenance cost, as well as reduces the overall capacity of the plant piping system. Since domestic wastewater is recognized as nutrient rich water, the recovery of nutrients using a crystallization technique may provide value added product called Struvite, which is a slow releasing fertilizer. Struvite precipitation occurs in an equimolecular concentration of Mg^{2+}, NH_4^+ and PO_4^{3-} at slightly alkaline conditions. Addition of a source of Mg is essential to maintain the favorable condition of PO_4 and Mg.**

Keywords: **Wastewater; Phosphorus; Struvite; Magnesium; Ammonical nitrogen Eco-friendly fertilizer.**

1. INTRODUCTION

Struvite precipitation is one the innovative physico-chemical processes which can majorly contribute for the removal of ammonia and phosphorus 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 (Sh. El Rafie et al., 2013).. Insufficient and improper treatment facilities of these effluents cause serious soil and water pollution, including eutrophication in the surrounding areas. Phosphorus and nitrogen enhance the growth of algal blooms in the water bodies (rivers, lakes and seas) worldwide, which reduce light penetration and available oxygen in the water bodies. Thus, eutrophication leads to aquatic death all over the world.

Phosphorus in wastewater is in one of the three forms, phosphate (also called orthophosphate), polyphosphate and organically bound phosphorus. Controlled reaction between phosphate, magnesium and ammonium ions provides sparingly soluble product called struvite ($MgNH_4PO_4.6H_2O$) which can be utilized directly in agriculture as a valuable mineral fertilizer. The required dosage of Mg^2+ salts ($MgCl_2$, $MgSO_4$, $Mg(OH)_2$, etc.) is undoubtedly the most significant operational expenses (OPEX) component associated with this approach, estimated to contribute up to 75% of the overall production costs (Lahav et al., 2013). The most common forms of nitrogen in wastewaters are ammonia (NH_3), ammonium ion (NH_4^+), nitrite (NO_2), nitrate (NO_3) and organic nitrogen.

Struvite yield one of the most nutritive fertilizers because it consists of Mg, N and P as micro and macro nutrients for soil fertilities, in addition it is a concentrated, granular, non-sludgy, non-odorous, and slow-release fertilizer and fairly valuable by-product. Struvite can be effectively used as a slow release fertilizer at high application rate without a risk of damaging plants. Suggested uses are diverse and include ornamental plants, young trees in forest, grass, orchards and potted plants (Sh. El Rafie et al., 2013).

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2. FACTORS INFLUENCING STRUVITE FORMATION

Predicting and controlling nucleation and crystal growth is all the more complex as it depends on a combination of factors such as the initial crystal states of the compounds, phenomena of matter transfer between solid and liquid phases, thermodynamics and kinetics of reaction, as well as several physic chemical parameters including: pH, supersaturation level, mixing, energy, temperature and the presence of foreign ions in the precipitating solution.

A. pH:

pH plays a vital role in struvite precipitation. The pH of dairy wastewater was found in the range of 6.035 ± 0.065 which was increased up to the pH 9.2 with the help of NaOH solution and it was observed that when the precipitation started, the pH of the solution decreases in the range of 8.74 - 8.98, fig 1., (Krishan A et al.,). MAP complex process is pH sensitive method. A complex becomes insoluble at pH above 8.5 and hence accurate control of pH has to be shown in precipitation operating conditions (Rafie Sh El et al.,).

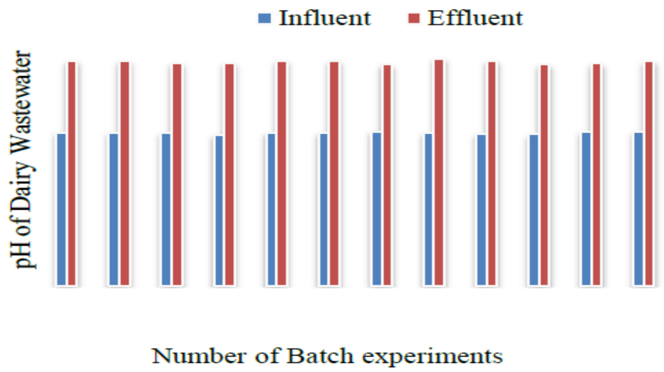

Fig 1. Impact of struvite precipitation on the pH of dairy wastewater. (Krishan A et al.,)

B. Temperature:

Kozik et al (2012) carried out in a DT MSMPR type crystallizer in 298 K with the Struvite crystals of mean size from ca. 23 to ca. 86 μm, of diverse homogeneity (CV 62 – 90%) were produced. As the solubility product is linked to the super-saturation state of the solution in which crystals may occur, the precipitation of Struvite is more difficult to obtain at high temperatures. Boistelle et al. (1983) effectively noticed a change between Struvite crystals obtained at 25º C and crystals obtained at 37º C. While at 25º C Struvite crystal were found “rectangular and prismatic”, at 37º C they were mainly “square and thick”. They also indicated that for high magnesium concentrations, high temperature could affect the nature of crystal formed, with for example Struvite transforming faster into newberyite ($MgHPO_4 \cdot 3H_2O$) than at lower temperature.

C. Aeration rate:

Yetilmezsoy and Zengin (2009) stated that a sufficient aeration time should be provided to achieve high removal efficiencies. They obtained about 93.4% NH_4-N removal with an aeration rate of 0.6 L min^{-1} within a period of 24 h. They also found the highest NH_4-N removal (95.3%) in 12 h reaction time with an aeration rate of 10 L min^{-1}. Lei et al. (2006) found about 60.2% ammonia removal with an aeration rate of 0.6 L min^{-1} in a reaction time of four hours. On the contrary, they achieved the same removal efficiency without aeration in a period of 24 h. He found that Struvite formation is proportional to the aeration rate and reached a plateau at around 0.73 L /min.

D. Fertilizer quality of Struvite:

Lim et al., (2012) showed that, Struvite might be considered as a main problem occurring in wastewater treatment plants, but it can be used in the production of fertilizers and soil conditioners. There is a significant demand for phosphorus as a fertilizer for agricultural purposes due to its slow release properties. If phosphorus recovery happens in form of Struvite, it can be used as a slow-release fertilizer which will not leach like conventional fertilizers. He studied the performance of Struvite as a fertilizer in comparison to other commercial fertilizers, and found that Struvite fertilizers were more effective in the growth of Chinese cabbage due to high levels of phosphorus, potassium, nitrogen, and magnesium. Fattah et al.,

(2008) explained the benefits of Struvite as heavy metals which are regulated in fertilizers for agricultural purposes. He showed that Struvite formation at certain conditions could be free of a wide range of heavy metals and other heavy metals which precipitated were much lower than the regulatory limits.

3. METHODOLOGY

Kozik A et al., conducted a laboratory experiment in a DT MSMPR (Draft Tube, Mixed Suspension Mixed Product Removal) type crystallizer in 298 K with molar ratio of 1:1:1. Magnesium chloride was taken as Mg source and concluded that Increase in pH from 8.5 to 10 resulted in decrease of crystal mean size from 37.9 to 23.2 µm and from 86.4 to 51.0 µm for elongation time 900 and 3600s, respectively. The Crystals produced at pH 10 lowers the mean sizes.

Sh. El Rafie et al., experimented on a samples from Chemical fertilizer industry`s streams. NaOH solution (1N) is used to adjust effluent streams pH to the required value Liquid bittern (LB) was added as low cost magnesium source, containing 73% magnesium. Struvite formation was later verified by analyzing the morphology and composition employing scanning electron microscope (SEM) and Xray Diffraction (XRD), respectively. The ammonia removal was observed about 50% to 80%. The yield of struvite was 0.5g/L to 1.15 g/L.

Kumar A et al., studied by taking a mixed wastewater sample from sewage treatment plant of SRM University. A Mixed Suspension Mixed Product Removal Batch Reactor (MSMPRBR) was used in his study. The pH of sample was increased with the help of Boyu aquatic animal air pump .Magnesium chloride is used as a magnesium source. He concluded that the pH of the wastewater sample was decreased after precipitation. An average of around 77% of BOD was removed after crystallization. The percentage of phosphate and ammonia removal was about 83% and 16% respectively.

Lahav O et al., used laboratory fluidized-bed struvite precipitation reactor by taking domestic wastewater and Using seawater NF brine as a magnesium source. P removal was higher than 90% and the struvite purity obtained was very high (95%), as demonstrated by both dissolution experiments and XRD analyses. The cost of magnesium production using the NF separation method was estimated to be less than 50% of the cost of magnesium chemicals, provided that the WWTP is located close to the sea.

Huang H et al., carried out experiment on simulated swine wastewater using modified zeolite at pH 8.5. The natural zeolite was modified by magnesium salts as the adsorbent material for ammonia–nitrogen. Results showed much better efficiencies of ammonia–nitrogen and phosphate removal than those by natural zeolite at the same pH. When the reaction condition was controlled at 110 g/L of modified zeolite at 40 min of reaction time, the ammonia–nitrogen and phosphate-removal efficiencies reached 82% and 98%, respectively.

Krishan A et al., experimented on a nutrient rich dairy wastewater in a Struvite Fed Batch Reactor. 30% of magnesium chloride solution was added as an Mg source and concluded that the concentration of total solid, total dissolved solids, total hardness and magnesium hardness were increased after the treatment but the concentration of calcium hardness was decreased. It was observed that the efficiency of BOD, COD, Phosphate and Ammonia removal was 66%, 87%, 93 % and 89% respectively. Application of struvite precipitation method will save the nutrients and reduce environmental pollution.

Fig; 2 Continuous DT MSMPR crystallizer unit with internal circulation of suspension. (Kozik A 2012)

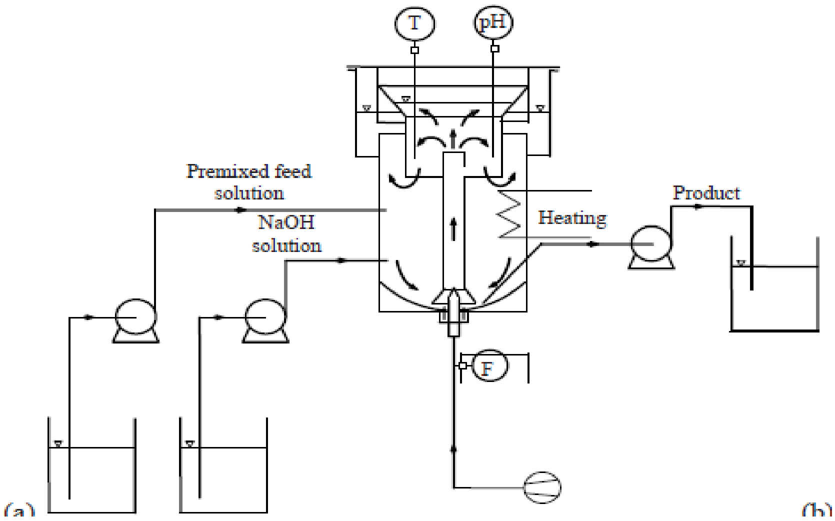

Fig: 3 Scheme of laboratory stand with gas–liquid jet pump DTM MSMPR.(Piotrowski K 2013)

4. 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 stoichiometric molar ratio of Mg^{2+}: NH_4^+-N: PO_4^{2-} was 1:1:1 which was sufficient for ammonia removal by 80%. The hazardous elements in wastewaters (mainly NH_4 and PO_4) might be converted to a valuable resource through this process. Struvite crystallization process is an effective eco-friendly process and is a slow-release valuable fertilizer that reduces the cost of production in agriculture. Production of Struvite from wastewaters will reduce the hazard of eutrophication in the water bodies by removing N and P.

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