



Recovery of Nutrients from Wastewater by Struvite Crystallization

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ABSTRACT

Discharge of untreated domestic wastewater often leads to eutrophication of receiving water body and create a septic condition, and accelerate sewage sickness in case of land-disposal. However, since domestic wastewater is recognized as nutrient rich water, the recovery of nutrients using a chemical precipitation and crystallization technique may provide value added product struvite, which is a slow releasing fertilizer. This research work shows the techno-feasibility struvite precipitation as an attempt for improving water quality, with simultaneous recovery of struvite as byproduct.

INTRODUCTION

In recent years, struvite has emerged as the most promising compound for recovery from wastewater plants. Struvite is a crystalline deposit and its chemical formula is $MgNH_4PO_4 \cdot 6H_2O$. It is slightly soluble in water and dehydrates in dry warm air. Numerous literature reports show the recovery of nutrients (especially nitrogen and phosphorous) from wastewaters in the form of struvite through anaerobic digestion (Battistoni et al. 2000, Nelson et al. 2003, Demiere et al. 2005, Ali 2007, Demirel & Othman 2009).

Nitrogen is an essential nutrient for plants and animals. The major contributors of nitrogen to wastewaters are human activities such as food preparation, showering, and waste excretion. The per capita contribution of nitrogen in domestic wastewater is about 1/5th of that for BOD. Total nitrogen in domestic wastewater typically ranges from 20 to 70 mg/L for low to high strength wastewater (Crites & Tchobanoglous 1998). Factors affecting concentration include the extent of infiltration and the presence of industries. Influent concentration varies during the day and can vary significantly during rainfall events, as a result of inflow and infiltration to the collection system. 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. Nitrogen in domestic wastewater consists of approximately 60 to 70 percent ammonia nitrogen and 30 to 40 percent organic nitrogen (Crites & Tchobanoglous 1998). Most of the ammonia nitrogen is derived from urea, which breaks down rapidly to ammonia in wastewater influent.

Total phosphorus (TP) in domestic wastewater typically

ranges between 4 and 8 mg/L but can be higher depending on industrial sources, water conservation, or whether a detergent ban is in place. Phosphorus is used in fertilizers, detergents and cleaning agents, and is present in human and animal waste. Phosphorus in wastewater is in one of the three forms, phosphate (also called orthophosphate) polyphosphate and organically bound phosphorus.

The major complexes and free ions present in struvite system are $MgOH^+$, $MgH_2PO_4^+$, $MgHPO_4$, $MgPO_4^-$, H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} , NH_3 , NH_4^+ , Mg^{2+} and PO_4^{3-} . The thermodynamic modelling response confirms that struvite precipitation commences in a supersaturated solution and supersaturation is a function of solution concentration (total magnesium, ammonium and phosphate) and pH value (Ali 2007). Precipitation of struvite is affected by several factors, such as pH, concentrations of Mg^{2+} , PO_4^{3-} and NH_4^+ , and the presence of other interfering ions, such as calcium (Ca^{2+}) (Demirel et al. 2005). It is highly pH dependent as activities of both NH_4^+ and PO_4^{3-} are affected by solution pH (Nelson et al. 2003). It has been well documented that pH for struvite precipitation is 8.0-10.7 (Oblinger et al. 1998). This optimum pH range is related to PO_4^{3-} solubility and the presence of N as NH_4^+ in solution. High NH_4^+ concentration enhances struvite precipitation and has the extra advantage of pH buffering in solution (Nelson et al. 2003). This work studies the recovery of struvite from domestic wastewater and impact of struvite precipitation on different water quality parameters.

MATERIALS AND METHODS

Table 1 gives the characteristics of the wastewater.

Design of batch reactor: A Mixed Suspension Mixed

Table 1: Mixed wastewater characteristics.

S.No.	Parameters	Values
1	pH	6.55
2	TDS (mg/L)	960
3	TS (mg/L)	12,484
4	COD (mg/L)	988.0
5	BOD (mg/L)	346.0
6	Total hardness (mg CaCO ₃ /L)	540.0
7	Calcium hardness (mg CaCO ₃ /L)	336.0
8	Magnesium hardness (mg CaCO ₃ /L)	204.0
9	Calcium ion (mg/L)	134.66
10	Magnesium ion (mg/L)	49.57
11	Available phosphate (mg/L)	21.79
12	Ammonical nitrogen (mg/L)	48.89

Table 2: Design criteria for holding tank and aeration tank.

<i>Design criteria for holding tank</i>	<i>Dimensions</i>
Diameter of reactor	200 mm
Height of cylindrical reactor	250 mm
Height conical part of reactor	100 mm
<i>Design criteria for aeration tank</i>	<i>Dimensions</i>
Diameter of aeration tank	100 mm
Height of aeration tank	200 mm

Product Removal Batch Reactor (MSMPRBR) of 12 liters volume, made of clear perspex was used in this study. The shape of reactor was cylindrical with conical base. 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 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 33 rpm, and it can be removed later from the reactor. Due to vibration, mixing was done as a first step and it was achieved by aeration pump of capacity 5 litre/minute. A schematic sketch of Mixed Suspension Mixed Product Removal Batch Reactor (MSMPRBR) is shown in Fig. 1.

Sampling of mixed wastewater for struvite crystallization: Grab samples of mixed wastewater were taken just after screening from sewage treatment plant of SRM University. The samples were taken in plastic cans of 10 litres capacity. The can was thoroughly rinsed twice with raw sample. The sample has to be taken every day before 4 hours of experiment start. The pH and total dissolved solid were determined at the sampling spot with the help of pH meter and TDS meter. Remaining other physico-chemical characteristics were analysed in lab within 2-4 hours of sampling except BOD. Experiments were started after characterization of the wastewater.



Fig. 1: Reactor setup.

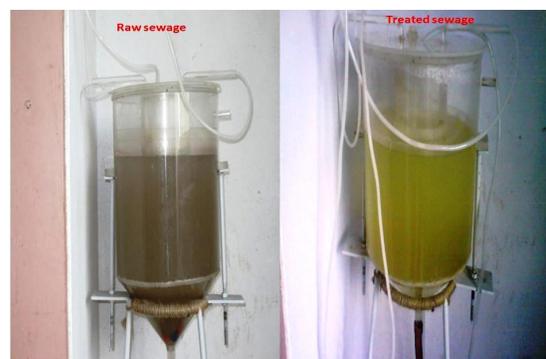


Fig. 2: Raw and treated mixed wastewater.



Fig. 3: Struvite crystal formed over the sludge of mixed wastewater with parent seed.

Crystallization of struvite with mixed wastewater: The MSMPRBR was cleaned with diluted HCl solution and washed with deionized water. The reactor was allowed for drying at room temperature (25°C). After cleaning the reac-

tor, it was filled with 8 liters of mixed wastewater. The pH of mixed wastewater was increased with the help of Boyu aquatic animal air pump (U-9900) at 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 7.5 mL/minute. The rate of magnesium chloride mixing may be varied according to the concentration of PO_4^{+} and NH_4^{+} in the sample. Then solution was seeded with 1 g of previously generated pure struvite as parent crystal. The mixing of solution was done by air pump itself till whole solution of magnesium chloride was finally added into the artificial wastewater; precipitate was formed at very low rate. The HRT of reactor was maintained about 5 hours. After 5 hours air stripping and addition of magnesium chloride solution was stopped and whole solution was kept for 24 hours for formation of precipitate in the reactor bottom. 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 which was finally separated by hand picking or by sieving with less than 45-63 μm ASTM standard sieves. Sludge was sieved by this sieve resulting in the struvite crystals (Figs. 2 and 3).

RESULTS AND DISCUSSION

Impact of struvite precipitation on the pH: The raw mixed wastewater pH was found in the range of 6.3-6.67. pH of the wastewater was increased with the help of aeration till the pH of solution attained 9.2. After that 1.5 liters of 30% magnesium chloride solution was mixed with solution. It was observed that when precipitation started, the pH of the solution decreases from its original pH 9.2. It was in the range of 8.72 to 8.90. The impact of precipitation on the pH is shown in Fig. 4.

Impact of struvite precipitation on the total dissolved solids (TDS): In the raw mixed wastewater, the concentration of TDS was found in the range of 960 -1130 mg/L. After the addition of 30% magnesium chloride, it was observed that the concentration of TDS value of the solution was sharply increased in the range of 4323-4467 mg/L. This shows that most of the MgCl_2 ended up in TDS, thus resulting in less than 100% recovery of magnesium chloride through struvite precipitation. The impact of precipitation is shown in Fig. 5.

Impact of struvite precipitation on the total solids (TS): In raw mixed wastewater, the concentration of total solid was found in the range of 12484-14000 mg/L. After the precipitation of struvite with sludge it was observed that the TS value of the solution was sharply decreased whereas the TDS

of solution was increased. This shows that the maximum amount of colloidal particles which were present in wastewater settled down with the struvite. After settlement of all the suspended material of the bottom of reactor, the solution gets very clear. The impact of struvite precipitation on total solids has been shown in Fig. 6. An average of around 37 % total solids was removed by this experiment.

Impact of struvite precipitation on the BOD and COD

concentration: The BOD of the raw mixed wastewater was in the range of 325 ± 9.6 mg/L. After the treatment, BOD of the solution sharply decreased and reached in the range of 74 ± 6.53 mg/L. The raw mixed wastewater itself contains large number of aerobic bacteria; during the aeration oxygen was also dissolved in the solution along with carbon dioxide. Due to high concentration of oxygen in the solution, the bacterial growth enhanced consuming the organic matter as food materials. Therefore, a sharp decline was observed in BOD concentration. As a result of decomposition the organically bound phosphate and ammonia were released in the solution and they are ready to participate in struvite precipitation. The impact of struvite precipitation on the BOD concentration is shown in Fig. 7. An average of around 77% of BOD was removed by this experiment. Similar reasons could be ascribed for COD reduction. The COD of the raw mixed wastewater was in the range of 928-1016 mg/L. After the treatment, COD of the solution got sharply declined in the range of 176-204 mg/L.

Impact of struvite precipitation on the concentration of

phosphate: The concentration of phosphate in the raw wastewater was in the range of 22.22 ± 0.3589 mg/L. After the precipitation of struvite, it was observed that the concentration of phosphate declined sharply in the range of 0.896 ± 0.234 mg/L. About 95% of phosphate was recovered in the form of various compounds of phosphate along with struvite. The impact of struvite precipitation on the concentration phosphate is shown in Fig. 8.

Impact of struvite precipitation on the concentration of

ammonia: The concentration of ammonia was found to be in the range of 48.53 ± 0.4 mg/L in the raw wastewater. After the precipitation of struvite, it was observed that the concentration of ammonia declined sharply in the range of 4.211 ± 0.056 mg/L. About 91% of ammonia was recovered in the form of various compounds of phosphorus along with struvite. The impact of struvite precipitation on the concentration of phosphate is shown in Fig. 9.

CONCLUSIONS

A 12 litres capacity mixed suspension mixed product removal batch reactor (MSMPRBR) was designed to perform the experiment. Based on the preliminary experimental

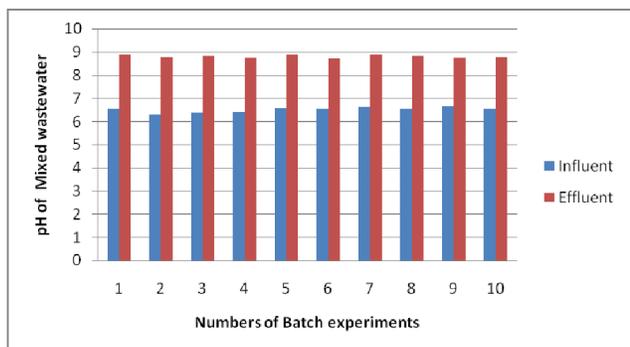


Fig. 4: Impact of struvite precipitation on the pH of mixed wastewater.

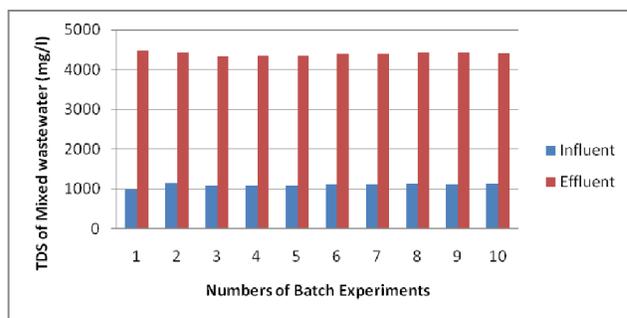


Fig. 5: Impact of struvite precipitation on TDS of mixed wastewater.

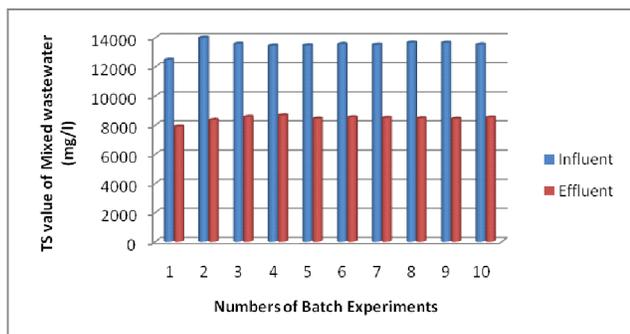


Fig. 6: Impact of struvite precipitation on TS of mixed wastewater.

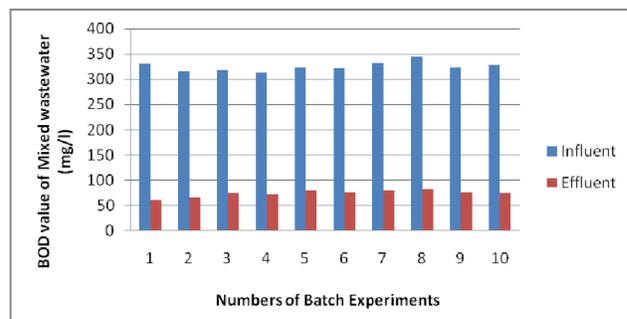


Fig. 7: Impact of struvite precipitation on the BOD of mixed wastewater.

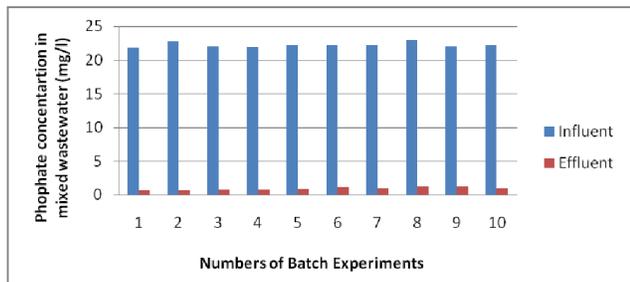


Fig. 8: Impact of struvite precipitation on the concentration of phosphate of mixed wastewater.

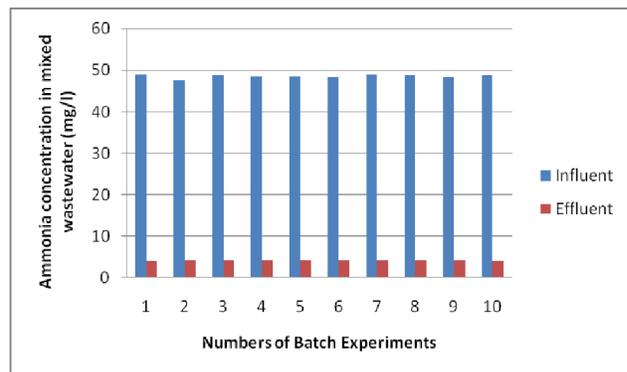


Fig. 9: Impact of struvite precipitation on the concentration of ammonia of mixed wastewater.

observations, the following conclusions can be drawn.

1. Struvite precipitation leads to pH increase in all the cases.
2. The concentration of total solids was decreased after the treatment whereas the concentration of total dissolved solids were increased.
3. Both, the BOD and COD showed remarkable decrease as a consequence of struvite precipitation.
4. The percentage of phosphate and ammonia removal was investigated and 83% phosphate and 16% ammonia was removed from the solution in the form of different complexes along with struvite.

REFERENCES

Ali, M.I. 2007. Struvite crystallization in fed-batch pilot scale and description of solution chemistry of struvite. *Chemical Engineering Research and Design*, 85(A3): 344-356.

Battistoni, P. Pavan, P. Prisciandaro, M. and Cecchi F. 2000. Struvite crystallization: A feasible and reliable way to fix phosphorus in anaerobic supernatant. *Water Research*, 34: 3033-3041.

Crites, R.W. and Tchobanoglous, G. 1998. *Small and Decentralized Wastewater Management Systems*. McGraw Hill.

Demirer, S.U. Demirer, G.N. and Chen, S. 2005. Ammonia removal from anaerobic digested dairy manure by struvite precipitation. *Process Biochem.*, 40: 3667-3674.

Demirer, S.U. and Othman, M. 2009., Removal of ammonia and phosphate from supernatant of anaerobically digested waste activated sludge by chemical precipitation. *Bioresource Technology*, 100: 3236-3244.

Nelson N.O., Mikkelsen, R.L and Hesterberg D.L. 2003. Struvite precipitation in anaerobic swine lagoon liquid: Effect of pH and Mg:P ratio and determination of rate constant. *Bioresource Technology*, 89: 229-236.

Ohlinger, K., Young, T. and Schroeder, E. 1998. Predicting struvite formation in digestion. *Water Research*, 32(12): 3607-3614.