Recovery of Nutrients from Dairy Wastewater by Struvite Crystallization

Amit Krishan[1], Ankita Srivastava[2]

[1]Assistant Professor, Department of Civil Engineering,

G. L. Bajaj Institute of Technology & Management, Greater Noida-201308 (UP), India

[2]Assistant Professor, Department of Civil Engineering,

Accurate Institute of Management & Technology, Greater Noida-201308 (UP), India

E-mail: krishan001amit@gmail.com,

Contact Number: +91-8595010856

Abstract— Discharge of untreated nutrient rich dairy industry wastewater is a problematic issue, which may cause pollution and eutrophication of receiving water. The recovery of nutrients using a chemical precipitation and crystallization technique will provide value added product struvite (MgNH4PO4.6H2O), known as magnesium ammonium phosphate hexahydrate, a slow releasing fertilizer from dairy wastewater. 20 liters capacity Struvite Fed Batch Reactor was designed to perform the experiment. In this study the characteristic of dairy wastewater was analyzed to assess the recovery potential of method and percentage of reduction in pollutant concentration. 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.

Keywords — Dairy wastewater, nutrient, struvite, precipitation, crystallization, crystal, recovery

1. INTRODUCTION

A great increase in the number of industries in India has led to the production of a large volume of complex wastes. Numerous works have been carried out on the assessment of freshwater pollution by the discharge of effluent from the industries [1]. Dairy industry is noted as one of the significant contributor to water pollution. The generation of wastewater due to washing of equipment, milk spillage, other milk products waste, wash-down of yard area contains urine and manure, detergents, spilled milk. Dairy waste is basically biodegradable, produces an undesirable odour and contains an appreciable quantity of oil and can have adverse effect on environment due to high Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS) and nutrients such as phosphorus and nitrogen.

The key source of nitrogen in milk or milk products is in the form of casein and whey proteins. Typically, milk with 3.7% fat would contain about 3.15% protein and about 295 mg/l of non-protein nitrogen [2]. Fresh raw milk would normally contain about 3-8 mg/l of ammonia nitrogen and no measurable nitrate [3]. It was reported that typical wastewater from dairy processing plants contains 15-180 mg of nitrogen/l with an average of 76 mg/l [4]. Raw wastewater from dairy facilities has a typical BOD of 2,500 mg/l. At a nitrogen concentration of 50 mg/l, the BOD to N ratio would be 50:1.The most common forms of nitrogen in wastewater are ammonia (NH_3), ammonium ion (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) and organic nitrogen. Phosphorus in wastewater is in one of three forms as phosphate (also called orthophosphate) polyphosphate, or organically bound phosphorus. One of the major problems caused by discharging biochemically treated wastewater effluents into lakes and streams is the eutrophication of these waters. This eutrophication is generally attributed to the discharge of fertilizing elements such as phosphorus and nitrogen. The impacts of excess nutrients on water quality have been well documented [5, 6, 7, 8]. The removal of phosphorus and nitrogen from dairy industry effluents appears to be a practical way of limiting algal blooms in the receiving waters. The removal of these elements by biochemical or chemical means appears to be feasible. Various laboratory and field studies have shown that the biochemical wastewater treatment processes can be modified such that significant removal of nitrogen and/or phosphorus can be attained [9, 10].

In recent years, struvite has emerged as the most promising compound for recovery of nutrient (especially nitrogen and phosphorous) from wastewater plants. Struvite ($MgNH_4PO_4.6H_2O$) is a white crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentration. It is a valuable slow-release fertilizer, the production of which could offset much of the cost of chemical treatment [11]. The basic chemical reaction to form struvite has been expressed as equation $Mg_2^+ + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O$ with $pK_s = 12.6$ at 25^oC [12, 13]. The precipitation of struvite is affected by several factors, namely the pH, the chemical composition of the wastewater (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 [14, 15]. Numerous literature reports show the recovery of nutrients from wastewaters in the form of struvite through anaerobic digestion [16, 17, 18, 19, 20].

The objective of this study is the recovery of nutrients based on the precipitation ability of struvite. In this study, the precipitation of struvite is investigated with the purpose to reduce harmful effects on the environment and retrieve nutrients.

2. MATERIALS AND METHODS

2.1 Characteristics of Dairy Wastewater

The concentrations of important constituent in a dairy wastewater sample are shown in Table 1.

Table 1—Characteristics of dairy wastewater

Constituent	Concentration
pH	6.035 ± 0.065
Ammonia	69.96 ± 1.16 mg/l
Phosphate	45.05 ± 0.45 mg/l
TDS	756.5 ± 35.5 mg/l
Total Solids	938 ± 60 mg/l
BOD	216.17 ± 4.17 mg/l
COD	890 ± 14 mg/l
Total Hardness	501.5 ± 13.5 mg/l as CaCO3
Calcium Hardness	348 ± 10mg/l as CaCO3
Magnesium Hardness	156.5 ± 16.5 mg/l as CaCO3

2.2 Design of Fed Batch Reactor

A Struvite Fed Batch Reactor was designed with a capacity of 20 liters. The shape of reactor was cylindrical with conical base. It was divided into two distinct parts; the upper part which was rectangular cuboids and the lower part of reactor was rectangular pyramid. The pyramidal part of reactor act as settling zone. The bottom of the reactor contains tap for removal of sludge, crystals and wastewater. A submersible pump was provided for proper mixing of wastewater, $MgCl_2.6H_2O$ solution and NaOH solution in the reactor. The schematic sketch of Struvite Fed Batch Reactor is shown in Figure 1.

Design criteria for holding tank

Diameter of reactor	= 260 mm
Height of cylindrical part of reactor	= 350 mm
Height of conical part of reactor	= 100 mm
HRT of holding tank	= 24 hr

2.3 Crystallization of struvite from Dairy Wastewater

Struvite crystallization from dairy wastewater using the Struvite Fed-Batch Reactor was performed in Chemistry Laboratory, Department of Chemistry, SRM University. About 12 batches of experiments were performed during February and March 2011.

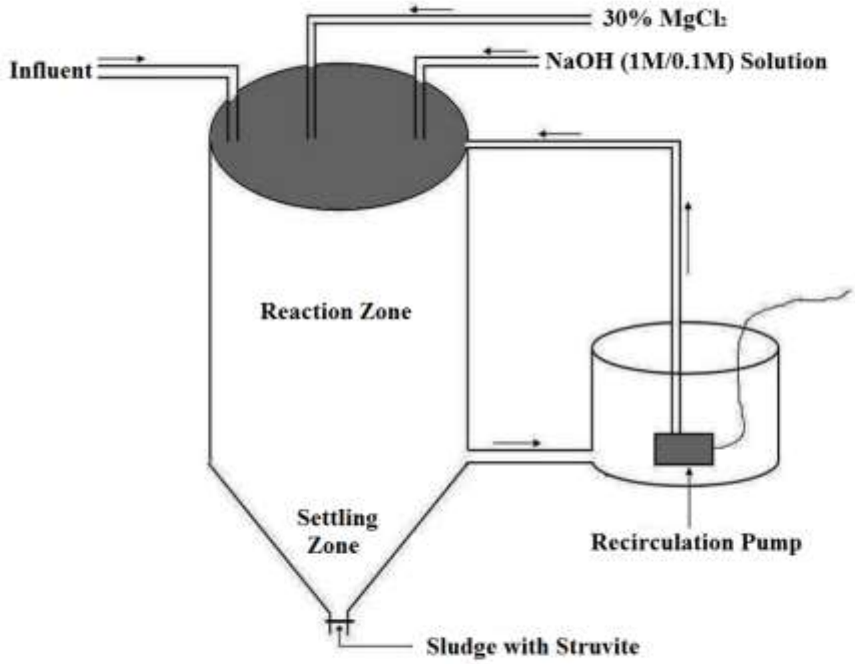

Figure 1. Schematic sketch of Struvite Fed Batch Reactor

The Struvite Fed Batch Reactor 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 reactor, it was filled with 14 liters of dairy wastewater. The pH of dairy wastewater was increased with the help of NaOH solution, 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 submersible pump till whole solution of magnesium chloride was finally added into the dairy wastewater and precipitate was formed at very low rate. The HRT of reactor was maintained about 5 hours. After 5 hours addition of NaOH and 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 45-63µm ASTM standard sieves. Sludge was sieved by this sieve resulting in the struvite crystals.

2.4 Sampling and Pre-treatment of Wastewater

Two wastewater samples were collected for analysis in each set of experiment, one sample from reactor input and another after the precipitation of struvite at reactor output. The samples were taken in plastic cane of 1 liter capacity labeled and stored in cool place (at 4^0C). All experimental analysis was done by using of standard guideline prescribed in 17th and 21st edition of APHA. Adequate amount of wastewater samples were taken for pre-treatment and mixed with the help of submersible pump for 10 minutes. The supernatant was used as sample for the analysis.

3. RESULTS AND DISCUSSION

3.1 Impact of pH on the struvite precipitation

pH plays a vital role in struvite precipitation. The experiment was to identify the optimum pH for struvite formation. 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. After that, 30% 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 8.74 - 8.98 from its original pH 9.2. The optimum pH range for struvite formation is 8.5 - 9.5 [21, 22].The impact of precipitation on the pH was shown in Figure 2.

3.2 Impact of Struvite Precipitation on the Ammonia and Phosphate concentration

Initially the concentration of ammonia and phosphate in the dairy wastewater was found in the range of 69.96 ± 1.16 mg/l and 45.05 ± 0.45 mg/l respectively, but after the precipitation of struvite it was observed that their concentration decline sharply in the range of 4.6 ± 0.5 mg/l and 4.76 ± 0.4 mg/l. About 89% ammonia and 93% of phosphate was recovered in the form of various compounds along with struvite. The impact of struvite precipitation on the concentration of ammonia and phosphate is shown in Figure 3 and 4.

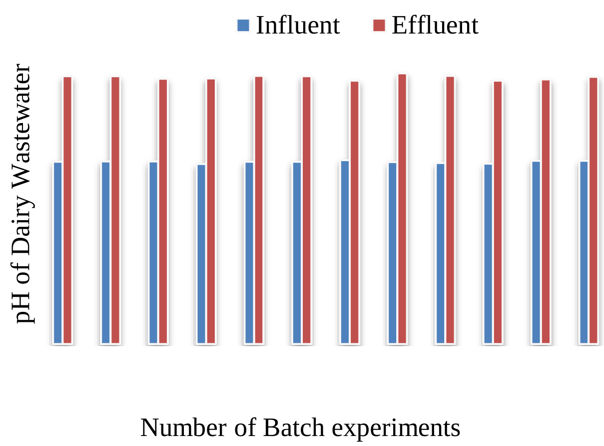

Figure 2.Impact of struvite precipitation on the pH of dairy wastewater.

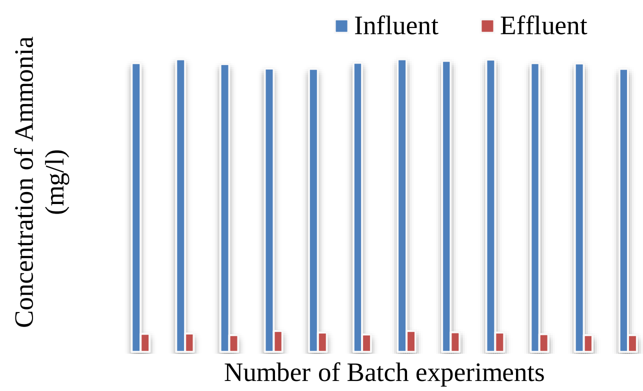

Figure 3.Impact of struvite precipitation on the concentration of ammonia of dairy wastewater

Metal salt precipitation is the most common approach for recovering nutrient from wastewater, which makes the precipitate unrecoverable for possible industrial processing into fertilizer [23, 24]. Nutrient recovery is possible, using existing technologies without metal salt precipitation from municipal wastewater [25, 26, 27, 28, 29]. It is economically feasible to recover 10%–80% of the nutrient flowing into wastewater treatment.

Recovering NH_4^+ is not only to recover the nutrients for agriculture purposes by forming the fertilizer as struvite but also to reduce the emission of greenhouse gases into the atmosphere significantly. Ammonia emission eventually contributes to atmospheric N input into natural or near natural ecosystems, not only promoting eutrophication but also causing N_2O emissions, thus being an indirect greenhouse Ammonia is not considered a direct greenhouse gas because of its short lifetime in the atmosphere. It is postulated, that 1% of emitted NH_3-N is converted to N_2O-N, and therefore it is possible to integrate NH_3 losses into Global warming potential [30]. Hence, the retrieval of NH_4^+ in this study by forming the chemical precipitation can recover a significant amount NH_4^+ and limit the amount of greenhouse gases.

3.3 Impact of Struvite Precipitation on Solids

In dairy wastewater, the concentration of TDS and TS was found in the range of 756.5 ± 35.5 mg/l and 938 ± 60 mg/l respectively. After the addition of NaOH and 30% magnesium chloride solution, it was observed that the concentration of TDS of the wastewater was sharply increased in the range of 1814 ± 30 mg/l which result in increase of TS in the range of 1872.5 ± 34.5 mg/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 wastewater. 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 dairy wastewater is shown in the Figure 5 and 6.

3.4 Impact of struvite precipitation on the BOD and COD concentration

The BOD and COD of the dairy wastewater were found in the range of 216.17 ± 4.17 mg/l and 890 ± 14 mg/l respectively which was decreased sharply in the range of 72.13 ± 3.46 mg/l and 112 ± 8 mg/l, after the struvite precipitation. The dairy 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 in the solution and they were ready to participate in struvite precipitation. The impact of struvite precipitation on the BOD and COD concentration has been shown in Figure 7 and 8. On an average around 66% of BOD and 87% of COD was removed by this experiment.

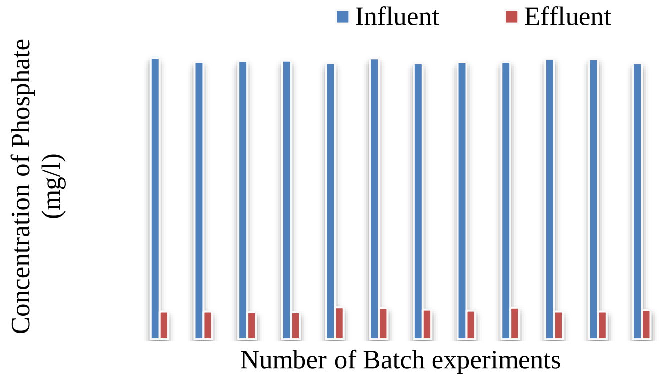

Figure 4. Impact of struvite precipitation on the concentration of phosphate of dairy wastewater

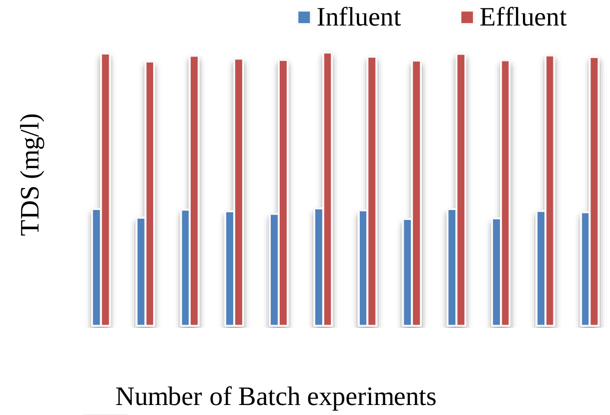

Figure 5.Impact of struvite precipitation on the concentration of TDS of dairy wastewater

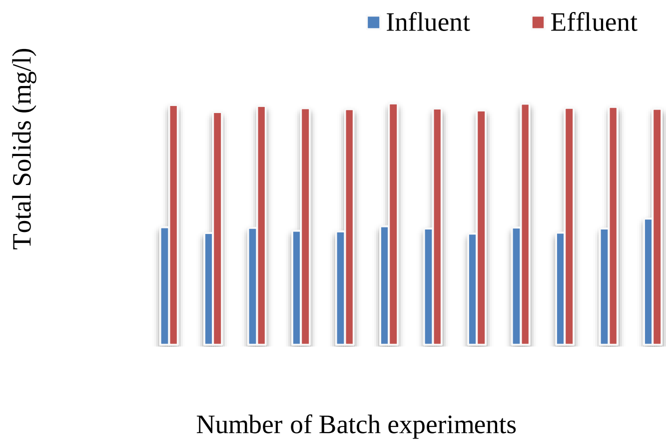

Figure 6.Impact of struvite precipitation on the concentration of TS of dairy wastewater

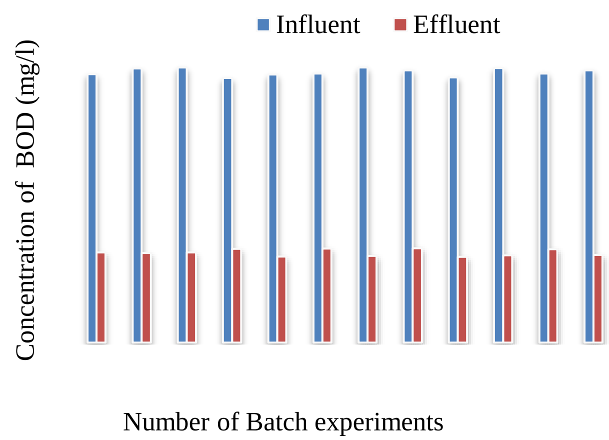

Figure 7. Impact of struvite precipitation on the concentration of BOD of dairy wastewater.

3.5 Impact of Struvite Precipitation on the Hardness

The total hardness of the dairy wastewater was found in the range of 501.5 ± 13.5 mg/l as $CaCO_3$. After the struvite precipitation, the concentration of total hardness sharply increased. The total hardness was high because magnesium was supplied from outside in the solution for struvite precipitation. There was no 100% recovery that's why maximum amount of magnesium was remaining in the solution and increases total hardness of the solution. It was lowered down in the further treatment of wastewater in different treatments units. The impact of struvite precipitation is shown in Figure 9. After the experiments the concentration of total hardness was found in the range of 1506 ± 26 mg/l as $CaCO_3$.

The calcium hardness and magnesium hardness of the dairy wastewater was found in the range of 348 ± 10 and 156.5 ± 16.5 mg/l as $CaCO_3$ respectively. After the precipitation of struvite, the concentration of calcium hardness decreased due to the precipitation of calcium phosphates has been observed in addition to or instead of struvite [31, 32]. Calcium is a common interfering ion to struvite formation in dairy manure [33]. But the concentration of magnesium hardness was sharply increased because magnesium was supplied from outside in the solution for struvite precipitation and there was no 100% recovery that's why maximum amount of magnesium was remaining in the solution. The impact of struvite precipitation is shown in Figure 10 and 11. After the experiments the concentration of calcium hardness and magnesium hardness was found in the range of 116 ± 8 and 1391.5 ± 31.5 mg/l as $CaCO_3$ respectively.

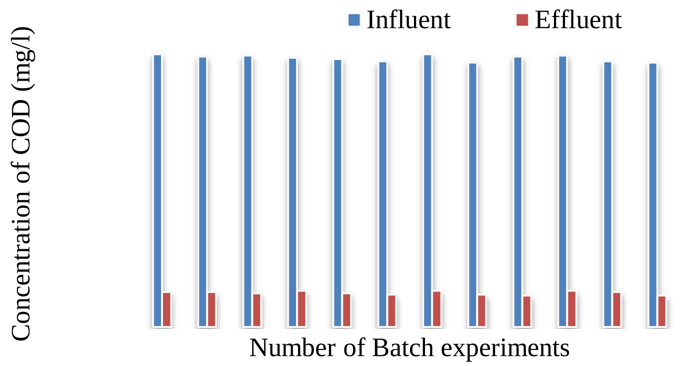

Figure 8. Impact of struvite precipitation on the concentration of COD of dairy wastewater

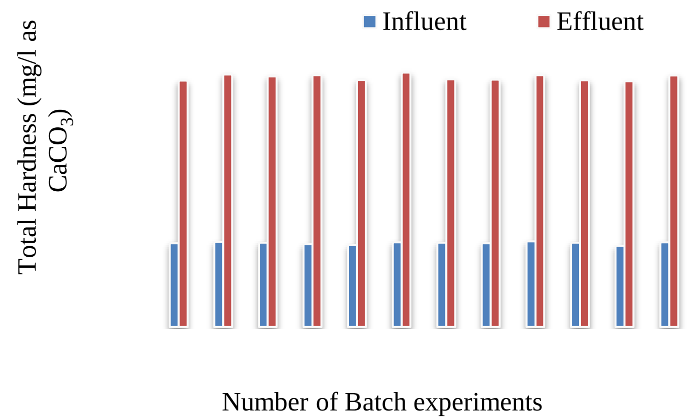

Figure 9. Impact of struvite precipitation on the concentration of Total Hardness of dairy wastewater

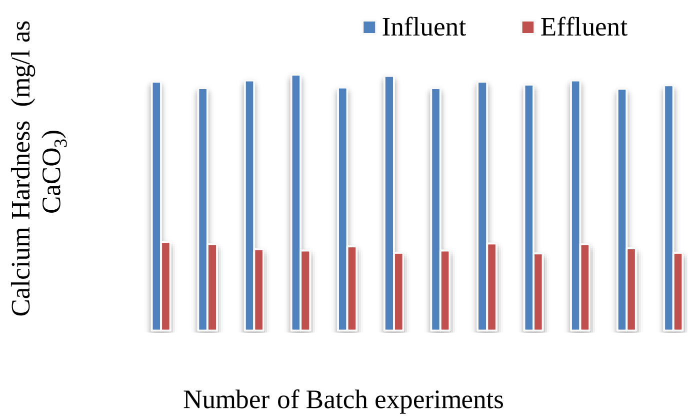

Figure 10. Impact of struvite precipitation on the concentration of Calcium Hardness of dairy wastewater

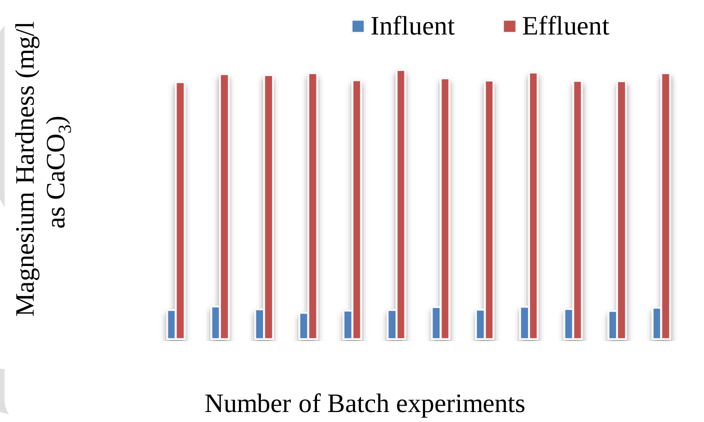

Figure 11. Impact of struvite precipitation on the concentration of Magnesium Hardness of dairy wastewater

4. CONCLUSION

In this study, struvite precipitation is used to recover nutrients from dairy wastewater. 20 liters capacity Struvite Fed Batch Reactor was designed to perform the experiment. Based on the preliminary experimental observations the conclusions drawn are:

The characteristic of dairy wastewater was analyzed to assess the recovery potential of method and percentage of reduction in pollutant concentration. The concentration of total solid and total dissolved solids were increased after the treatment and it was found in the range of 1784- 1844 and 1838- 1907 mg/l respectively.

As the result of experiments the concentration of total hardness and magnesium hardness was increased and it was found in the range of 1480-1532 and 1360-1423 mg $CaCO_3$/l respectively but calcium hardness was decreased and it was found in the range of 108- 124 mg $CaCO_3$/l.

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.

REFERENCES:

[1] Rama, Rao S.V., Singh, V.P. and Mall, L.P., Biological methods for monitoring water pollution level. Studies at Ujjain In B Gopal and J.S. Singh edited. Glimpses of ecology, 1978, 341-348.

[2] Ballou, L.U., Pasquini, M., Bremel, R.D., Everson, T. and Sommer, D., Factors affecting herd milk composition and milk plasmin at four levels of somatic cell counts. J. Dairy Sci., 1995, 78, 2186-2195.

[3] Harper, W. F. and Blaisdell, J. L., State of the art of dairy food plant wastes and waste treatment. Proceedings of the Second National Symposium on Food Processing Wastes, Denver (Colorado), USA, March, 1971, 23–26.
[4] Soederhjelm, P. and Lindqvist, B., The ammonia content of milk as an indicator of its biological deterioration or ageing. Milchwissenschaft, 1980, 35, 541-543.
[5] Daniel, T. C., Sharpley, A. N., Edwards, D. R., Wedepohl, R. and Lemunyon, J. L., Minimizing surface water eutrophication from agriculture by phosphorus management. J. Soil Water Conserv. Suppl., 1994, 49, 30-38.
[6] Correll, D. L., The role of phosphorus in the eutrophication of receiving waters: A review. J. Environ. Qual., 1998, 27, 261-266.
[7] Sims, J. T., Simard, R. R. and Joern., B. C., P losses in agricultural drainage: Historical perspective and current research. J. Environ. Qual., 1998, 27, 277-293.
[8] Edwards, A. C., Twist, H. and Codd, G. A., Assessing the impact of terrestrially derived phosphorus on flowing water systems. J. Environ. Qual., 2000, 29, 117-124.
[9] Sawyer, C. N., Biological engineering in sewage treatment, sewage Wks J. 16, 1944, 925-935.
[10] Ludzack, F. J. and Ettinger, M. B., Controlling operation to minimize activated sludge effluent nitrogen. Wat. Poll. Contr. Fed., 1962, 34, 920-931.
[11] Liao, P. H., Gao, Y. and Lo, K. V., Chemical precipitation of phosphate and ammonia from swine wastewater. Biomass and Bioenergy, 1993, 4(5), 365-371.
[12] Siegrist, H., 1996. Nitrogen removal from digester supernatant comparison of chemical and biological methods. Water Science and Technology, 1996, 34, 399-406.
[13] Tunay, O., Kabdasli, I., Orhon, D. and Kolcak, S., Ammonia removal by magnesium ammonium phosphate precipitation in industrial wastewater. Water Science and Technology, 1997, 36, 225-228.
[14] Battistoni, P., Fava, G., Pavan, P., Musacco, A. and Cecchi, F., Phosphate removal in anaerobic liquors by struvite crystallization without addition of chemicals: preliminary results. Water Resources, 1997, 31, 2925-2929.
[15] Stratful, I., Scrimshaw, M. D. and Lester, J. N., Conditions influencing the precipitation of magnesium ammonium phosphate. Water Resources, 2001, 35, 4191-4199.
[16] Doyle, J. D. and Parsons, S.A., Struvite formation, control and recovery. Water Resources, 2002, 36, 3925-3940.
[17] Battistoni, P., Pavan, P., Prisciandaro, M. and Cecchi, F., Struvite crystallization: A feasible and reliable way to fix phosphorus in anaerobic supernatant. Water Research, 2000, 34, 3033-3041.
[18] Nelson, N. O., Mikkelsen, R. L. and Hesterberg, D. L., Struvite precipitation in anaerobic swine lagoon liquid: Effect of pH and Mg:P ratio and determination of rate constant. Bioresource Technology, 2003, 89, 229-236.
[19] Demirer, S. U., Demirer, G. N. and Chen, S., Ammonia removal from anaerobic digested diary manure by struvite precipitation. Process Biochem., 2005, 40, 3667-3674.
[20] Ali, M.I., Struvite crystallization in fed-batch pilot scale and description of solution chemistry of struvite. Chemical Engineering Research and Design, 2007, 85(A3), 344-356.
[21] Demirer, S.U. and Othman, M., Removal of ammonia and phosphate from supernatant of anaerobically digested waste activated sludge by chemical precipitation. Bioresource Technology, 2009, 100, 3236-3244.
[22] Booker, N. A., Priestley, A. J. and Fraser, I. H., Struvite formation in wastewater treatment plants: opportunities for nutrient recovery. Environmental Technology, 1999, 20, 777-782.
[23] Buchanan, J. R., Mote, C. R. and Robinson, R. B., Struvite control by chemical treatment. Transactions of the American Society of Agricultural Engineers, 1994, 37, 1301-1308.
[24] Donnert, D. and Salecker, M., Elimination of phosphorus from waste water by crystallization. Environ. Technol., 1999b, 20, 735-742.
[25] Donnert, D. and Salecker, M., Elimination of phosphorus from municipal and industrial waste water. Water Sci. Technol., 1999b, 40, 195-202.
[26] Stratful, I., Brett, S., Scrimshaw, M.B. and Lester, J.N., Biological phosphorus removal, its role in phosphorus recycling. Environ. Technol., 1999, 20, 681-695.
[27] Driver, J., Lijmbach, D. and Steen, I., Why recover phosphorus for recycling, and how? Env. Tech., 1999, 20, 651-662.
[28] Durrant, A. E., Scrimshaw, M. D., Stratful, I. and Lester, J.N., Review of the feasibility of recovering phosphate from wastewater for use as a raw material by phosphate industry. Environ. Technol., 1999, 20(7), 749-758
[29] Strickland, J., Perspectives for phosphorus recovery offered by enhanced biological P removal. Environmental Technology, 1999, 20(7), 721-725.
[30] Woods, N.C., Sock, S.M. and Daigger, G.T., Phosphorus recovery technology modeling and feasibility evaluation for municipal wastewater treatment plants. Environmental Technology, 1999, 20(7), 663-679.
[31] Wulf, S., Maeting, M., Bergmann, S. and Clemens, J., Simultaneous measurement of NH3, N2O and CH4 to assess efficiency of trace gas emission abatement after slurry application. Phyton (Horn, Austria), 2001, 41(3), 131–142.
[32] Harris W. G., Wilkie A. C., Cao X.., Sirengo R., 2008. Bench-Scale Recovery of Phosphorus from Flushed Dairy Manure Wastewater. Bioresour. Technol., 99 (8), 3036–3043.
[33] Zeng, L. and Li, X., Nutrient Removal from Anaerobically Digested Cattle Manure by Struvite Precipitation. J. Environ. Eng. Sci., 2006, 5(4), 285–294.