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EXTRACTION OF NUTRIENTS FROM DAIRY WASTEWATER IN THE FORM OF MAP (MAGNESIUM AMMONIUM PHOSPHATE) AND HAP (HYDROXYAPATITE)

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ABSTRACT

Dairy wastewater when released from the industry is highly rich in organic matter, suspended solids, oil and grease, fats, nitrogen, phosphorous and calcium. After disposal it may cause water as well as land eutrophication and can block soil pores thus resulting in reduced levels of soil infiltration. When send to the treatment units this dairy wastewater also results in crystalline deposits. Dairy wastewater is classified as nutrient rich wastewater containing sufficient amount of nitrogen, phosphorous and calcium that can be separated or extracted by suitable methods. The extraction of these nutrients is done using a lab scale batch reactor of desired efficiency needful to justify this issue and find a solution to it. The process of extraction of nutrients is performed using a Mixed Suspension Mixed Product Removal Batch Reactor of suitable dimensions in the form of Magnesium Ammonium Phosphate and Hydroxyapatite. These nutrients being a slow released fertilizer will provide value to the crop production and land yield, further reducing BOD, COD and TSS of the wastewater making it safer to dispose. Dairy wastewater is taken from an industrial source which is firstly characterized, diluted and then fed into the reactor in the presence of suitable seed material resulting in formation of crystals. Experiments performed for the formation of Magnesium Ammonium Phosphate and Hydroxyapatite are separately carried out in different batches. The key focus of this project is to enhance the efficiency of dairy wastewater treatment units and prevent crystallization during treatment process.

Keywords: Magnesium Ammonium Phosphate (MAP), Hydroxyapatite (HAP), Batch Reactor, Dairy wastewater, Crystallization.

INTRODUCTION

Rapid growth of industries resulted in release of waste and toxic substances into the environment, creating health hazards, affecting flora and fauna. Besides, like many industries have serious waste disposal problems, the dairy industries are also facing, causing water and soil pollution with its released effluents. Dairy waste waters is highly rich in nutrients and organic content especially those which are essential for plant growth and commercially being used in the form of fertilizers. Nitrogen (N), Phosphorous (P) and Potassium (K) are the primary nutrients that are consumed by plants in large amount and can be extracted from industrial wastewaters in the form of magnesium ammonium phosphate ($MgNH_4PO_4.6H_2O$) and Hydroxyapatite also called as HAP i.e. $Ca_5 (PO_4)_3(OH)$ that can be used as fertilizer supplying P, N, Mg and Ca to the plants simultaneously with no unnecessary components in the fertilizer[1-5]. Dairy industry in India is expected to grow rapidly and have the waste generation and related environmental problems are also assumed increased importance. Poorly treated wastewater with high levels of pollutants caused by poor design, operation or treatment systems creates major environmental problems when discharge to surface water or land. Such problems include contamination and deoxygenating of streams and waterways by direct discharge or runoff of inadequately treated wastewater, excessive concentration of nutrients such as nitrogen and phosphorous in surface and subsurface water bodies. This contributes to excessive growth of plants and algal blooms, which makes the downstream water unsuitable for domestic, agriculture and industrial use. According to the water (Prevention & Control of pollution) act 1974 as a result of growth of industries and the increasing tendency to urbanization the problem of pollution of river and streams has assumed considerable importance. It had become essential to ensure the industrial effluents are not allowed to be discharged into the water courses without adequate treatment. It was estimated in 2001, by the U.S. Geological Survey (USGS), that the global reserve life of phosphate ore was approximately 90 years, therefore recovery of nutrients from wastewater will help to meet the future demands of fertilizers for plant growth[6-9].

Despite the production of a smaller mean crystal size, the proposed continuous MSMPR operation achieved higher production capacity with shorter mean residence time and comparable product yield as in batch[1].Indirect dosage of pure and industrial MgO resulted in a general improvement of 20% of NH_4-N reduction except when the presence of other ions in the solution was consistent.Struvite precipitation leads to pH increase and decrease in total solids, BOD and COD, and the percentage removal of phosphate and ammonia was 83% and 16% respectively[2].The applicability of MAP precipitation process for the recovery of high strength of NH_4 as N from UASB wastewater effluent can be done using three combinations of chemicals $MgCl_2.6H_2O$+KH_2PO_4, $MgSO_4.7H_2O$+$NaHPO_4.7H_2O$ and MgO+85% H_3PO_4[3].The Ca ion is notable for PO_4 ions hindering struvite precipitation because it reacts with phosphate as well as ammonia[4].Decrease of available PO_4-P concentration in the digester can minimize phosphorous precipitation, reducing the maintenance problems associated with struvite deposits[5].Wastewater leads to soil acidification and premature eutrophication in surrounding waterways due to the presence of excess ammonium and phosphate. Occasionally, strong nutrient loading in waste water stream forms solid deposits and causes clogging of wastewater distribution system[6].Precipitation of struvite is highly pH dependent, as activities of both NH_4 and PO_4 are affected by solution pH. This optimum pH range (8.9 - 9.25) is related to PO_4 solubility and the presence of N as NH_4 in solution. High NH_4 concentration enhance struvite precipitation and have the advantage of pH buffering in solution and worked on recovery of nutrient from wastewater in the form of struvite by anaerobic method[9].Irrigation with high TDS (Total Dissolved Solids) results in decrease in optimal crop production[10].Physico-chemical characteristics and fertilizing efficiency of dairy effluent is highly alkaline in nature and contains large amounts of suspended and dissolved solids resulting in high BOD (3892 mg/l) and COD (9682 mg/l) [10-12].

EXPERIMENTAL

The characteristics of industrial dairy wastewater are given in Table 1.

Design of batch reactor

A mixed suspension mixed product removal batch reactor (MSMPRBR) of 12.06 litres volume, made of clear Perspex was used in this project. The shape of reactor is cylindrical with conical base. Volume of cylindrical part is 11.31 litres and of conical part is 0.75 litres. A cylindrical aeration tank was installed in the upper part of the reactor for aeration of wastewater. The lower part of reactor acts as settling zone for MAP and HAP crystals, and an outlet was provided for removal of sludge and crystals. Another outlets are provided at upper and lower part for removal of wastewater, if wastewater flowing continuously in the reactor. A mechanical operated double blade mixer is installed in the middle of the reactor of capacity 43 rpm, attached with a DC motor fixed on top of the reactor. Due to vibration and rotation, mixing was done as a first step and it was achieved by aeration pump of capacity 7 litre/minute. A schematic sketch of Mixed Suspension Mixed Product Removal Batch Reactor (MSMPRBR) is shown in Fig. 1.

Table 1: Raw Dairy Wastewater Characteristics

S. No.	Parameters	Units	Average Value
1	pH	NA	6.6
2	COD	mgl^{-1}	2790
3	BOD	mgl^{-1}	1350
4	TSS	mgl^{-1}	6975
5	Oil & Grease	mgl^{-1}	4190
6	Ca^{2+}	mgl^{-1}	121

7	Mg^{2+}	mgl^{-1}	77
8	TKN	mgl^{-1}	229
9	PO_4^{3-}	mgl^{-1}	526
10	NH_4^+	mgl^{-1}	69

Table 2: Design Criteria of Reactor

Design Criteria for Holding Tank	
Parameters	**Dimensions**
Diameter of Reactor	120mm
Height of cylindrical part	1000mm
Height of conical part	200mm
Design Criteria for Aeration Tank	
Diameter of aeration tank	100mm
Height of aeration tank	200mm

Sampling of Dairy Wastewater for Crystallization

Grab samples of dairy wastewater were taken just after screening from treatment plant of Dairy Industry. The samples were taken in plastic cans of 10 litres capacity. The can was thoroughly rinsed twice with raw sample. The pH and total dissolved solid were determined at the sampling spot with the help of pH meter and TDS meter. Remaining other physic-chemical characteristics were analysed in lab within 2-4 hours of sampling except BOD. Experiments were started after characterization of the wastewater.[13-15]

Crystallization of MAP and HAP with Dairy Wastewater

The MSMPRBR was cleaned with diluted HCl solution and washed with deionised water. The reactor was allowed for drying at room temperature (25°C). After cleaning the reactor, it was filled with 7 litres of dairy wastewater. The pH of wastewater is increased by adding NaOH Solution to the feed, to obtain the optimum pH range for the crystallisation of MAP and HAP which lies in the range of 8.5 to 9.5.

Crystallization of MAP (Magnesium Ammonium Phosphate)

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 PO_4^+ and NH_4^+ in the sample. Then solution was seeded with 1 g of previously generated MAP as parent crystal. The mixing of solution was done by air pump and the mechanical mixers till whole solution of magnesium chloride was finally added into the 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 desiccators for drying with interfering air for 10 hours. Finally, filtrate was air dried at room temperature. The MAP 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 MAP crystals.[16-18]

Crystallization of HAP (Hydroxyapatite)

Two litres of 30% calcium chloride solution was added into reactor at the rate of 7.5mL/minute. The rate of calcium 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 HAP as parent crystal. The mixing of solution was done by air pump and mechanical mixer till whole solution of calcium chloride was finally added into the 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 calcium 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 desiccators for drying with interfering air for 10 hours. Finally, filtrate was air dried at room temperature. The HAP 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 HAP crystals.

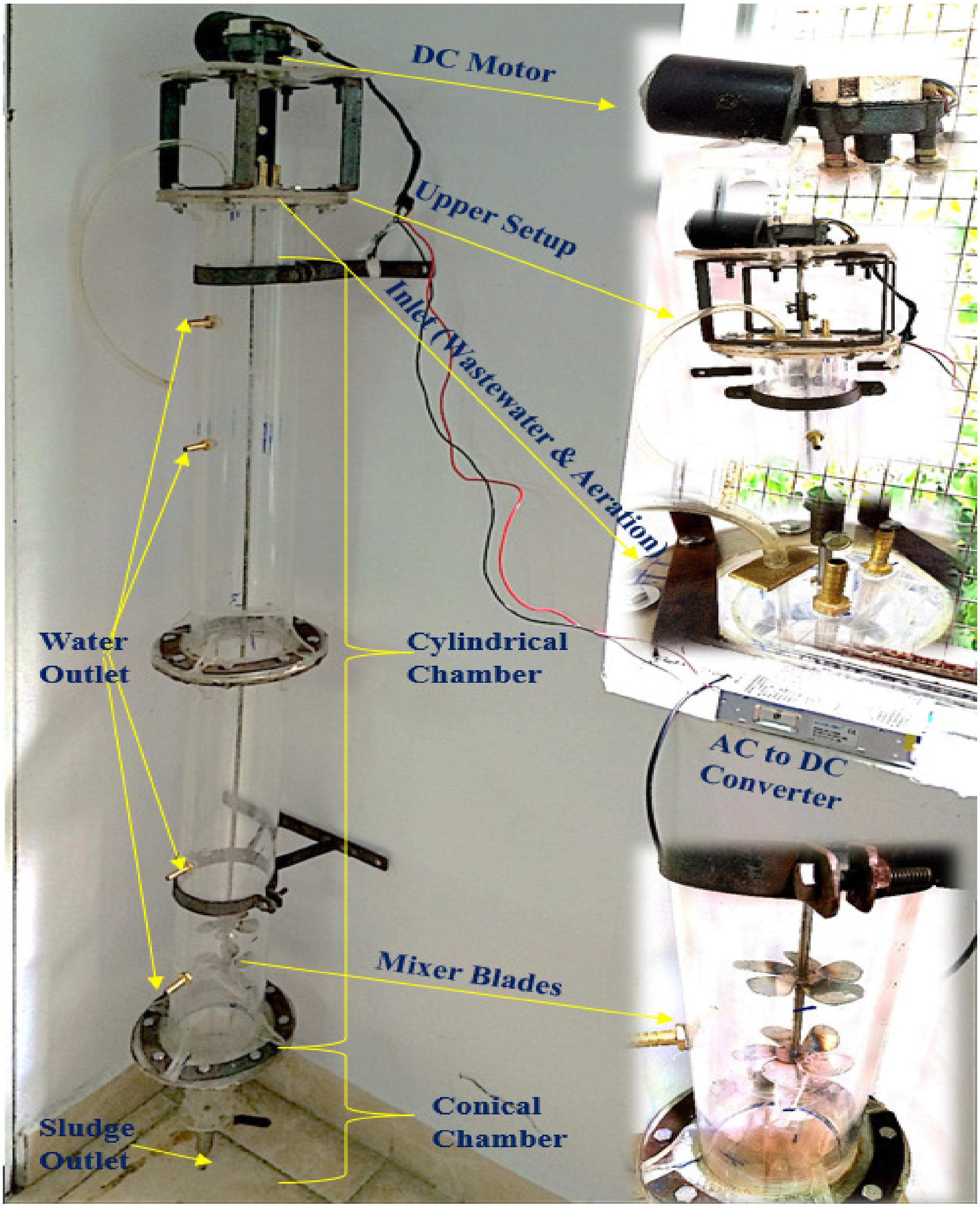

Fig.-1: Reactor Setup

RESULTS AND DISCUSSION

Impact of MAP and HAP crystallization on pH

The raw dairy wastewater pH was found in the range of 6.1-6.9. pH of the wastewater was increased to 9.2 by the addition of NaOH solution. After that 2 litres of 30% magnesium chloride solution and calcium chloride solution was mixed with the wastewater in different batches of experiment. It was observed that when crystallization started, the pH of the solution decreases from its original pH 9.2. It was in the range of 8.6 to 8.9. The impact of precipitation on the pH is shown in Figure-2.

Impact of MAP and HAP crystallization on the BOD and COD concentration: The BOD of the raw dairy wastewater was in the range of 1300-1400 mg/L. After the treatment, BOD of the solution sharply decreased and reached in the range of 250-350 mg/L. The raw dairy 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 MAP and HAP crystallization. The impact of MAP and HAP crystallization on the BOD concentration is shown in Figure-3.

Fig.-2: Impact of MAP and HAP crystallization on pH

An average of around 75% of BOD was removed by this experiment. Similar reasons could be ascribed for COD reduction. The COD of the raw dairy wastewater was in the range of 2750-2850 mg/L. After the treatment, COD of the solution got sharply declined in the range of 650-750 mg/L.

Impact of MAP and HAP crystallization on the total suspended solids (TSS)

In raw dairy wastewater, the concentration of total suspended solid was found in the range of 6500-7500mg/L. After the crystallization of MAP and HAP with sludge it was observed that the TSS 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 MAP and HAP. After settlement of all the suspended material at the bottom of reactor, the solution gets very clear. The impact of MAP and HAP crystallization on total suspended solids has been shown in Fig. 4. An average of around 45 % total suspended solids were removed by this experiment. After the experiment the observed values of TSS were found to be in the range of 3000-4000 for both MAP and HAP crystallization.

Impact of MAP and HAP Crystallization on the concentration of phosphate

The concentration of phosphate in the raw dairy wastewater was in the range of 500-550mg/L. After the crystallization of MAP and HAP, it was observed that the concentration of phosphate declined sharply in the range of 15-25mg/L. About 95% of phosphate was recovered in the form of various compounds of phosphate.

Impact of MAP and HAP crystallization on the concentration of ammonia: The concentration of ammonia was found to being the range of 65-75mg/L in the raw dairy wastewater. After the crystallization of MAP and HAP, it was observed that the concentration of ammonia declined sharply in the range of 5-10mg/L in the case of MAP and 35-45mg/l in the case of HAP. About 90% of ammonia was recovered in the form of various compounds of phosphorus.

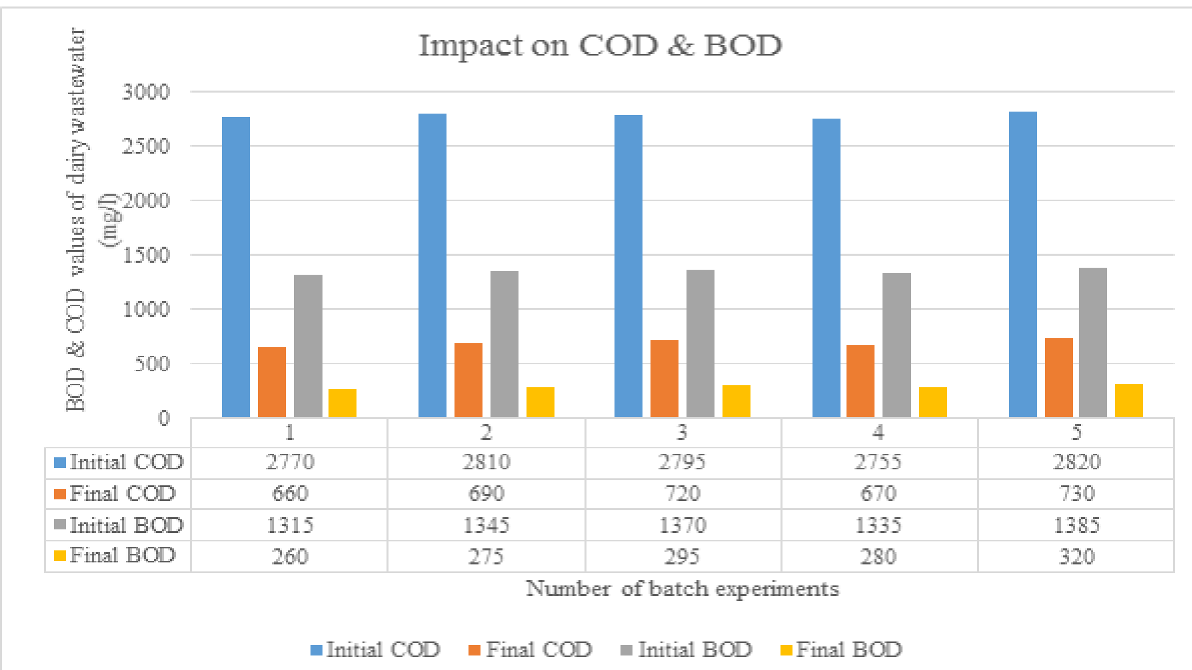

Fig.-3: Impact of MAP and HAP crystallization on COD & BOD values

CONCLUSION

MAP and HAP crystallization leads to pH increase in all the cases. The concentration of total suspended solids was decreased after the treatment whereas the concentration of total dissolved solids were increased. Both, the BOD and COD showed remarkable decrease as a consequence of MAP and HAP crystallization. The percentage of phosphate undergone crystallization was investigated and it was observed that approximately 70% phosphate was crystallized from the solution in the form of MAP and HAP. The percentage of ammonia undergone crystallization was investigated and it was observed that approximately 10-20% ammonia was crystallized from the solution in the form of MAP and HAP.

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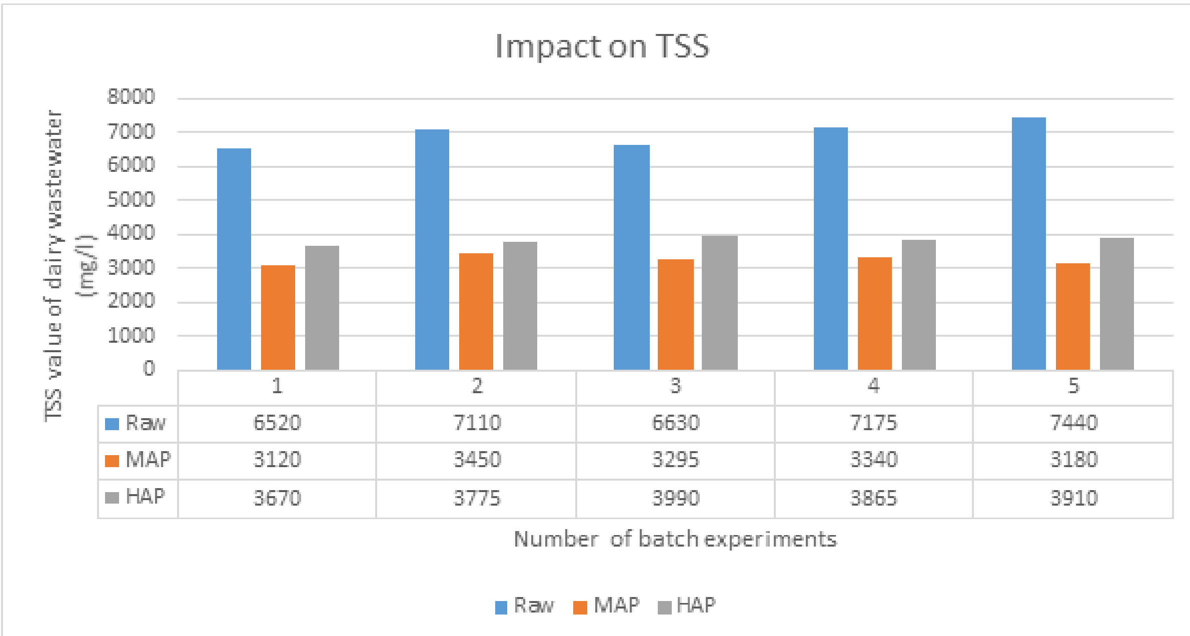

Fig.-4: Impact of MAP and HAP crystallization on the total suspended solids (TSS)

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