

# Formation of Struvite Crystals from Domestic Wastewater using Magnesium Carbonate as an Mg Source

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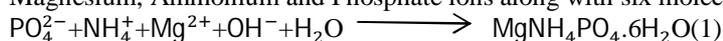
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**ABSTRACT:** Experimental work concerning the process of removal of phosphorus and nitrate from domestic wastewater and is recovered as Struvite. The main problem of these nutrients in wastewater causes eutrophication when left without treatment. Therefore it is much necessary to limit these nutrients when left to receiving water bodies. Struvite crystals are formed with the combination of Phosphate, Nitrate and Magnesium along with water. Magnesium Carbonate is used as a source of Magnesium in this study. The pH of the raw wastewater is raised to 10 using 1M NaOH solution. The equimolar ratio of Phosphate and Magnesium Carbonate used is 1:1. The main aim of this study is to find out the optimum conditions by conducting batch studies various stirring time, settling time, pH conditions and the removal efficiencies of phosphate and nitrate was observed to 96.20% and 98.30% respectively at 0.5 hour of stirring time. The impact of Struvite crystals on hardness was also studied. The Struvite crystal structures were studied using SEM images.

**KEYWORDS:** Phosphate, Nitrate, Struvite, Domestic Wastewater, Magnesium carbonate

## I. INTRODUCTION

Phosphate and nitrate is a toxic pollutant commonly found in domestic wastewater. High concentration of these nutrients causes eutrophication of surface water bodies when left without proper treatment, leading to death of aquatic organisms. Most of the phosphorus and nitrogen in domestic wastewater is the product of our eating habits and food preparation, body exudates washed off in the bath or shower and products washed from clothes. Cleaning chemicals also contribute organic compounds in varying amounts. Total nitrogen in domestic wastewater typically ranges from 20 to 70 mg/L for low to high strength wastewater (Crites & Tchobanoglous 1998). The growth of Struvite at treatment plant pipes increases pumping and maintenance cost, as well as reduces the overall capacity of the plant piping system. It is highly pH dependent as activities of both  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  are affected by solution pH (Nelson et al. 2003). Since domestic wastewater is recognized as nutrient rich water, the recovery of nutrients using a crystallization technique will give a product called Struvite, which is a slow releasing fertilizer. It incorporates a chemical reaction among Magnesium, Ammonium and Phosphate ions along with six molecules of water. (Equation 1)



Due to low influent alkalinity, alkali addition is necessary for crystallization process and for pH adjustment. MAP is a slow releasing fertilizer with a chemical formula of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  and a mixed fertilizer which can be treated as phosphorus fertilizer. The important factors affecting the struvite formations are pH, stirring time, molar ratio, temperature, presence of foreign particles. pH acts a major part in crystallizing because the crystal structure forms in alkaline condition. Different alkaline conditions give different morphological structures of Struvite crystals. The main objective is to study the different parameters of domestic wastewater before and after the Struvite formation and to study the influence of different factors such as stirring time, settling time, dosage, pH on removal of phosphate and

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nitrate and recovery as Struvite. Generally, wastewaters from anthropogenic, livestock, or municipal leachate contains less magnesium compared with nitrogen and phosphate. So, it is necessary to add a source of Mg to optimize the struvite crystallization process. (Tunay et al., 1997, Suzuki et al., 2005, 2007). Magnesium carbonate supports the crystal structure of struvite.

## II. MATERIALS AND METHODS

### 2.1 Design of batch reactor

A crystallizer reactor of 15 liters volume, made of clear Perspex was used in this study. The design criteria of crystallizer reactor are shown in table 1. The reactor was made cylindrical with tapering bottom which acts as settling zone. Valves are provided both at the bottom of tapering end as well as cylindrical zone to collect the sludge and supernatant respectively. A mechanical stirrer is used for continuous mixing of wastewater. Speed setter was used to adjust the rpm. A schematic sketch of crystallizer reactor is shown in fig 1.



Fig. 1. Crystallizer Reactor

Table 1. Design criteria of crystallizer reactor

REACTOR STRUCTURE	DIMENSION
Diameter of reactor	20cm
Height of cylindrical reactor	60cm
Height of tapering bottom	15cm

### 2.2 Sampling of domestic wastewater

A grab sampling of domestic wastewater was carried out from Kesare wastewater treatment plant, Mysuru. The samples were taken just after the screening at a single point. The samples were collected in cans of capacity 20 liters and initial physico-chemical parameters were analyzed in the laboratory as shown in table 2.

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**Table 2.**Physico-Chemical parameters of Kesareraw wastewater before Struvite formation.

PARAMETERS	RANGE
pH	6.4-7.9
Total hardness	260-370
Ca hardness	130-150
Mg hardness	120-196
Phosphate	43.5-92.82
Nitrate	37.12-52.45
Magnesium	19.72-28.14
COD	752-3200
BOD5	480-620

## 2.3 Methodology

The domestic wastewater sample after initial characterization was put into the crystallizer reactor. The pH of wastewater sample was raised to 10 using 1M NaOH solution. A calculated amount of Magnesium Carbonate was added into the reactor with a molar ratio of 1:1(P:Mg). The Mechanical stirrer was placed inside the reactor by adjusting the rpm to 75. The purpose of using stirrer is to thoroughly mix up the added chemicals. After switching off the stirrer the wastewater sample in the reactor was allowed to settle down. The supernatant water at the top was taken from the valve and is analyzed for certain parameters in the laboratory (table 3). The sludge at the bottom is taken out and is kept for drying at a room temperature for 24 hrs. or can be dried at hot air oven at 50°C for 24hrs. A series of batch studies were conducted by varying stirring time, settling time, pH and dosage to find out the optimum condition for the removal and recovery of Phosphorus and nitrate as struvite. The Morphology of struvite crystals were studied by taking SEM images.

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## III. RESULTS AND DISCUSSIONS

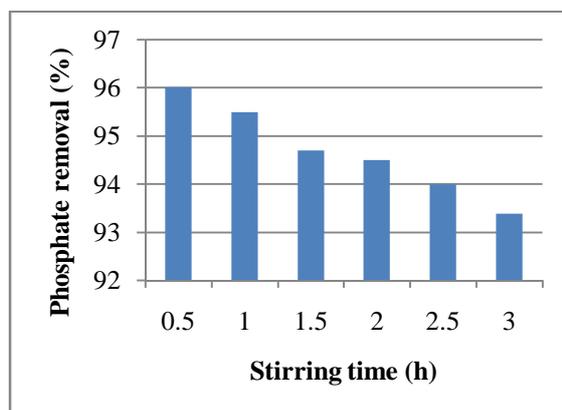
### 3.1 Influence of Struvite formation on Phosphate removal

The Phosphate concentration in raw wastewater was about 46.425mg/l. After Struvite formation the concentration of phosphate in wastewater was observed to decrease at 0.5hr of stirring when compared to other stirring time. Therefore about 96% of Phosphate was removed for 0.5h of stirring time and was recovered as Struvite. As the stirring time increases the removal efficiency of phosphate decreases because the amount of phosphate adds to the wastewater due to breakage of crystals.

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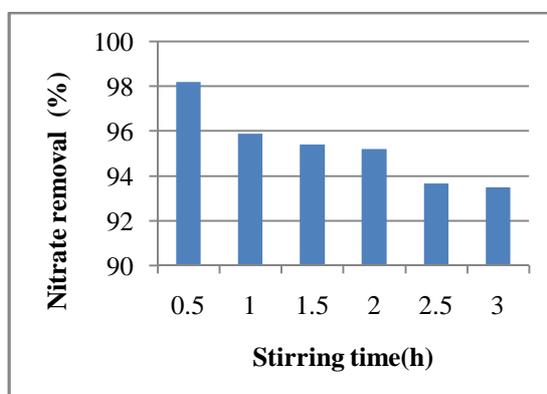
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**Fig 2.** Various batch studies were conducted for different stirring time and 96% of phosphate is removed for 0.5 hr stirring time and is recovered as Struvite

### 3.2 Influence of Struvite formation on Nitrate removal

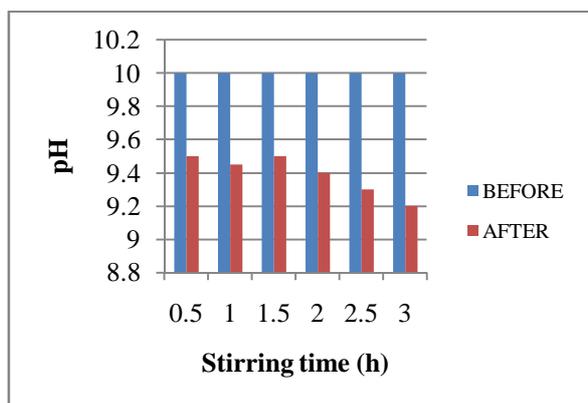
The Nitrate concentration in raw wastewater was about 44.570mg/l. Afterstruvite formation the concentration of Nitrate was observed to decrease at 0.5hr of stirring time when compared to other stirring time. Therefore about 98.2% of Nitrate was removed for 0.5h of stirring time and was recovered as Struvite.



**Fig. 3.** Various batch studies were conducted for different stirring time and 98.2% of Nitrate is removed for 0.5 hr stirring time and is recovered as Struvite. Magnesium carbonate removes nitrate more when compared to phosphate.

### 3.3 Influence of Struvite formation on pH

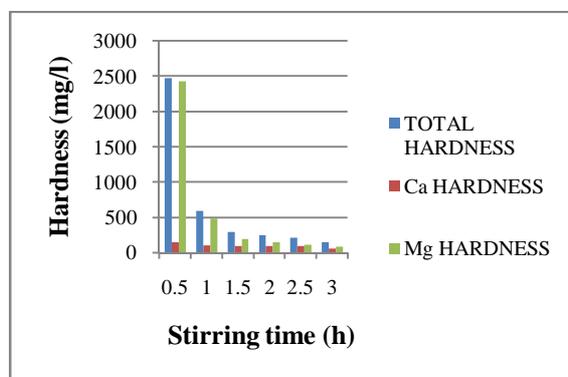
The pH of the raw wastewater was 6.7 and it was increased to 10 using 1M NaOH solution and is kept constant for different stirring time. The pH of the treated wastewater was measured as shown in the fig 4. There was a slight decrease in the pH for all stirring time; this is because the formation of Struvite takes place in alkaline condition as in Equation 1.



**Fig. 4.** Increase in pH in all the cases because Struvite formation and after its formation it slightly decreases as Struvite forms in alkaline conditions

### 3.4 Influence of struvite formation on Hardness

Formation of struvite from wastewater showed very good results in declining the hardness content. The total hardness, calcium hardness and magnesium hardness in raw wastewater was found to be 320mg/l, 152mg/l and 200mg/l respectively. After the formation of Struvite, hardness decreases as the stirring time increases as shown in fig 5.



**Fig. 5.** Total and Magnesium hardness has increased as magnesium carbonate is added and as the stirring time increases due to chemical reaction hardness has decreased.

Here, the total hardness and magnesium hardness has increased approximately to 2500mg/l. It is due to the addition of magnesium carbonate. Magnesium Carbonate used as Mg source increases the magnesium hardness and carbonate tends to increase total hardness. Calcium hardness is already present in water. As the stirring time increases from 0.5h to 1h, both magnesium hardness and total hardness has suddenly decreased nearly to 500mg/l. This is due to the reaction that takes place between magnesium carbonate and water in alkaline condition. (Equation 3)



Magnesium hydroxide settles down at the bottom and sodium carbonate competes with magnesium and carbonate and prevents the bonding between them acting as a resin by softening the water while reducing hardness from wastewater. Hardness of wastewater can be maintained within the standards before disposing to receiving water bodies by Struvite treatment.

### 3.5 Influence of settling time on Struvite formation

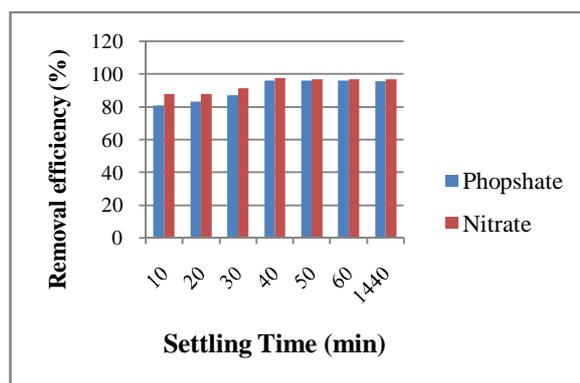
A batch studies were conducted for various settling time and its effect on removal and recovery of phosphate and nitrate from wastewater was observed. The heavy particles were allowed to settle down at the bottom and the

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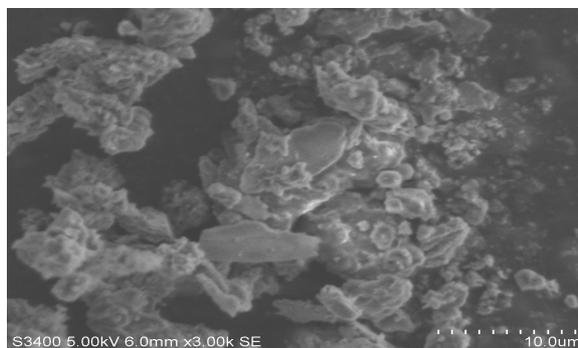
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supernatant water was analyzed. The initial concentration of P and N were kept at 52.11mg/l and 43.23g/l respectively and the different settling time is provided. The removal efficiency of both the nutrients was observed at 40min of settling.



**Fig. 6.** The settling time was given till 1hr with an interval of 10 min and Phosphate and Nitrate removal was observed. The removal efficiency was noted highest at 40 min of settling time.



**Fig. 7.** Scanning Electron Microscope image of Struvite crystals formation with pH 9 and at a settling time of 24 hrs with a stirring time of 1 hr with Magnesium carbonate as a magnesium source.

## IV. CONCLUSIONS

The process of Struvite formation reduces high amount of phosphate and nitrate from domestic wastewater which helps in controlling eutrophication of surface water and death of aquatic organisms. Magnesium carbonate used as a Magnesium source removed 96.2% and 98.3% of Phosphate and Nitrate respectively. COD, BOD and hardness showed remarkable decrease as a consequence of Struvite formation. This process will convert the hazardous waste into non-hazardous nutrient source as a fertilizer.

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