

## Separation of Struvite from Sewerage Water and its Evaluation as Phosphatic Fertilizer

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### Abstract

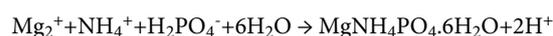
Magnesium ammonium phosphate hexahydrate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), commonly known as struvite is a crystalline mineral of low solubility. In wastewater treatment facilities, separating phosphorus by conversion to struvite could reduce its content in the wastewater. The experiment conducted for local wastewater sources to identify better source and recover struvite for phosphatic fertilizer evaluation. Chemical precipitation through pH elevation and ( $\text{Mg}^{2+}:\text{NH}_4^+:\text{N}:\text{PO}_4^{3-}:\text{P}$ ) molar ratio were used to recover  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  as struvite from sewerage water of different sites. To recover (MAP) magnesium ammonium phosphate hexahydrate from the four different sources, chemicals including  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_3\text{PO}_4$  were applied at molar ratio ( $\text{Mg}^{2+}:\text{NH}_4^+:\text{N}:\text{PO}_4^{3-}:\text{P}=1.2:1:1$ ) and at different pH ranging from 8.0 to 11.0. Results indicated that maximum P removal was obtained as 87% at pH 10.5 from the source of I-9 sector containing high levels of P. For N results indicated that maximum N removal was obtained as 67% at pH 10.0 from the same source of P removal. In the experiment among various combinations, comprising of Mg:N:P ratio, pH levels and stirring speeds, the stirring speed of 250 rpm for 30 minutes was more desirable for struvite precipitation process. The MAP precipitation significantly reduced the contents of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  in sewerage water at different sites. So, it is necessary to develop the optimum conditions for small-scale and commercial production of struvite, because struvite recovery is technically feasible and economically beneficial. Therefore, this technology provides opportunities to recover phosphorus sustainably from sewerage water and preserve phosphorus reserves.

**Keywords:** Precipitation; Struvite separation; Stirring speed; Chemical ratio; Sewerage

### Introduction

Phosphorus (P) is an essential plant nutrient, and in agricultural and industrial development it has a major contribution. Wastewater containing high levels of P has become a major source of pollution in the water bodies. Therefore, it's an important priority to maintain water quality by the removal of P from wastewater. For P removal, various chemical and biological processes have been developed, such as biological nutrient removal processes, metal precipitation, enhanced biological phosphorus removal processes, constructed wetland systems and the struvite crystallization process [1]. Furthermore, wastewater is one of the potential sources of phosphorus recovery [2].

In surface water, the discharge of phosphates may lead to eutrophication and blooming of algae. Therefore, to control phosphate pollution, removal of P from wastewater is essential. Now a days, phosphorus removal by chemical method is one of the best technology to achieve effluent standards [3]. Among these processes recovery of phosphorus can be readily achieved by crystallization as struvite magnesium ammonium phosphate (MAP) hexahydrate, which can be further utilized as a valuable slow-release fertilizer [4,5]. Struvite crystallization occurs under alkaline conditions according to the reaction shown as follows:



Some forms of nitrogen (ammonia, nitrate and nitrite) and phosphorus (orthophosphate and monophosphate) affect the aquatic life and produce toxicity in the wastewater. Removal of nitrogen and phosphorus from wastewaters is essential before discharging it into the water streams for pollution-free and eco-friendly environment. So, many countries are paying attention to water pollution resulting from wastewater and have tightened legislation and discharging standards. Moreover, in the wastewater, macronutrients are often discharged to the natural water bodies without managing eutrophication and other issues in water cycle. To facilitate nutrient recovery, it is of great interest to develop proper technologies and maintain the quality of wastewater effluent [6]. The MAP hexahydrate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) called struvite, is a white inorganic crystalline mineral, soluble in acid not in water, alkali and ethanol, density  $1.71 \text{ g cm}^{-3}$ , and is considered as a slow release fertilizer [7]. A modification of struvite has been proposed in the perspective of competition in the market as a fertilizer with diammonium phosphate (DAP) and triple superphosphate, where struvite should be treated with phosphoric acid [8]. Struvite has been proven technically feasible and economically beneficial. Struvite contains 12.6% P and 5.7% N by weight; the phosphate is entirely citrate-soluble and the fertilizer analysis in oxide form with 9.9% Mg [9]. Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) also has a high  $\text{P}_2\text{O}_5$  content compared with established fertilizers, and is an excellent slow release

fertilizer that does not “burn” roots when applied in excess due to its low solubility in pH neutral solutions [10]. Two main factors are concerned in struvite crystallization process: the molar ratio of Mg:N:P and the pH value of wastewater. Since the solubility of struvite decreases with the increase in pH [11] so it can be recovered under alkaline conditions.

Estimated phosphorus in detergents as 44 TP/year for (2010 data, plus 3 TP/year in personal care products. In pet foods phosphorus is estimated at 28 TP/year as inflows of phosphorus into the urban area. Inputs to the urban area’s agriculture as fertilizers were estimated to be 16 TP/year, and in animal feeds and fodder 1 TP/year. Other inputs (newspaper, atmospheric deposition and packaging) total 10 TP/year. Further, it has been predicted that each year, the P demand would increase by 1.5% [12].

With the depletion of phosphorus resources phosphorus recovery from wastewater streams is receiving more and more interests worldwide [13]. Presently, technology of recycling N and P from all kinds of wastewater as MAP precipitation is receiving focus by the scientists and industrialists [14,15].

Currently, limited research has been conducted on struvite crystallization on the effects of Mg and PO<sub>4</sub> supplements. Further research is required to determine the suitable level of Mg or Ca salts and PO<sub>4</sub> for struvite crystallization during MAP precipitation. This study was carried out to recognize the effects of exterior Mg and PO<sub>4</sub> addition and to determine the satisfactory pH and stirring speed for maximum struvite formation from wastewater.

Further, the plan of this work is to learn the precipitation problems in a wastewater treatment process. This work is a primary step to minimize the bad effects of wastewater by this treatment and finding solutions for phosphorus crises.

## Materials and Methods

The present study was conducted in the year 2013-2014 in the laboratories of the department of soil science and soil and water conservation and in the central research laboratory of Pir Mehr Ali Shah Arid Agriculture University Rawalpindi. The detailed of the study is given below.

### Collection and preparation of samples

Samples from sewerage water were collected from the entrance point of wastewater stream. Replicated samples were taken from selected locations, I-9 sector wastewater treatment plant (Islamabad), Nala Lai near Soan River Rawalpindi, H-8 sector Islamabad and Dhok kala khan in labeled plastic bottles. This study comprises sampling of waste water from these locations.

The laboratory experiment was carried out with three replications of each location. All the samples were kept at 4°C. All the analyses were performed at room temperature. Raw sewerage wastewater samples, which were collected during the study, have wide range of nutrient concentrations.

### Chemicals used in map/struvite precipitation

In this study, two chemicals namely: magnesium chloride hexa hydrate (MgCl<sub>2</sub>.6H<sub>2</sub>O) and tri sodium phosphate (Na<sub>3</sub>PO<sub>4</sub>) delivers good phosphorus treatment at relatively low cost. When precipitating chemicals are introduced in wastewater, they form inorganic crystals

with increasing pH levels. According to stoichiometric calculation (Mg<sub>2</sub><sup>+</sup>: NH<sub>4</sub><sup>+</sup>-N: PO<sub>4</sub><sup>3-</sup>-P=1.2:1:1), are the required dosages of chemicals for crystallization of struvite (Table 1).

Samples (g/mol)	Amount of NH <sub>4</sub> <sup>+</sup> -N in 400 mL of sewerage water (g)	Mg and P sources	Molecular weight	Amount of chemicals	
I-9(sector)	0.0184	MgCl <sub>2</sub> .6H <sub>2</sub> O Na <sub>3</sub> PO <sub>4</sub>		203.3 164.0	0.321 0.216
Nala Lai	0.0184	MgCl <sub>2</sub> .6H <sub>2</sub> O Na <sub>3</sub> PO <sub>4</sub>		203.3 164.1	0.314 0.211
H-8(sector)	0.0184	MgCl <sub>2</sub> .6H <sub>2</sub> O Na <sub>3</sub> PO <sub>5</sub>		203.3 164.2	0.258 0.173
DK Khan	0.014	MgCl <sub>2</sub> .6H <sub>2</sub> O Na <sub>3</sub> PO <sub>6</sub>		203.3 164.3	0.244 0.164

**Table 1:** Dosages of chemicals in 400 mL of the sewerage water at the stoichiometric ratio (Mg<sub>2</sub><sup>+</sup>:NH<sub>4</sub><sup>+</sup>-N:PO<sub>4</sub><sup>3-</sup>-P = 1.2:1:1).

### Struvite separation

Experiment was conducted for different experimental conditions which were investigated including pH levels (8.0, 8.5, 9.0, 9.5, 10.0, 10.5 and 11.0), Mg:N:P molar ratio (1.2:1:1) and with stirring speeds of 250 and 300 rpm. With these different parameters when one parameter was varied, the remaining parameters were kept constant. All experiments were carried out at room temperature. Two combinations of stirring speeds, seven combinations of pH and chemicals including MgCl<sub>2</sub>.6H<sub>2</sub>O+Na<sub>3</sub>PO<sub>4</sub> were conducted to precipitate the sewerage water.

Struvite separation were carried in order to maintain the ratio of Mg:N:P with amounts of Mg (MgCl<sub>2</sub>.6H<sub>2</sub>O) and PO<sub>4</sub>-P (Na<sub>3</sub>PO<sub>4</sub>) ions to be added was determined by stoichiometric calculation considering initial concentrations of ions in samples. Among these combinations, comprising of Mg:N:P ratio 1.2:1:1, pH values 8.0, 8.5, 9.0, 9.5, 10.0, 10.5 and 11.0; and stirring speed of 250 and 300 rpm for 30 min was used for MAP/struvite precipitation. In each MAP precipitation process, 100 mL of sewerage water was first poured into 100 mL flask and then chemicals used as magnesium and phosphate sources were added as required dosages. Samples were stirred continuously on a magnetic stirrer for about 15 min until an equilibrium state in terms of a stable pH was reached. After the chemicals addition the pH adjustment were made using 2N or 5N, NaOH solution. The samples were stirred continuously on stirrer for about 30 minutes, after that the mixture was allowed to settle down for 60 minutes in order to separate the precipitated crystals at the bottom of flask from liquid. Supernatant samples were collected and analyzed for further analysis.

### Analytical Methods

**Determination of pH:** All the samples were analyzed for pH using a calibrated pH meter through the method described by Page, et al. [16]. The sample was added in 50 mL conical flasks and reagent A and B were made as described in ammonium molybdate method. 10 mL of reagent B was added in the sample and volume was made. Blue colour developed after 30 minutes. The absorbance of the samples was measured at 880 nm wavelength. A blank was also run with the

samples. A series of standard solutions containing 0, 2, 4, 6 and 8 with the suitable volume of stock solution were made with distilled water.

50 mL of sample was distilled by distillation apparatus and added with about 100 mL of distilled water. Boric acid indicator was prepared by adding 20 g of boric acid in 900 mL hot distilled water and 20 mL of mixed indicator in it, later volume was made. After the distillation the distillate was titrated against 0.02 N H<sub>2</sub>SO<sub>4</sub> till the pinkish colour reappears. Magnesium concentration was determined with an atomic absorption spectrophotometer.

**Struvite analysis:** After MAP crystallization, precipitates were dried at 45°C in an oven for 2 days then weighed and analyzed for PO<sub>4</sub><sup>3-</sup>-P by dissolving in 0.1 M HCL and P contents were measured by ascorbic acid method using a spectrophotometer [17].

**Statistical analysis:** The data calculated were subjected to statistical analysis by using suitable statistical technique. The data obtained were subjected to analysis of variance (ANOVA) and LSD test was applied at 5% level of significance.

## Results and Discussion

This study was conducted to evaluate the quality of struvite precipitated in sewerage wastewater from different sources through various pH levels, with the addition of various P:Mg ratios and different stirring speeds. Results on various quality parameters of wastewater and struvite have been statistically interpreted and discussed in the following paragraphs:

### Characteristics of original sewerage water

The pH of original sewerage water collected from four sites ranged between 7.28-7.81 with mean value of 7.59 (Table 2). The pH value 7.81 of the sewerage water in Nala Lai (Rawalpindi) source was greater than that of all the other sources.

Locations	pH	PO <sub>4</sub> <sup>3-</sup> - P (mg L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> -N (mg L <sup>-1</sup> )	Mg <sup>2+</sup> (mg L <sup>-1</sup> )
I-9(sector)	7.51	59.5	46.0	42.0
Nala Lai	7.81	56.0	45.0	39.0
H-8(sector)	7.71	31.2	37.0	37.0
DK Khan	7.28	21.2	35.0	32.0
Average	7.59	42.0	40.8	37.5

**Table 2:** Characteristics of the sewerage water collected from four sites.

Phosphorus contents of sewerage water samples ranged from 21.2 to 59.5 mg L<sup>-1</sup> with the mean value of 42.0 mg L<sup>-1</sup>. The highest phosphorus contents (59.5 mg L<sup>-1</sup>) were in sewerage water from I-9 sector (Islamabad) being greater than that of all other sources. The NH<sub>4</sub><sup>+</sup> contents of sewerage water samples ranged from 35.0 to 46.0 mg L<sup>-1</sup> with mean value of 40.8 mg L<sup>-1</sup>. The NH<sub>4</sub><sup>+</sup> contents of I-9 sector sewerage water were 46 mg L<sup>-1</sup> being greater than that of all other sources. The Mg<sup>2+</sup> contents of sewerage water samples ranged from 32.0 to 42.0 mg L<sup>-1</sup> with mean value of 37.5 mg L<sup>-1</sup>. The Mg<sup>2+</sup> contents of I-9 sector sewerage water were 42 mg L<sup>-1</sup> being greater than Mg<sup>2+</sup> contents of all other sites.

The results indicated that pH of all sewerage waters was within the normal range even it contained a lot of acidic and basic materials transported from different industries or households. Further, the sewerage water continuously receives waste water containing organic matter. Contents of phosphorus and magnesium in sewerage water were in medium to high range; it could be due to continuous enrichment of sewerage water with residential and industrial wastes containing organic materials. The excreted P is dissolved into wastewater and transported to the sewerage system or infiltrates down to the groundwater. The NH<sub>4</sub><sup>+</sup> concentration in sewerage water was low being less than the normal range. This could be due to dilution of wastewater with rain water being added in the sewerage system a few days before sampling time. All these physico-chemical process parameters also depend on wastewater effluent's origin and treatment technology. Hence, this study was undertaken to optimize the conditions for struvite crystal formation and to provide a new data set under various process conditions.

### Weight of struvite crystals

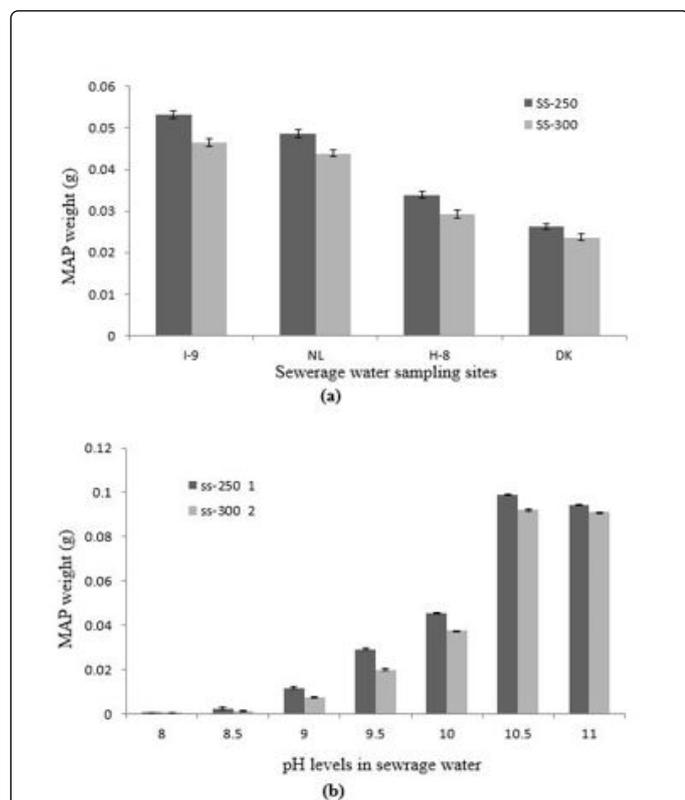
Struvite formation in the sewerage water after struvite precipitation process was significantly affected by variation in the stirring speeds and pH levels employed in sewerage water samples from different sources. Weight of struvite crystals under two stirring speeds was as 0.041 g at 250 and 0.036 g at 300 rpm. It reflected that 250 rpm stirring speed was more favourable and caused significantly greater precipitation. Low levels of stirring speed are appropriate for struvite precipitation because when precipitates are formed, they settle easily at the bottom. Ryu and Lee [18] found that among various stirring speeds 250 rpm was more suitable for MAP precipitation process. Several physico-chemical characteristics also influence these parameters such as mixing energy [19] (Figures 1-3).

Weight of struvite crystals in the sewerage water was also significantly affected by the pH levels. Weight of struvite crystals at pH 10.5 was highest (0.096 g) showing greater amount of struvite crystals than under all other pH levels. At pH 8.0, weight of struvite crystals was lowest because struvite precipitation process occurred at higher pH levels. So, this pH level of 10.5 was more desirable because most of the phosphorus was converted to the struvite crystals. Struvite precipitation process is highly pH dependent because the activities of both PO<sub>4</sub><sup>3-</sup> and NH<sub>4</sub><sup>+</sup> are pH dependent. At pH 8.0, the crystallization process was slow and at pH 10.5 the crystallization process was so high that white crystals were settled at the bottom. Supersaturation and pH have been reported to be the most influential parameters for struvite crystallization. Struvite is highly soluble under acidic pH and highly insoluble in alkaline pH [20].

Mass of struvite crystals formed in sewerage water collected from four sites differed significantly from each other. The highest weight of struvite crystals was that of I-9 sector (0.050 g), showing greater precipitation. Original analysis of wastewater showed that phosphorus contents were different with respect to sites. More crystals formation from I-9 sector site was due to higher contents of phosphorus in the original sewerage water. In general, struvite formation can be divided into two stages: nucleation and growth. Crystal formation primarily occurs by nucleation from combination of constituent ions called embryos and nuclei growth in sequence, i.e, enlargement of crystal until equilibrium. However, predicting or controlling these stages are complex as it is controlled with various physico-chemical factors, such as solution pH, mixing, crystal sizes, temperature and the presence of

foreign impurities [21]. Municipal wastewater contains variable amounts of N and P along with organic and inorganic substances.

struvite crystals obtained at higher pH levels in a range of 8.0 to 12.0 [26].



**Figure 1:** Weight of precipitated struvite crystals as influenced by stirring speed (a) from four sampling sites, and (b) at various pH levels.

Interactive effect of sampling sites with stirring speeds is shown in Figure 1a. Struvite crystals in the sewerage water after struvite precipitation process at different sites were significantly affected by the stirring speeds. Weight of struvite crystals ranged between 0.024 to 0.053 g. The highest weight of struvite crystals (0.053 g) was recorded in the sewerage water from I-9 sector site processed at 250 rpm stirring speed. Ryu and Lee [18] reported that among from various stirring speeds 250 rpm was the most appropriate for MAP precipitation process. Low levels of stirring speed are favourable for struvite precipitation because when precipitates are formed they settle easily at the bottom. It appears as irregular, unshaped and coarse crystals [22,23]. Further, the presence of impurities in solution can block or inhibit struvite crystals formation. These impurities may also increase or decrease the crystal size [24].

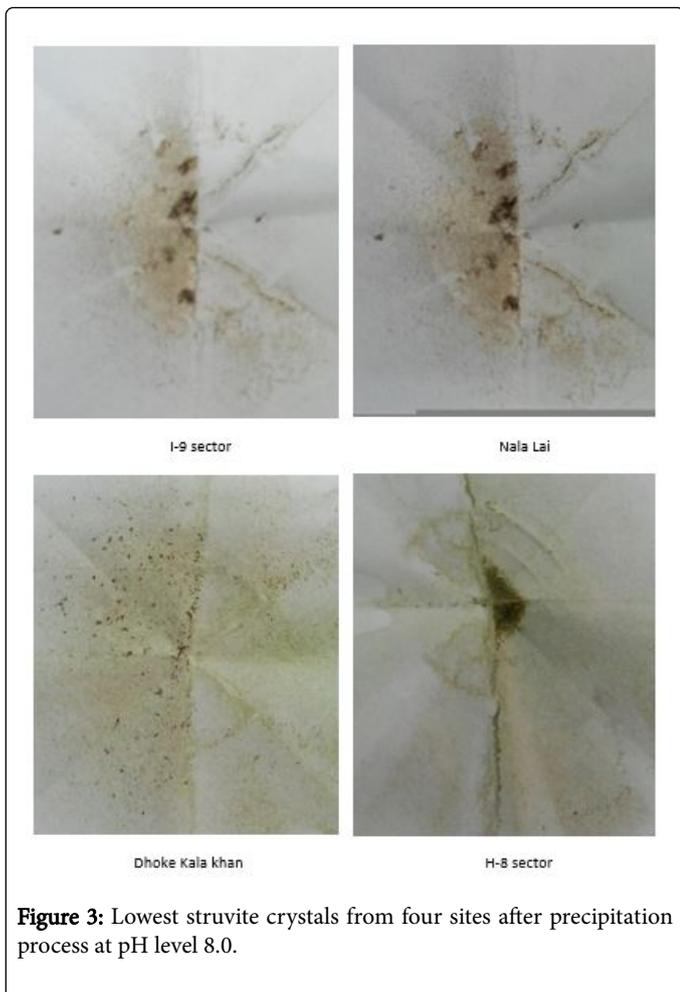
Interaction of sampling sites with the pH was also significant. Weight of struvite crystals ranged between 0.00 to 0.115 g, the highest weight of struvite crystals (0.115 g) was recorded in sewerage water sampled from I-9 sector site treated at 10.5 pH. The crystals form in an alkaline condition [25]. The crystals weight of I-9 sector site was higher due to the higher phosphorus contents in the original sewerage water, and crystals weight of Dhoke Kala Khan site was lowest due to lower phosphorus contents in the original sewerage water. Higher pH levels are suitable for crystallization process because greater weight of



**Figure 2:** Highest struvite crystals from four sites after precipitation process at pH level 10.5.

Weight of struvite crystals in the sewerage water were significantly affected by the interaction of various pH levels and stirring speeds (Figure 1b). Struvite crystals ranged from 0.001 to 0.099 g, the highest one at pH level of 10.5 with 250 rpm stirring speed. So, pH plays an important role in struvite precipitation process. Struvite precipitation is highly pH dependent [27]. At pH 8.0 the crystallization process was slow and at pH 10.5 the crystallization process was so high that white crystals were settled at the bottom. Higher pH was more desirable for struvite crystallization process because maximum crystals were obtained at higher pH levels [28] obtained the minimum struvite solubility between pH 10.3-10.7. This indicates that the effect of mixing was not only accelerates nucleation process but is also effective in the removal of nitrogen and phosphorus through struvite formation.

Interaction among stirring speed  $\times$  pH  $\times$  sampling sites of sewerage water was also statistically significant. Struvite crystals weight ranged between 0.00 to 0.116 g, and the highest one (0.116 g) found in I-9 sector site samples treated at pH 10.5 and 250 rpm of stirring speed. The crystals weight of I-9 sector site was higher due to the higher phosphorus contents in the original sewerage water. Crystal's weight of Dhoke Kala Khan site was lowest due to the lower phosphorus contents in the original sewerage water. Through simultaneous precipitation of phosphorus and nitrogen [29], some of the reported benefits include production of a slow release fertilizer [30].



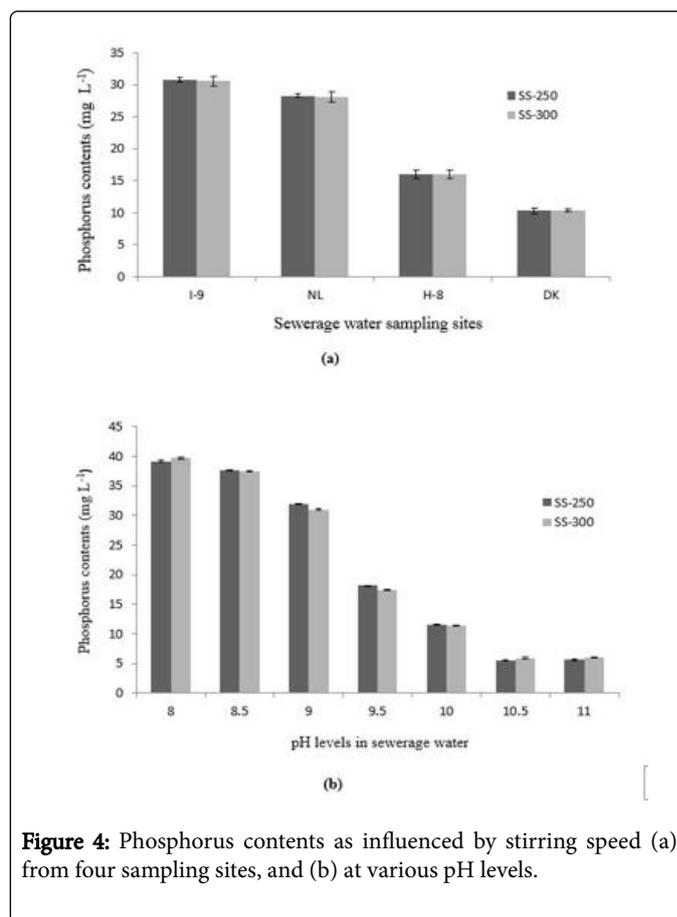
**Figure 3:** Lowest struvite crystals from four sites after precipitation process at pH level 8.0.

### Phosphorus contents in sewerage water

Phosphorus contents in the sewerage water after struvite precipitation process were significantly affected by variation in the stirring speeds and pH levels employed in sewerage water samples from different sources. Phosphorus contents under two stirring speeds were as  $21.3 \text{ mg L}^{-1}$  at 250 and  $21.4 \text{ mg L}^{-1}$  at 300 rpm. It reflected that 250 rpm stirring speed was more favourable and caused significantly greater precipitation. Low levels of stirring speed are satisfactory for struvite precipitation because when precipitates are formed they settle easily at the bottom. Ryu and Lee [18] found that among from various stirring speeds 250 rpm was more suitable for MAP precipitation process. Mixing energy showed strong results on the number of crystals formed and as a result, on their size [31].

Phosphorus contents in the sewerage water were also significantly affected by the pH levels. The lowest phosphorus contents at pH 10.5 were  $5.72 \text{ mg L}^{-1}$  showing greater phosphorus removal than under all other pH levels. So, this pH level of 10.5 was more desirable because most of the phosphorus was converted to the struvite crystals. So, the higher pH level was suitable for crystallization process because greater amount of struvite crystals obtained at high pH. Struvite precipitation process is highly pH dependent because the activities of both  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  are pH dependent [32].

During the struvite precipitation process phosphorus contents of sewerage water collected from four sites differed significantly from each other. The lowest phosphorus contents were that of I-9 sector ( $29.1 \text{ mg L}^{-1}$ ), showing greater phosphorus removal from I-9 sector site. These results showed that phosphorus contents were different with respect to sites, because there were more contents of phosphorus in the original sewerage water of I-9 sector site. Wastewaters contain a greater amount of organic matter, phosphorus and nitrogen [33] (Figure 4).



**Figure 4:** Phosphorus contents as influenced by stirring speed (a) from four sampling sites, and (b) at various pH levels.

After struvite precipitation process phosphorus contents in the sewerage water at different sites were significantly affected by the stirring speeds (Figure 2a). The phosphorus contents ranged between  $10.3$  to  $30.8 \text{ mg L}^{-1}$ . The lowest phosphorus contents ( $10.3 \text{ mg L}^{-1}$ ) were recorded in the sewerage water from Dhoke Kala Khan site processed at 250 rpm stirring speed. Low levels of stirring speed are favourable for struvite precipitation because when precipitates are formed they settle easily at the bottom. Ryu and Lee [18] found that among from various stirring speeds 250 rpm was the more active for MAP precipitation process.

Interaction of sampling sites with pH was also significant. Phosphorus contents in the sewerage water collected from different sites ranged between  $3.5$  to  $56.7 \text{ mg L}^{-1}$ . The lowest phosphorus contents  $7.53 \text{ mg L}^{-1}$  was recorded in sewerage water sampled from I-9 sector site with 10.5 pH. Ali [34] stated that the formation of struvite depends upon the reactant concentration and solution pH. Higher pH levels are suitable for crystallization process because greater precipitation obtained at higher pH. Solution pH is one of the important factor for the removal of nutrient such as nitrogen and

phosphorus from solution by struvite precipitation [35]. So, pH plays an important role in struvite precipitation process. The MAP precipitation success depends on different factors but pH of the solution is one of the main factor [36].

Phosphorus contents in the sewerage water after struvite precipitation process were significantly affected by the interaction of various pH levels and stirring speeds (Figure 2b). Phosphorus contents ranged from 5.53 to 39.75 mg L<sup>-1</sup>, the lowest one at pH level of 10.5 with 250 rpm stirring speed. Low levels of stirring speed and high levels of pH are useful for struvite precipitation. Several physico-chemical characteristics also influence these parameters such as mixing energy [37]. Struvite precipitation process is highly pH dependent because the activities of both PO<sub>4</sub><sup>3-</sup> and NH<sub>4</sub><sup>+</sup> are pH dependent.

Interaction among stirring speed × pH × sampling sites of sewerage water was also statistically significant. Phosphorus contents ranged between 3.47 to 56.07 mg L<sup>-1</sup>, and the lowest one (7.13 mg L<sup>-1</sup>) was found in I-9 sector site samples treated at pH 10.5 and 250 rpm of stirring speed. Ali [34] found that the formation of struvite depends upon the reactant concentration and solution pH. Precipitates formed at alkaline pH and settled at the bottom with low stirring speed. Struvite precipitation process is pH dependent and 250 rpm stirring speed was more desirable, because higher percentage of P removal achieved through struvite formation with increase in solution pH.

### Phosphorus removal from sewerage water

Phosphorus removal in the sewerage water after struvite precipitation process was non-significant by variation in stirring speeds employed in sewerage water samples from different sources. Phosphorus removal under two stirring speeds was as 49.15% at 250 and 49.37% at 300 rpm. It reflected that Phosphorus removal in the sewerage water as influenced by stirring speed and pH variation from different sources (%) (Figure 5).

Applied stirring speed was non-significant. So, applied stirring speeds were not suitable for P removal contents. Uludag-Demirer and Othman [38] stated that there was no significant effect of stirring on struvite precipitation. Statistical analysis indicated that there was no significant effect of introducing the stirring speeds of 250 rpm or more than 250 rpm on the removal percentage of P. In the current experiment, with the increase in levels of stirring speed there was no significant effect on phosphorus removal. Several physico-chemical characteristics influence these parameters, such as mixing energy [39].

Phosphorus removal in the sewerage water after struvite precipitation process was also significantly affected by the pH levels. Phosphorus removal at pH 10.5 was highest (84.05%) showing greater phosphorus removal than under all other pH levels. So, this pH level of 10.5 was more desirable because most of the phosphorus was converted to the struvite crystals. So, higher pH levels were suitable for crystallization process because maximum struvite crystals obtained at high pH levels. Struvite precipitation process is highly pH dependent because the activities of both PO<sub>4</sub><sup>3-</sup> and NH<sub>4</sub><sup>+</sup> are pH dependent [40].

After struvite precipitation process, phosphorus removal of sewerage water collected from four sites differed significantly from each other. The lowest phosphorus removal was that of H-8 sector was (48.16%) and that of Dhoke Kala Khan was 50.79%, showing greater phosphorus removal. Britton et al. [41] reported 30-90% P removal with NaOH addition. These results showed that phosphorus contents were different with respect to sites, because there were less contents of

phosphorus in the original sewerage water of Dhoke Kala Khan but phosphorus removal percentage from this wastewater was high. On the other hand, it is important to remove the environmentally harmful free ammonia and phosphorous, as controlled precipitation of struvite in the sewerage and other wastewater channels [42].

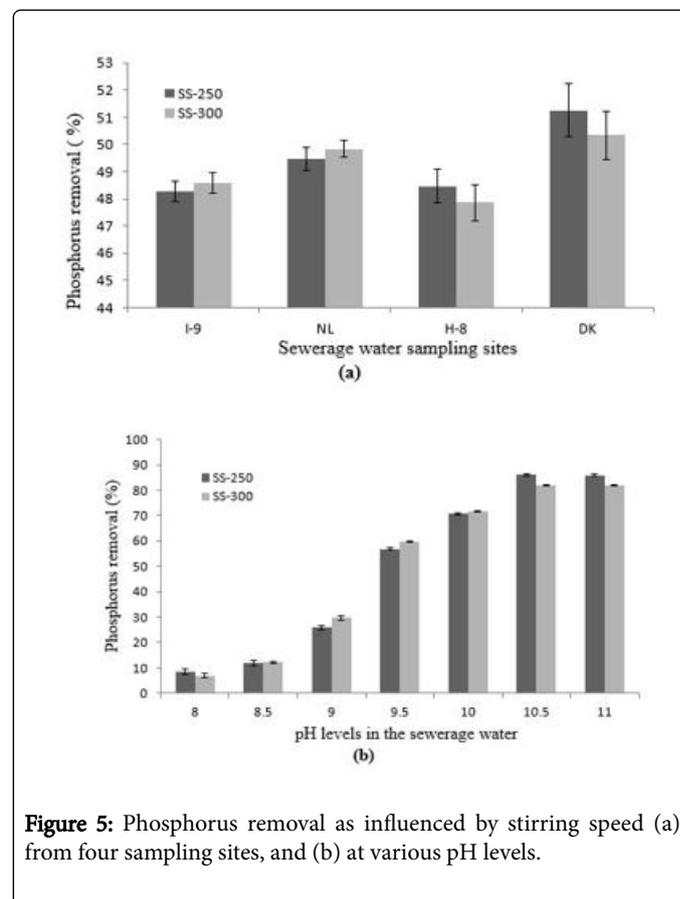


Figure 5: Phosphorus removal as influenced by stirring speed (a) from four sampling sites, and (b) at various pH levels.

Interactive effect of sampling sites with stirring speed is shown in Figure 3a. Phosphorus removal in the sewerage water after struvite precipitation process at different sites was non-significant with respect to stirring speed. Uludag-Demirer and Othman [38] reported that there was no significant effect of stirring on struvite precipitation. The phosphorus removal ranged between 47.86 to 51.25%. The highest phosphorus removal (51.25%) was recorded in the sewerage water from Dhoke Kala Khan site processed at 250 rpm stirring speed. Ryu and Lee [18] stated that among from various stirring speeds 250 rpm was more a suitable for MAP precipitation process. Low levels of stirring speed are favourable for struvite precipitation because when precipitates are formed they settle easily at the bottom under low stirring speed.

Phosphorus removal in the sewerage water collected from different sites was also significantly affected by the pH levels, ranged between 3.35 to 87.33%. The highest phosphorus removal (87.33%) was found in sewerage water sampled from I-9 sector site with 10.5 pH. Tao et al. [43] also reported 84-92% P removal in the wastewater by higher pH levels. Solution pH is one of the important factor for the removal of nutrient such as nitrogen and phosphorus from solution by struvite precipitation [35,44]. Higher pH was suitable for crystallization process because greater amount of struvite crystals obtained at higher

pH. The MAP precipitation success depends on different factors but pH of the solution is one of the main factor [25].

Removal percentage of phosphorus in the sewerage water after struvite precipitation process was significantly affected by the interaction of various pH levels and stirring speeds (Figure 3b). Phosphorus removal ranged from 6.9 to 86.1%, the highest one was 86.1% at pH level of 10.5 with 250 rpm stirring speed. Sakthivel et al. [36] found that P removal results were also greater than the 84% with NaOH addition.

Interaction among stirring speed  $\times$  pH  $\times$  sampling sites of sewerage water was also statistically significant. Phosphorus removal ranged between 2.4 to 88%, and highest one (88.0%) was found in I-9 sector site samples treated at pH 10.5 and 250 rpm of stirring speed. Uludag-Demirer and Othman [38] reported that there was no significant effect of stirring on struvite precipitation. Struvite precipitation process is pH dependent. More crystals obtained with the increasing pH levels. De-Bashan and Bashan [45] reported that a pH value greater than 7.5 is precondition for struvite crystallization. The both  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ion activities are pH dependent [46].

## Conclusion

The MAP precipitation significantly reduced the contents of  $\text{PO}_4^{3-}$  in sewerage water from different sites. This study shows that struvite recovery from sewerage water is technically feasible. Therefore, this technology provides opportunities to recover phosphorus sustainably from sewerage water and preserve phosphorus reserves. The recovery of struvite is technically feasible and economically beneficial so, it's necessary to develop the optimal conditions for small-scale and commercial production of struvite.

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