

Impact of Magnesium Source on the Yield and Structure of struvite

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Abstract— Magnesium ammonium phosphate, also known as struvite, is a salt that forms spontaneously in water that contains equimolar ratios of its components - phosphates, magnesium and ammonia. Recently, researchers have studied struvite precipitation with an intention to recover phosphorus. Wastewater has been identified as a suitable source to synthesize struvite to recover phosphorus instead of discarding it to surface water bodies in large quantities. Municipal wastewater is rich in phosphorus and toxic nutrients like ammonia which negatively impact the environment and pollute natural water sources. Struvite synthesis provides an opportunity to beneficiate wastewater and then removed ammonia and phosphate can be used as a slow-release fertilizer. The drawback of using wastewater is that magnesium is usually the limiting ion and it must be added as a precursor to allow for struvite precipitation. Various magnesium sources have been used in previous studies and compared based on the quality of the struvite they form, cost, availability, morphology and the yield of struvite. This study focused on the use of magnesium oxide (MgO) and calcined magnesite (MgCO₃) as magnesium sources to precipitate struvite. Experimental results showed that MgCO₃ had a greater precipitate yield than MgO, MgO had a higher phosphorus recovery and the ammonia recovery was approximately equal to that of MgCO₃.

Keywords— Struvite, Wastewater, Magnesium, Phosphorus

I. INTRODUCTION

The recovery of struvite (MgNH₄PO₄•6H₂O) is quite an established activity because it has been identified as a feasible method to recover phosphorus from wastewater. Laboratory scale experiments have been conducted on struvite precipitation for various research topics and wastewater sources. Municipal wastewater has been reported as the source of significant amounts of phosphorus [1]. The removal of ammonia from wastewater through struvite precipitation has been explored by researchers and proven as efficient. Ammonia-nitrogen is removed from water using air stripping, biological nitrification-denitrification, breakpoint chlorination, ion exchange or chemical precipitation [1][3]. The removal of both phosphorus and ammonia from wastewater limits their

environmental impact; they promote eutrophication on surface water bodies which in turn affects water quality and all aquatic living organisms [4] and [5]. Struvite precipitation serves the purpose of recovering these nutrients for reuse and protecting the aquatic environment from pollution. Struvite can be used as an alternative fertilizer because of the high nutrient recovery efficiency from its precipitation and its slow nutrient release characteristics into the soil [3]. The reuse of phosphorus is beneficial because it is a finite resource, the phosphate rock is approaching possible depletion in the world; therefore the use of struvite as fertilizer has the potential to close the open phosphorus cycle and reduce the rate of phosphate rock mining [1], [6] and [7].

For struvite precipitation to occur, the molar ratio between magnesium, phosphate and ammonia (Mg:PO₄:NH₄) in the wastewater needs to be 1:1:1 but magnesium is usually the limiting ion in the water [8]. The reaction is dependent on the Mg:P:NH₄ molar ratio, temperature, mixing energy, reaction time and pH. A magnesium source needs to be added to the wastewater as a precursor to increase the magnesium concentration and allow for an equimolar stoichiometric ratio between the ions for struvite precipitation. Struvite precipitation is spontaneous, with an optimal temperature range of 15°C - 35°C and an alkaline pH range of 9-10.5 has been reported as optimal [1] and [3]. The reaction is affected by the presence of foreign ions, the co-precipitation of other compounds with struvite affect its purity, quality and yield. Research has recently shifted on finding alternative magnesium sources to use for struvite precipitation. The use of commercial magnesium salts is costly and this has contributed to the slow development of struvite precipitation at large scale. The use of affordable, energy-efficient and easily accessible magnesium sources has been explored by many researchers and their experiments were successful but with a few disadvantages. These alternatives included desalination brine, seawater, wood ash, bittern and by-product magnesite [2], [6] and **Error! Reference source not found.** The main disadvantage is the presence of competing ions in these magnesium sources. A Feedstock Sustainability Index was developed by [1] and it ranks wastewater sources according to their suitability for struvite precipitation. Fertilizer industry wastewater, cochineal insects processing wastewater, human urine and landfill leachate were ranked higher than municipal wastewater. For industrial scale, the use of these top-ranked wastewater sources will be efficient if the target is to maximize struvite yield and nutrient recovery.

Most of the studies have used MgCl₂ as the source of magnesium [5, 6] for the precipitation of struvite from

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wastewater; however, our previous review [7] reported that the source of magnesium could influence the properties of struvite. This study aims to compare struvite produced from two sources of magnesium, MgO and MgCO₃, the comparison is based on the quality of struvite and the yield obtained from each magnesium source.

II. MATERIALS AND METHODS

A. Sampling

Wastewater was collected from Zeekoegat wastewater treatment works in Pretoria, South Africa (25°37'15"S 28°20'05"E). The water was collected from a digester's supernatant liquid known to have significant concentration levels of ammonia and phosphates. The constituents of the sewage wastewater were determined and are presented in Table I and Table II.

B. Chemicals and reagents

Two different magnesium sources were used as precursors for struvite synthesis, namely, magnesium oxide (MgO) and calcined magnesite (MgCO₃). (MgO) was purchased from Associated chemical enterprises, South Africa and it was used as an analytical grade, the calcined cryptocrystalline magnesite is a local magnesium source and it was used without any further treatment.

C. Experimental procedure

Suspended solids in the wastewater were filtered using 150 mm ashless filter paper. Batch experiments were conducted at lab-scale and at varied Mg/P molar ratios in triplicates. Temperature range, pH range, mixing energy and mixing time were kept constant. The Mg/P ratios studied were 1:1 and 1.2:1, temperature range of the wastewater was kept between 21°C - 25°C and the pH range was 10.00 - 10.50. 500 mL of the filtered raw sample was used for every run in 1L beakers, the experiments were conducted in triplicates for each magnesium source at the two different Mg/P ratios. Magnetic stirrers were used to mix the solutions for 30 minutes and the beakers were sealed with parafilm. The residence time was varied for some of the runs to test the relationship between residence time and yield. Residence times of 3 hours, 18 hours and 48 hours were used. The crystals formed were filtered and collected through vacuum filtration (through the 150 mm ashless filter paper) and dried in an oven overnight at 38°C. The residual water from each run was filtered through 0.45µm syringe filters before they were sent for analysis. The initial pH of the raw wastewater was 7.10.

D. Dosage

Equation (1) was used to calculate the percentage of magnesium available in each of the magnesium sources to ensure that the right amount of magnesium (in grams) was added to the wastewater for struvite precipitation to take place.

Percentage composition by mass

$$= \frac{\text{molar mass of element} \times N}{\text{molar mass of compound}} \times 100 \quad (1)$$

Where N is the number of that element in the compound.

The data in Table I was used to calculate the suitable magnesium dosage to achieve the Mg/P ratio of 1:1 for the first run of experiments and 1.2:1 for the second run of experiments.

III. ANALYTICAL METHODS

The ion concentrations of PO₄³⁻, NH₄⁺ in the raw water sample were analyzed by ion chromatography (IC) Metrohm make - Compact 930 AnCat Flex IC Chromatograph, and the Mg ions and other metals were analyzed using an inductively coupled plasma-optical emission spectrometry (ICP-OES) Agilent make - ICP OES 725. The residual water was analyzed to determine the concentration of the remaining ions in the water after struvite precipitation. The dried crystals were measured on a bench scale to determine the yield in grams.

TABLE I: IC RAW WASTEWATER CONSTITUENTS IN MG/L

Component (mg/L)	IC result
PO ₄ ³⁻	543.217
NH ₄ ⁺	559.114
Cl ⁻	76.009
SO ₄ ²⁻	30.530
Na ⁺	70.938
K ⁺	82.651
NO ₃ ⁻	7.545

TABLE II: ICP RAW WASTEWATER CONSTITUENTS IN MG/L

Component (mg/L)	ICP result
Mg ²⁺	48.305
Ca ²⁺	44.799
Na ⁺	64.804
K ⁺	82.527

IV. RESULTS AND DISCUSSION

A. Yield

The dry struvite crystals from each run were measured separately and the yield results are given in Table III and Table IV. The yield of the synthesized struvite (in grams) increased with the magnesium source dosage. Residence time of 48 hours and less did not have an impact on the yield of struvite, there was no significant difference in mass when residence time was 3 hours, 18 hours and when it was changed to 48 hours.

TABLE III: YIELD OF STRUVITE CRYSTALS AT 1:1 MG/P RATIO

Magnesium source	Run 1 (g)	Run 2 (g)	Run 3 (g)
MgO	1.692	1.659	1.632
MgCO ₃	2.707	2.599	2.571

TABLE IV: YIELD OF STRUVITE CRYSTALS AT 1.2:1 MG/P RATIO

Magnesium source (g)	Run 1 (g)	Run 2 (g)	Run 3 (g)
MgO	1.741	1.728	1.756
MgCO ₃	2.852	2.875	2.884

B. Efficiency of Phosphorus and ammonia recovery

Phosphorus and ammonia recoveries were calculated using Equation (2).

Nutrient recovery

$$= \left(\frac{X_{initial} - X_{final}}{X_{initial}} \right) \times 100\% \tag{2}$$

Where X is the nutrient in mg/L.

The IC report of the residual water indicates that 99.7% of the PO₄³⁻ was removed from the raw water when MgCO₃ was used as a pre-cursor at a Mg/P ratio of 1:1. When the Mg/P ratio was increased to 1.2:1, the percentage removal was 98.5%, indicating that the equimolar ratio was optimal for the calcined magnesite magnesium source. The removal of ammonia was 83.4% at a Mg/P ratio of 1:1 and it increased to 89.9% when the Mg/P was increased to 1.2:1. The pH was kept at 10.00 throughout the reactions.

The calcined magnesite is a good magnesium source for nutrient recovery, it also provided the highest yield compared to MgO. It can thus be used to clean wastewater from these nutrients to prevent eutrophication. In both cases, the phosphorus and ammonia recovery is very high and this is favorable if the struvite is to be used as a slow release fertilizer. The IC results of the residual water (at Mg/P ratio of 1:1) are presented in Table V. Table VI presents the results at Mg/P ratio of 1.2:1. All data were considered acceptable because the standard deviation of the samples is less than 10%.

TABLE V: 1:1 - IC RESIDUAL WASTEWATER RESULTS IN MG/L FOR MGCO₃

Component (mg/L)	Run 1	Run 2	Run 3
Mg ²⁺	109.337	141.753	120.401
PO ₄ ³⁻	1.310	1.608	-
NH ₄ ⁺	76.298	96.078	94.111
SO ₄ ²⁻	34.480	36.217	36.543
Na ⁺	137.753	137.867	116.752
Ca ²⁺	17.658	13.833	21.472

-: Not detected

TABLE VI: 1.2:1 - IC RESIDUAL WASTEWATER RESULTS IN MG/L FOR MGCO₃

Component (mg/L)	Run 1	Run 2	Run 3
Mg ²⁺	123.780	146.520	130.760
PO ₄ ³⁻	5.980	10.920	6.820
NH ₄ ⁺	59.390	54.820	55.080
SO ₄ ²⁻	40.510	38.420	34.330
Na ⁺	61.250	64.460	58.780
K ⁺	75.060	78.510	76.48
Ca ²⁺	14.850	24.700	23.980
NO ₃ ⁻	20.440	14.790	11.710

All the PO₄³⁻ was successfully removed from the raw water when MgO was used at a Mg/P ratio of 1:1. When the Mg/P ratio was increased to 1.2:1, the percentage PO₄³⁻ removal was 98.8% and this indicates that the equimolar ratio was optimal for a MgO pre-cursor. The addition of MgO into the wastewater increased the pH from 7.10 to approximately 10.50 and it was observed that dosage does affect pH because when the Mg/P ratio was increased, the pH increased to 10.80. This increase in pH might be the reason why the recovery of PO₄³⁻ decreased by 1.2%. A PO₄³⁻ recovery of 98.8% is still high and the struvite crystals are eligible to be reused.

At a Mg/P ratio of 1:1, 83.9% ammonia was removed and it increased to 89.5% when the Mg/P ratio was increased to 1.2:1.

It is observed that for both magnesium sources, an increase of their dosage increases the ammonia removal, the phosphorus removal decreases but the effect is not very significant. Both recoveries at a Mg/P ratio of 1.2:1, pH between 10 and 10.80, temperature of 24°C and a mixing time of 30 minutes were viable. Residence time did not affect nutrient recovery.

The IC results of the MgO residual water (at Mg/P ratio of 1:1) are presented in Table VII and Table VIII presents the results at Mg/P ratio of 1.2:1.

All data were considered acceptable because the standard deviation of the samples is less than 10%.

TABLE VII: 1:1 - IC RESIDUAL WASTEWATER RESULTS IN MG/L FOR MGO

Component (mg/L)	Run 1	Run 2	Run 3
Mg ²⁺	192.690	192.690	192.643
PO ₄ ³⁻	-	-	-
NH ₄ ⁺	96.964	96.964	76.594
Cl ⁻	79.471	79.471	79.842
SO ₄ ²⁻	33.842	33.613	33.931
Na ⁺	73.318	67.172	74.719
K ⁺	80.779	80.779	75.177
Ca ²⁺	11.028	11.154	14.952

-: Not detected

TABLE VIII: 1.2:1 - IC RESIDUAL WASTEWATER RESULTS IN MG/L FOR MGO

Component (mg/L)	Run 1	Run 2	Run 3
Mg ²⁺	176.55	179.81	193.21
PO ₄ ³⁻	6.540	5.780	7.900
NH ₄ ⁺	66.470	53.900	55.550
SO ₄ ²⁻	35.310	46.560	32.990
Na ⁺	65.030	60.830	59.550
K ⁺	79.580	75.700	73.99
Ca ²⁺	11.440	8.580	3.330
NO ₃ ⁻	25.590	19.980	11.780

V. CONCLUSION

The aim of this study was to synthesize struvite from different magnesium sources and assess the quality. The results indicate that the magnesium sources used are efficient for nutrient recovery. The results show how the dosage and type of magnesium source affect the precipitate yield and the nutrient recovery. It was observed that the yield is dosage sensitive, an increase if the Mg/P ratio increases. An increased magnesium dosage (1.2:1 Mg/P ratio), increases the recovery of ammonia by >5% compared to when the ratio was 1:1. Phosphorus recovery was not affected significantly, the recovery was decreased by <2%, this applies to both magnesium sources. To maximize the removal of both nutrients, the 1.2:1 ratio should be used.

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