

Phosphorus Recovery from Source-Separated Urine under Hydrothermal Conditions

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Introduction

Phosphorus is an important fertilizer. However, due to dwindling resources and high energy required for extraction, the price of phosphate fertilizers is increasing². Also, phosphorus needs to be removed from wastewater to decrease harmful environmental impacts. Nutrients released into the environment can cause eutrophication, or excess plant and algae growth¹ that has negative ramifications in ecosystems and economies. If a phosphorus-based fertilizer replacement could be recovered from wastewater, it could be sold to offset the costs of treatment and reduce eutrophication.

Source-separated urine is the separation of urine from feces at the source, rather than leaving them to be treated together. Though mostly used in developing countries and in a few European countries³, its implementation shows promise for nutrient recovery. Urine accounts for only about 1% of total wastewater volume, yet it contains 50% of the total phosphorus⁴. From urine, phosphate can be precipitated in the form of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). Struvite can be used as a fertilizer, and its effectiveness compares well with mineral phosphate fertilizers used currently².

Hydrothermal treatment is the simulation of high temperature and pressure conditions present under the Earth's crust for the formation of minerals. Typically, a hydrothermal reaction is any reaction that occurs above room temperature at a pressure greater than 1 atm in a closed system⁵. Some studies exist on struvite crystallization from hydrothermal treatment of wastewater⁶, but little data exists for the hydrothermal treatment of source-separated urine for phosphate recovery. This study aims to investigate the precipitation of struvite from source-separated urine at both ambient and hydrothermal conditions to determine if a hydrothermal treatment increases the precipitation of struvite.

Materials and Methods

Synthetic Urine

Synthetic human urine was used in both ambient and hydrothermal tests. Synthetic urine was used due to easier management and little difference between it and real urine⁷. The compositions of both synthetic fresh urine (SFU) and synthetic hydrolyzed urine (SHU) are

summarized in Table 1 and were adapted from previous literature⁸.

Table 1 – Compositions of Synthetic Urine⁸

Chemical (mol/L)	SFU	SHU
Urea as N	0.500	-
NaCl	0.044	0.060
Na_2SO_4	0.015	0.015
KCl	0.040	0.040
NH_4OH	-	0.250
NaH_2PO_4	0.020	0.014
NH_4HCO_3	-	0.250
MgCl_2	0.004	-
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.004	-
pH	6	9
Ionic strength	0.15	0.47

Chemical Modelling

Version 3.1 of Visual MINTEQ (VM) was used to model mineral speciation at ambient conditions. The compositions of synthetic urine listed in Table 1 were examined, with the addition of varying concentrations of added magnesium chloride (MgCl_2). The pH and level of hydrolysis were also varied.

After the program ran, the saturation indices were examined to pick out solids that might form. These solids were added to the list of possible solids, and the simulation was performed again before extracting data.

Ambient Conditions

Sixteen separate tests were run at ambient conditions. The variations between each of these are summarized in Table 2. Magnesium must be added in order to see a significant amount of phosphate precipitation. This was done by adding varying levels of MgCl_2 . Each solution was prepared then stirred constantly for eight days to allow them to come to equilibrium. A sample of the solutions was taken and filtered after 1, 4, and 8 days. These samples submitted for inductively coupled plasma optical emission spectrometry (ICP-OES) to determine phosphorus and magnesium concentrations after precipitation had occurred. After the eighth day, any precipitate that formed was also collected for possible later analysis.

Table 2 – Ambient Condition Variation Summary

Parameter	Values
pH	6, 9, & 11
Added MgCl_2	0M, 0.007M, 0.014M, & 0.028M
% Hydrolysis	0% (SFU) & 100% (SHU)

Hydrothermal Conditions

The same solutions as summarized in Table 2 were tested under hydrothermal conditions, except combinations at pH 11 or with 0.007 M added MgCl_2 , which were omitted in the interest of time. Each solution

was subject a hydrothermal treatment at 75, 150, 225, and 300°C. For each test, the prepared solution was sealed in a hydrothermal reactor, then allowed to sit in a sand bath at the correct temperature for 30 minutes. Each solution was collected after the hydrothermal treatment and prepared for ICP-OES. Any precipitate that formed was also collected for possible later analysis.

Results and Discussion

Visual MINTEQ

Figure 1 (SFU) and Figure 2 (SHU) both depict phosphate concentration at equilibrium. A lower phosphate concentration indicates more phosphate precipitation. For SFU, more phosphate precipitated at an increased pH. For SHU, phosphate precipitation was best between a pH ~7 to a pH ~9. Both SFU and SHU showed an increase in phosphate precipitation when the concentration of added magnesium was increased.

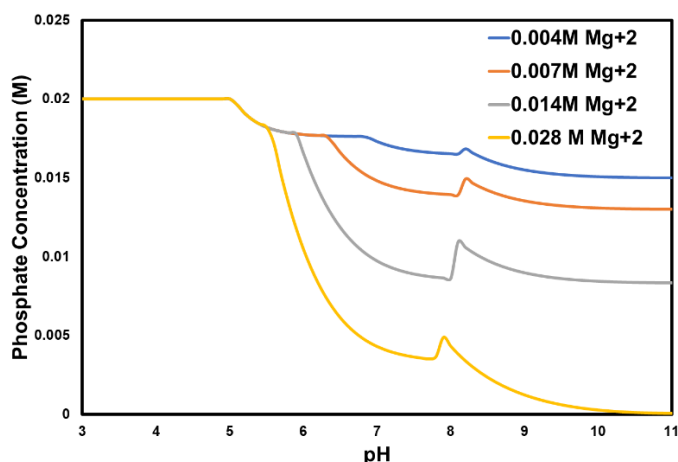


Figure 1: Phosphate concentration in SFU at equilibrium for variable pH and different added magnesium concentrations.

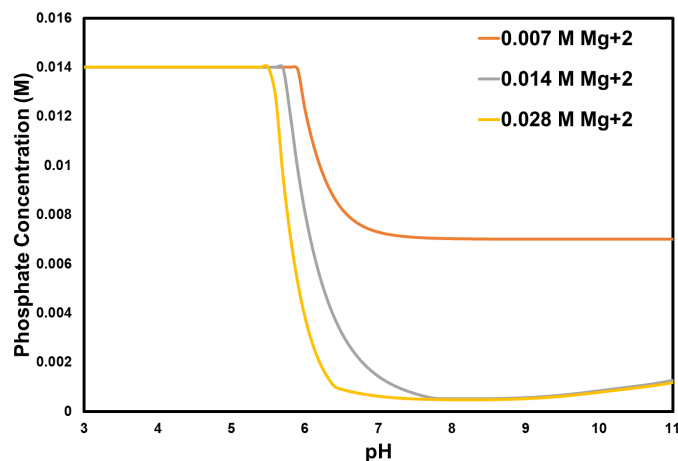


Figure 2: Phosphate concentration in SFU at equilibrium for variable pH and different added magnesium concentrations.

Ambient Conditions

ICP-OES results have not been received at this time. As such, it is not possible to state at which ambient conditions struvite best precipitated. However, some qualitative observations can be given, as well as the precipitates that VM predicted for each ambient condition.

Nearly all the SFU tests showed precipitation. The precipitate is unlikely to be struvite because the half-life for the uncatalyzed hydrolysis of urea is estimated to be on the order of years⁹, so there is likely to be no ammonium present for struvite formation in these solutions. VM indicated that at pH 6 and at varying additions of MgCl₂, hydroxyapatite (HAP) and MgHPO₄·3H₂O would precipitate. At a pH of 9 or 11 and varying additions of MgCl₂, HAP and Mg₃(PO₄)₂ were predicted to precipitate. While the desired mineral struvite it likely not being formed, phosphorus is still being removed from the urine.

All the SHU tests that had added MgCl₂ showed precipitation. VM indicated that only struvite would precipitate for a pH of 9 with a molar ratio of magnesium to phosphate of 1:2. All other solutions had predicted precipitation of both struvite and magnesite (MgCO₃). MgCO₃ will form in small quantities unless magnesium is present in excess relative to phosphate, i.e. molar ratio >1. Aside from this case, the desired mineral struvite should be the main product for the SHU tests.

Hydrothermal Conditions

ICP-OES results have not been received at this time. As such, it cannot be stated whether the hydrothermal treatment increased struvite precipitation in either SFU or SHU. VM is only reliable for ambient conditions, so it cannot predict mineral speciation for hydrothermal treatment.

The pH of the solutions was measured after hydrothermal treatment. For SFU, the pH changed from ~6 before treatment to about ~9 after treatment for temperatures at 150°C and higher. This indicates that hydrothermal treatment caused the rapid hydrolysis of urea, and struvite may have formed in SFU, when it likely did not at ambient conditions. If this is the case, struvite could be obtained from fresh urine quickly, rather than having to wait for the urine to hydrolyze naturally to recover a phosphate fertilizer.

Conclusions

Based on computer models, struvite will only form in hydrolyzed urine unless some degree of hydrolysis occurs in fresh urine. Though struvite does not precipitate from fresh urine, phosphorus is still removed via other minerals. It is unclear if hydrothermal conditions improved struvite precipitation. Fresh urine does appear to undergo hydrolysis during treatment, which would reduce the time required to obtain struvite from source-separated urine.

Once numerical results are obtained, the practicality of using a hydrothermal treatment for struvite precipitation will be assessed. If the results are promising, these tests will be replicated and seek more data on the hydrolysis of urea at both ambient and hydrothermal conditions. Struvite crystals will also be examined using electron microscopy. The hydrothermal treatment may form a crystal that makes phosphate more bioavailable.

References

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