



Storage of urine as a pre-treatment for struvite recovery

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ABSTRACT

Struvite (magnesium ammonium phosphate) is a bioavailable fertilizer that has had been successfully recovered from traditional wastewater treatment plant effluents. Since urine is a richer and more concentrated source of phosphorus, it makes sense to recover struvite from the urine collected in dry toilets.

Traditional struvite recovery from wastewater effluents requires the addition of a caustic to increase pH and achieve supersaturated conditions necessary for precipitation. This work demonstrates that, by utilizing the urease-driven pH increase, the requirement for a pH modifier disappears, and thus additional cost, is removed.

By removing calcium and other non-desirable compounds and allowing the pH to naturally attain an ideal working range, only magnesium needs to be added to recover a pure struvite product. It is shown then, that the storage of urine is an essential step to recovering struvite, not in fact, an obstacle to overcome.

INTRODUCTION

As the finite phosphorus resources which buoy global agriculture deplete [1], the billions without adequate sanitation increase, and the limited supply of freshwater becomes undrinkable, we must rapidly develop the understanding and technology necessary to adapt to a changing world. In light of the prohibitively expensive infrastructure that is inappropriate to most parts of the world, the significant requirements of freshwater, the valuable nutrient losses, and the concerns over residual disposal, it is obvious that the current paradigm of water-based sanitation will not be sustainable indefinitely. However, despite growing localized acceptance of alternative EcoSan systems [2,3] widespread urine separation and collection is a ways off. This research addresses this reality gap by proposing a method for nutrient recovery that is accessible, acceptable and sustainable.



The University of British Columbia has long been a pioneer in the field of phosphorus removal. Researchers were among the first to lay the foundation of Bio-P mechanisms (i.e. the hyper-accumulation of phosphorus by organisms) [4,5,6] whereas current research focuses on the removal and recovery of phosphorus in the form of struvite [7,6,8,9]. Struvite ($MgNH_4PO_4 \cdot H_2O$) is a renewable phosphate fertilizer that has been recovered from wastewater and sold in Japan since the 1990s [10]. The UBC technology for struvite recovery has been operational for several years, but to date, struvite has only been harvested from dilute waste streams. The concurrence of this technology with the need to turn urine into a more useful, manageable resource, naturally points the way to struvite recovery.

As interest in urine separation has grown, so has the need to better understand the complex urine dynamics. Recent research has shown that urine, in the presence of urease, shows a rapid increase in pH and ammonia concentration [11,12] and Udert et al have shown that as a result of this natural conversion, spontaneous precipitation of calcium-based compounds is induced [13,14]. Further work has actually shown that struvite can be recovered in the laboratory with sterile urine and the use of a caustic for pH control [15,16].

Building on this growing body of knowledge, the goal of this research was not only to recover pure struvite from urine, but to do so a) without the addition of a caustic for pH control and b) to do so in a way that could be replicated outside of laboratory controlled conditions. A key feature of this research was to understand how dilution, storage, and faecal contamination would impact the feasibility of using urine as a feedstock for struvite recovery. This was important since a real-world struvite recovery system would fail if the basic truths of urine collection were ignored. The experimental work aimed to replicate a source-separation/collection system, and therefore, the following axioms were held to be true:

- fresh urine will never be available for processing; urine must be stored
- urease is ubiquitous and urine will not remain sterile once in the system
- some amount of flush or cleaning water will always be present in collected urine

Not only were these factors acknowledged in the research, they were integrated and taken advantage of, such that the system could be optimized as a whole. This work links the real world experiences of urine collection and storage with the science of struvite recovery in order to take us one step closer to the ultimate goal of a truly holistic approach to water conservation, sustainable sanitation and nutrient recovery.

METHODS

Previous work utilized synthetic urine that was prepared as per the method given by Griffith [17]. The results of that work were presented elsewhere (BCWWA, Conference Proceedings, May 2006). Although synthetic urine is commonly used in urological



research, the solution used contained only the eleven most prevalent constituents in urine and was therefore, only a preliminary model. The results presented here are part of a larger investigation with real urine in order to account for the presence of organic and non-organic compounds that could alter the behaviour of the matrix.

Urine Collection

Twelve volunteers were recruited to provide a 24-hour urine sample. The participants collected their urine over the course of 24 hours and anonymously returned the samples the following morning. The age and sex of the participant was recorded and before the unlabelled samples were mixed, the volume of each was recorded. Of the twelve participants, 8 were men and 4 were women and the average age was 30 years. The average volume collected from each person was 1.5 L and 18.3 L in total was collected. The collected urine was mixed into a composite sample. The composite urine mixture was used immediately.

Factorial Design

A factorial experimental design was used to examine the effect of flushing water (dilution), faecal contamination (prevalence of urease), and storage (reaction time) on urine.

By varying the dilution, the amount of water that may be permissible or even useful to dilute stored urine in order to prepare it for phosphorus recovery, could be determined. Three levels of dilution were investigated- full strength (FS), half strength (1/2 S), and quarter strength (1/4 S) whereby the urine was used pure, diluted by half or diluted by a factor of 4.

Urease is the urea specific enzyme that hydrolyzes urea to ammonia and carbonic acid via the following reaction:



By adding varying amounts of urease to urine, we could determine the amount of faecal contamination that could beneficially be used to prepare urine for struvite recovery. Primary effluent from the UBC Pilot plant was used as a source of faecal urease. Three levels of faecal contamination were examined: no contamination (pure urine), 10 % primary effluent/urine vol/vol (10 %), and 25 % primary effluent/urine vol/vol (1/4 S) whereby the urine solution (regardless of its dilution) was replaced by 0 %, 10 % or 25 % of the total volume. Figure 1 shows a schematic diagram of the solution matrix.

The set of nine mixtures was replicated for quality control; set “a” mixtures (1a-9a) were the test samples and set “b” mixtures (1b-9b) were used as controls.

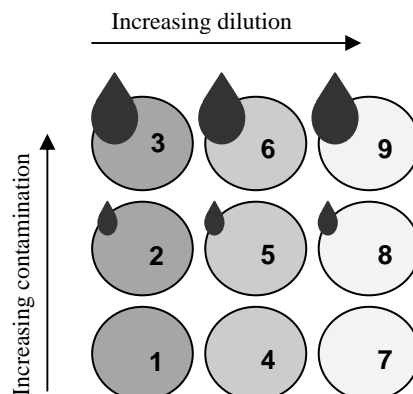


Figure 1. Experimental design.

Each 1-L mixture was prepared in a 1-L Nalgene, wide-mouth jar with a screw-top lid and was stored at room-temperature (approximately 22 °C). Lids were left on the samples when they were not being examined and were open for the duration of the testing and sampling.

Spontaneous Precipitation

The urine solutions (1a-9a and 1b-9b) were monitored daily for changes in pH and conductivity and samples were taken daily (approximately 10 mL) to measure ammonia, phosphate, magnesium and calcium. Samples were filtered with a Millipore 0.45 µm filter and preserved with 5 % H₂SO₄ to pH 2 and stored at 4 °C until they could be analyzed. The solutions were left until the pH and ammonia concentration had increased such that the ion activity product (IAP) exceeded the solubility limit for compounds capable of precipitation from urine, e.g. calcium, hydroxyapatite, and struvite (for a complete discussion see Udert et al [13]). In previous work with synthetic urine, we observed that precipitation occurred at a pH of, or greater than 8. The same trend was observed in this investigation.

Once a precipitate had formed, the supernatant was decanted and filtered with a Whatman #52 Filter to remove the crystalline solids. The filtrate was re-sampled for all the parameters described above. It should be noted however that only solutions 1a-9a were filtered; solutions 1b-9b were untouched but were monitored continuously unless otherwise noted.

Struvite Precipitation

In order to induce struvite precipitation, magnesium was added to the post-precipitation filtrate. Struvite is also known as MAP, or magnesium ammonium phosphate (MgNH₄PO₄·6H₂O). Magnesium was added in excess such that the magnesium to phosphate ratio was approximately 1.7:1. Magnesium solutions were prepared using MgCl₆H₂O and distilled water so that the solution would have a negligible effect on the pH. After the magnesium addition, the mixture was shaken for 60 seconds and left to react for 1



hour. After the reaction phase, all parameters were measured and samples were taken. The precipitate (struvite) was then filtered with a 0.45 μm Millipore filter, the precipitate was saved for analysis and the filtrate was reanalyzed.

Controls and Variations

The methods described in the above section are the methods used to remove calcium and form struvite in samples 1a-9a. Samples 1b-9b were used as controls; they were sampled and monitored in an identical manner as set “a” but any precipitate was left in solution and no magnesium was added. However, some changes were made: sample 2b was filtered and dosed with magnesium in order to allow for direct comparison to sample 2a. Mixtures 3b and 7b were dosed with magnesium before spontaneous precipitation occurred so that the precipitate from raw urine could be compared to the struvite formed following calcium removal.

Chemical Analysis

Ammonia and phosphate were measured with a Lachat QuikChem 8000 flow injection instrument. Calcium, magnesium, aluminium, iron and potassium were measured with a Varian Inc. SpectrAA220 Fast Sequential Atomic Absorption Spectrophotometer. Atomic absorption was used to measure all of the elements except for potassium, which was measured with atomic emission. A Bruker D8 Advance powder X-ray diffractometer, equipped with copper radiation and a graphite monochromator, was used to identify the crystal structure. Crystal constituents were measured by dissolving 100 mg of struvite crystals in 50 mL 0.5 % nitric acid and analyzing the solution using atomic absorption as described above.

RESULTS

Composition

Compared to the typical values for urine, the average values of constituents measured (ammonia, phosphate, calcium, magnesium) were about 50% lower than typical values. Table 1 shows typical values as reported in Documenta Geigy [18] and the values recorded from the sample population.

Table 1. Typical and measured concentrations (ppm) of selected urine constituents.

	PO ₄ -P	NH ₄ -N	Mg	Ca
Documenta	637	1001	120	230
Measured	450	300	70	70

The authors hypothesize that the values differed in nutrient levels because several of the subjects submitted very large, and thus dilute, 24-hour samples. Metal values were likely



lower because of the very soft water in Vancouver, but the reason for disproportional N:P levels is not clear.

Ammonia and pH

When urease hydrolyzes urea, ammonium is produced, which in turn, increases the pH of the solution. All urease-spiked urine mixtures, when left for sufficient time (1-4 days), achieved a pH of approximately 9. The solutions with the highest percentage of wastewater added reached the maximum pH the most quickly; the solutions with the smaller amounts reached pH 9 with a lag time of several days. The maximum ammonia concentration achieved was directly related to the original amount of urea present in the mixture, which is directly related to the degree of dilution and the percentage wastewater addition in the sample. Similarly, the rate of ammonia increase was directly related to percentage of wastewater present.

Spontaneous Precipitation

Precipitation consistently happened when the urine mixture, regardless of composition, reached a pH greater than or equal to 8. Precipitation occurred in a predictable fashion that varied primarily with dilution and secondly with faecal contamination (urease). The first mixtures to precipitate were the most dilute with the higher percentages (10 and 25%) of urease: solutions 6, 8 and 9. The second set of mixtures to precipitate were those that were less diluted but still with a high proportion of urease: solutions 2, 3, and 5. The urine mixtures with no added urease were last to precipitate: solutions 1, 4, and 7. Although the equipment was sanitized with bleach and steps were taken to keep the urine sterile. The fact that precipitation occurred in the “uncontaminated” mixtures is the reality of the ubiquitous nature of urease.

Calcium Removal

The amount of calcium removed via spontaneous precipitation was taken to be the difference between the calcium in solution before and after precipitation. The data presented in Figures 2a and 2b show both the percentage and the total mass of calcium and phosphorus that was removed through spontaneous precipitation.

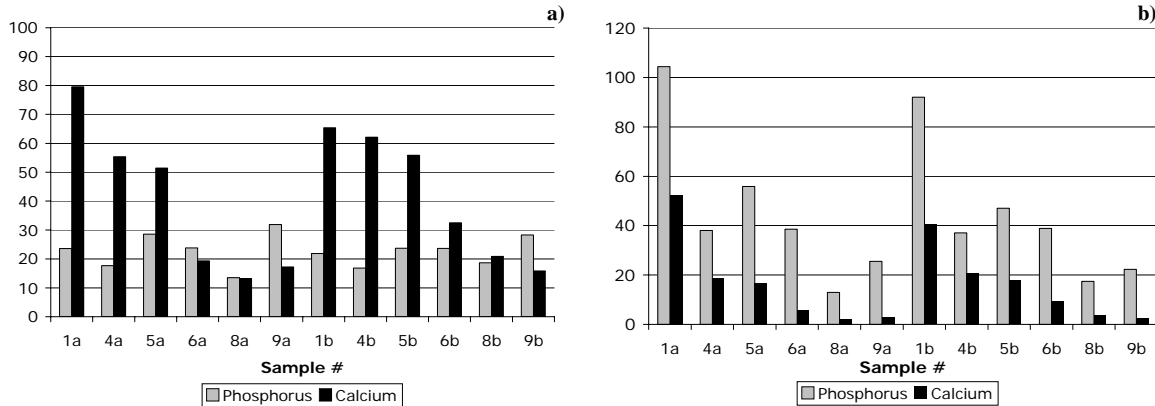


Figure 2. a) Percentage and b) mass of total Ca and PO₄-P removed.

In Figure 2a it is interesting to note that, while the percentage of phosphorus lost to precipitate is independent of initial concentration and is in the range of 13-31 %, the percentage of calcium removed varies directly with the dilution of the solution. Similarly, Figure 4b shows that the mass of phosphorus and calcium removed varies with the strength of the urine. Both figures show data sets “a” and “b” as evidence of the reproducibility.

Struvite Recovery

Phosphorus

The goal of struvite recovery is to maximize phosphorus removal whilst minimizing contamination. Shown in Figure 3a is the direct relationship between the amount of phosphorus that can be recovered and the strength of the urine. The fate of phosphorus in both data sets “a” and “b” is compared in Figure 3b.

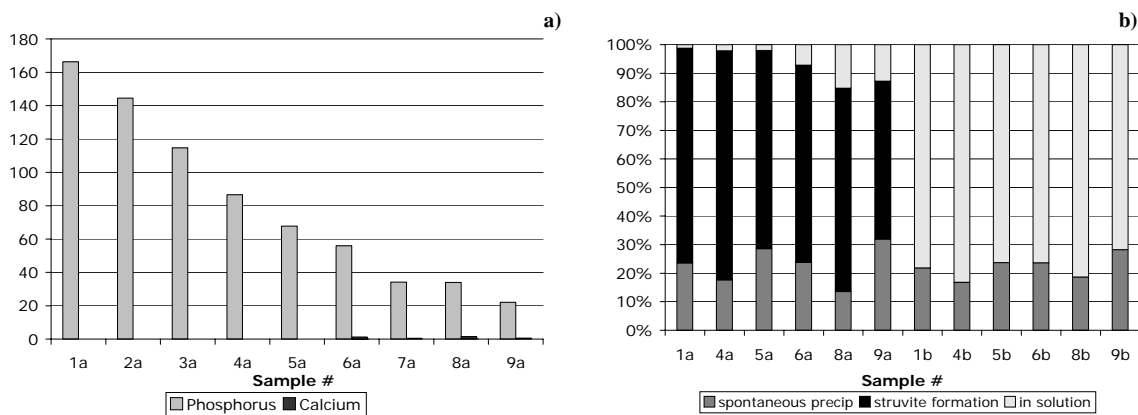


Figure 3a) Mass and **b)** percentage removal of phosphorus in the form of struvite.

Regardless of the initial mass of phosphorus present in the mixture, on average 25 % of phosphorus in solution is lost to spontaneous precipitation. Comparing the two data sets, it is clear that the remainder, about 70 %, can be removed in the form of struvite. Also, there is decreased removal (on a mass and percentage basis) with increased dilution.



Purity of Crystals

The recovered struvite crystals were analyzed for four of the most common contaminants in struvite: calcium, phosphorus, iron, and aluminium. Iron and aluminium were consistently below the method detection limit (0.02 and 2 ppm respectively). Potassium and calcium were consistently near the detection limit and never more than 0.5 % of the crystal mass. Since these are the most common contaminants, the struvite produced is likely over 99 % pure.

CONCLUSIONS

The success of the growing commercial struvite industry is based on a solid foundation of research, which has nearly perfected the recovery of phosphorus from dilute waste streams. No such foundation exists for the recovery of struvite from urine. The findings presented here will be useful in the continued work towards recovering struvite from human urine as a means of obtaining a reliable and cost-effective, slow release fertilizer.

Unless urine is stored under very sterile conditions and is transported quickly, spontaneous precipitation will occur. Increased levels of urease and dilution hasten the onset of precipitation. Calcium removal decreases from a maximum of about 80 % to a minimum of about 10 %, with increasing dilution and increasing contamination. Approximately 25 % of the phosphorus in solution will precipitate out of solution.

Struvite can be recovered from the urine matrix that remains following spontaneous precipitation and on average, 70 % of the phosphorus in urine can be recovered in the form of struvite. However, the percentage and mass of phosphorus recovered as struvite decreases with increased dilution. High quality struvite (~99 % pure) can be recovered from human urine when post-precipitation urine is dosed with magnesium before a pH of 9.

By allowing stored urine to increase in pH naturally, a virtually calcium free matrix that is ideal, both in terms of pH and composition, for struvite recovery, can be produced. By simplifying the struvite recovery process, and in the process, reducing the cost of chemical and infrastructure controls, the possibility of struvite recovery from urine comes closer to reality.



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