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# A comparative study of phosphorus recovery as struvite from cow and human urine

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ABSTRACT

With increase in world population and demand, phosphorus minerals are being exploited for its application as a fertilizer. At the same time, nutrient-loaded wastewaters cause eutrophication and algal blooms in aquatic bodies. Struvite ($MgNH_4PO_4{\cdot}6H_2O$) crystallization can be a sustainable approach to recover nutrients from effluents rich in magnesium, ammonium and phosphate for use as a slow-releasing fertilizer. In this regard, urine can be considered as an appropriate source for phosphorus recovery as struvite. This manuscript is a comparative study of struvite precipitation from cow and human urine. It deals with the variations in the physicochemical characteristics of urine and its effect on the quantity and quality of struvite. It was found that the phosphate recovery efficiencies were higher than 90% in both the cases. However, the struvite yield was almost twice in human urine (1.34 g/L) than cow urine (0.76 g/L). Further, Fourier-Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD) analysis confirmed the crystallinity and molecular bonding of the struvite crystals.

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## 1. Introduction

The amount of wastewater generated is increasing day by day with rise in urbanization and industrialization. However, the water treatment and recycling facilities are limited, leading to release of these nutrient-rich effluents in natural inland rivers and lakes. These actions resulted in unpleasant effects such as algal blooms and eutrophication of the water bodies [1,2]. On the other hand, the non-renewable phosphorus resource which is the primary source for fertilizer production worldwide is getting depleted and expected to get exhaust in the next 50–100 years. Instead, the valuable nutrients (phosphorus, nitrogen, potassium) can be recovered from wastewater and used for the production of a sustainable fertilizer [3].

Urine from domestic municipal wastewater contributes the most to the nutrient value of wastewater. Chemical analysis of urine shows that it is rich in several nutrients and minerals that can serve as plant growth substances. Both cow and human urine contains high concentrations of phosphate, nitrogen and potassium rendering it to be a sustainable alternate to conventional chemical fertilizers [4,5]. However, the direct use of liquid urine in agricultural fields is restricted due to consequences of low nitrogen fixing capacity, over dosage of nutrients, collection and transportation difficulties. It has been proven in literature and reality that struvite production is a promising and successful technology for recovery of nutrients and application on a large scale [6,7].

Struvite is a crystalline compound comprising of magnesium, ammonium and phosphate in an equimolar (1:1:1) ratio. The theoretical value of struvite is said to be 12.6%, 9.9% and 5.7% of phosphate, magnesium and ammonium, respectively, as per American Public Health Association (APHA) standard methods. It is insoluble in polar solvents; hence, can be easily recovered at an alkaline pH from nutrient-rich effluents and used as a slow-releasing fertilizer. In case of urine, the magnesium concentration is very low and requires external supply of magnesium for struvite formation [7]. Urine is an easily available and potential source of nutrients as an individual human being alone can produce 1–1.5L of urine per day, leading to generation of 500L per capita per year. It is reported that around 12,176 tons of struvite can be manufactured every day from cow urine being produced in India, of which 365 kg will be sufficient enough to fertilize 2.6 ha of land [7,8]. Also, it is noteworthy that the heavy metal concentration in struvite is lesser than

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that in actual urine and almost negligible to that present in commercial fertilizers.

Several studies have been carried out for struvite production using human and cow urine. Prabhu *et al.* (2013) [7] used urine collected from Indian dairy cows for struvite precipitation with brine as the magnesium source. Analysis of struvite confirmed 5.85%, 3.16%, and 0.56% of phosphate, magnesium and ammonium, respectively. An optimum concentration of 2 g struvite/kg of soil was used for the growth of *Vigna radiata*. Purnomo *et al.* (2019) [9] used a continuous flow reactor for struvite production from cow urine with 54% phosphate recovery. Latifian *et al.* (2014) [8] used calcinated human urine and achieved phosphorus recovery of 92%. Nevertheless, struvite studies on cow urine are very limited compared to human urine.

The scope of this study is to compare the characteristics of cow and human urine, and decide their suitability for struvite production. Physicochemical parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), salinity, phosphate, ammonium, nitrate and calcium concentrations were analyzed to gain an overall perspective on the process viability using urine. Lab-scale batch experiments of struvite precipitation were carried out to estimate the phosphorus recovery and struvite yield from each of the sources. From these studies, the appropriate medium for struvite production on a large-scale can be explored further for real-time studies.

## 2. Materials and methods

### 2.1. Urine sample collection and storage

#### 2.1.1. Cow urine

The fresh cow urine samples were collected from a cattle-shed near National Institute of Technology Rourkela, India. After collection, the samples were pooled together and stored in a dry air-tight plastic container at 4℃. During the study period, the samples were trifurcated and stored at ambient room temperature (25 ± 2℃) until suitable pH conditions were obtained (>9 ± 0.2) as a result of ureolysis.

#### 2.1.2. Human urine

The undiluted fresh human urine samples were collected from healthy male and female donors deprived of any medical complications between the ages of 20–35 years. The samples were pooled and stored at 4℃ in sealed plastic containers till further analysis. For further analysis, the samples were trifurcated and maintained at ambient room temperature (25 ± 2℃) to enhance urea hydrolysis until the required pH conditions (>9 ± 0.2) were attained.

### 2.2. Urine characterization

The characterization of urine was performed after the samples were thawed down to room temperature. Various physicochemical parameters of urine such as pH, EC, TDS, salinity, phosphate, ammonium, nitrate and calcium were measured. pH, EC, TDS and salinity were estimated using multiparameter water quality meter from Lab-man Scientific Instruments Pvt. Ltd. (India) (Model No: LMMP-30). Ammonium, nitrate and calcium ion concentrations were measured using appropriate ion selective electrodes (ISE) from Vernier software & Technology (USA). Phosphate concentration was determined by spectrophotometric method (Murphy and Riley) using stannous chloride and ammonium molybdate at an absorbance of 650 nm in a double beam UV–visible spectrophotometer (Model 2230, Systronics, India). All the experiments were carried out in triplicates.

### 2.3. Struvite precipitation

In order to precipitate struvite, batch experiments were carried out using real-time urine samples with external addition of magnesium. In this study, magnesium chloride hexahydrate ($MgCl_2\cdot 6H_2O$) procured from HiMedia (India) was chosen as the source of magnesium. It was added to 500 ml of urine in a 1:1 ($PO_4^{3-}$: $Mg^{2+}$) molar ratio to initiate hydrogen bond formation between the ions. Then, the samples were agitated at 150 rpm for 30 min in an incubator shaker to enhance nucleation and crystal growth. After sufficient mixing, the samples were kept undisturbed for a retention period of 12 h to improve settling of crystals. Following this, three-quarter of the supernatant volume was decanted and the rest containing sediments of struvite was centrifuged at 6000 rpm for 20 min. The recovered crystals were then left for drying overnight at 40 °C. The amount of phosphate recovered was calculated using **Eq. (1)** as follows:

$$\eta_P\% = \frac{P_I - P_R}{P_I} \quad (1)$$

Where, $P_I$ and $P_R$ are initial and residual concentrations of phosphate (mg/L) and $\eta_P\%$ is the percentage efficiency of phosphate recovered [10]. The struvite yield was calculated as the amount of dried struvite crystals obtained after precipitation.

### 2.4. Struvite characterization

The struvite crystals were characterized for their molecular bonding and functional groups using Fourier-Transform Infrared Spectroscopy (FTIR) analysis in which the sample was recorded in the range 400–4000 $cm^{-1}$ (Spectrum Two FTIR, Perkin Elmer (India). The crystallinity of the material was confirmed by X-ray Diffraction (Bruker AXS D8 Advance with Davinci Design) with Fe filter and LYNXEYE detector. The crystals were scanned at a rate of 4° (2θ) $min^{-1}$ in the range of 10-70°.

## 3. Results and discussion

### 3.1. Comparison of physicochemical characteristics of cow and human urine

Physiochemical parameters play an important role in comprehending the composition and chemical characteristics of a sample. In this study, the physicochemical factors of cow and human urine such as pH, EC, TDS, salinity, phosphate, ammonium, nitrate and calcium were analyzed and compared. These parameters will help in figuring out the suitable medium and conditions for efficient struvite recovery. pH is the most vital characteristic determining the formation of struvite. It can be seen in Table 1 that the pH of urine at the time of collection is slightly acidic. However, with increase in storage time, the pH tends to increase as a result of urea hydrolysis. The urease enzyme secreted by bacteria present in urine catalyzes ureolysis leading to formation of ammonium. This

**Table 1**
Physicochemical parameters of fresh urine of cow and human used in the study

| Physicochemical parameters | Cow urine | Human urine |
|---|---|---|
| pH | 6.8 ± 0.12 | 6.7 ± 0.07 |
| Conductivity (mS/cm) | 16.5 ± 0.03 | 15.15 ± 0.05 |
| TDS (ppt) | 8.2 ± 0.02 | 7.57 ± 0.01 |
| Salinity (psu) | 9.7 ± 0.05 | 8.79 ± 0.04 |
| Phosphate (mg/L) | 197.83 ± 3.52 | 232.24 ± 2.19 |
| Ammonium (mg/L) | 35.3 ± 0.59 | 27.39 ± 3.4 |
| Nitrate (mg/L) | 3522.39 ± 15.46 | 10.01 ± 0.35 |
| Calcium (mg/L) | 0.3 ± 0.05 | 7.76 ± 0.98 |

process will provide an apt alkaline environment for struvite crystallization [11,12]. In this case, after prolonged storage of urine samples for 8 days approximately, the pH reached 9.02 ± 0.06 and 9.12 ± 0.02 for cow and human urine, respectively. It is said in literature that pH in the range of 8–9.5 is conducive for struvite formation. Hence, the samples were stored accordingly and utilized for further experiments [13,14].

Electrical conductivity is also an essential criterion that helps in understanding the extent of ureolysis. The conductivity of both the urine samples were almost similar in the initial stages. With increase in hydrolysis, the conductivity of the medium also increased. Similarly, the TDS and salinity of cow and human urine are almost the same and increase with storage as a consequence of bacterial activity [6,15].

Phosphate and ammonium ions in urine are the ones that are directly associated in struvite formation. Phosphate ions are usually present in the form of orthophosphates, while ammonium ions are formed from urea dissociation [16,17]. The phosphate concentration in cow and human urine are 197.83 mg/L and 232.24 mg/L, respectively. There is only a slight variation in concentration, which eventually decreases during storage due to spontaneous precipitation of struvite. However, the ammonium concentration kept increasing till the time of maturation (pH > 9) because of urea hydrolysis.

A significant variation can be observed in the nitrate concentration between the two urine samples. Cow urine had nitrate levels >3500 mg/L, while human samples had only 10 mg/L of nitrate. This difference in chemical composition depends on the bodily conditions, size, dietary habits and climatic conditions of the location. Yet, it was found in the experiments that nitrate did not have any effect on struvite precipitation as the concentration remained almost the same before and after precipitation of struvite. In contrast, the calcium concentration was quite higher in human urine (7.76 ± 0.98 mg/L) than in cow urine (0.3 ± 0.05 mg/L).

### *3.2. Phosphorus and struvite recovery from cow and human urine*

After attaining the favorable conditions for struvite crystallization, phosphate concentration of the urine samples was estimated and $MgCl_2{\cdot}6H_2O$ was added in a 1: 1 ($PO_4^{3-}$: $Mg^{2+}$) ratio. The amount of struvite obtained after precipitation was dried and weighed for struvite yield estimation. Similarly, the residual phosphate in the supernatant was measured and percentage of phosphate recovered was calculated as per Eq. (1). It can be seen in Fig. 1 that the phosphate recovery in cow urine is relatively higher than in human urine. However, the recovery efficiencies of both the nutrient sources were >90% making them a suitable medium for struvite production. In contrast, the struvite yielded from human urine was almost twice than from cow urine. This can be attributed to higher phosphate present in human urine. Though the phosphate recovery rate was higher in cow urine, for commercial scale production of struvite, use of human urine would be a viable option. Apart from this, changes in the calcium concentration were also observed. The calcium levels reduced to 0.1 mg/L and 0.4 mg/L in cow and human urine respectively, owing to formation of small amounts of calcium and magnesium phosphates [1,18].

### *3.3. Qualitative analysis of struvite recovered from cow and human urine*

The quality of the struvite obtained was tested using characterization techniques such as Fourier-Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD). The FTIR spectrum of struvite precipitated from cow and human urine can be seen

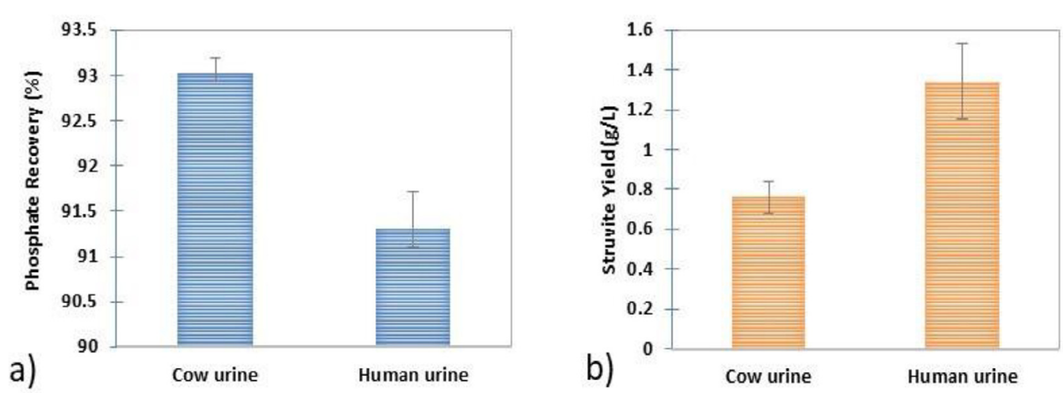


**Fig. 1.** Recovery of a) Phosphate and b) Struvite yield from cow and human urine

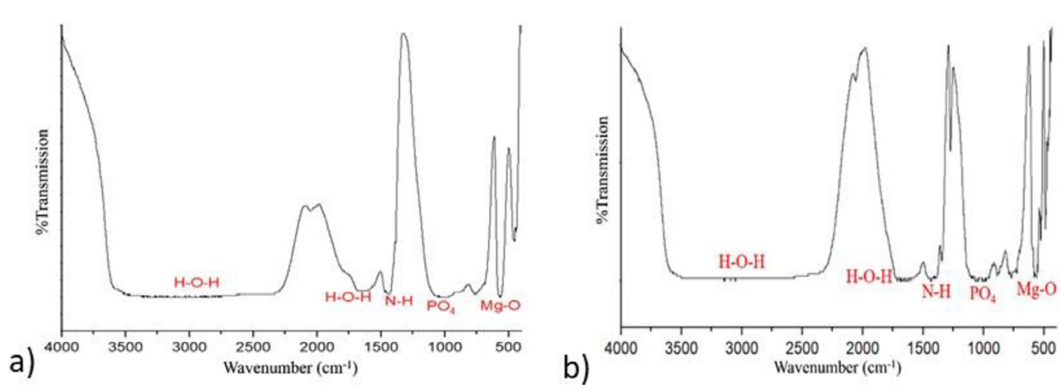


**Fig. 2.** FTIR spectrum of struvite crystals recovered from a) Cow and b) Human urine

**Table 2**
Vibrational assignments and wavenumbers of struvite crystals obtained from cow and human urine

| Bond/Vibrational Assignments | Wavenumber ($cm^{-1}$) | | |
|---|---|---|---|
| | Reference [19,20] | Cow urine | Human urine |
| H-O–H stretching vibrations of water | 3275.2–3521.6 | 3313.0, 3459.2 | 3501.5 |
| H-O–H stretching vibrations of cluster of water molecules of crystallization | 2314.0–2478.61 | 2329.5 | 2321.25 |
| H-O–H bending molecules of vibrations | 1653.05–1704.5 | 1688.5 | 1689.5 |
| N–H stretching vibrations | 1444.0–1647.0 | 1450.25, 1595.5 | 1448.0, 1597.5 |
| Asymmetric stretching vibrations of $PO_4$ | 1022.31–1239.4 | 1039.25, 1069.5 | 1043.5, 1079.5 1103.0 |
| Mg-O stretching | 543.0–753.0 | 567.25, 750.5 | 569.5, 722.5, 767.5 |

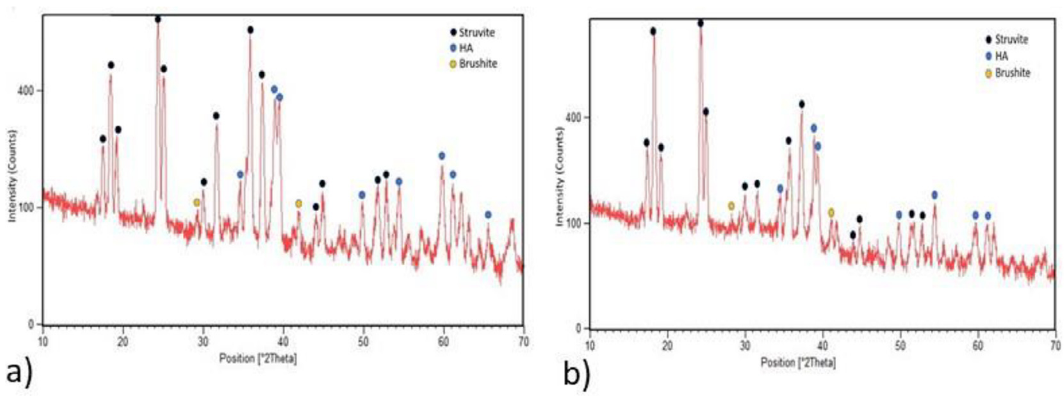


**Fig. 3.** XRD pattern of struvite crystals recovered from a) Cow and b) Human urine.

in Fig. 2. The comparison of the characteristic absorbance peaks is shown in Table 2. The main peaks between 1038 and 1080 $cm^{-1}$ were due to the absorption of $PO_4$ molecules in struvite. The peaks at 1450.0 $cm^{-1}$ and 1448.0 $cm^{-1}$ in Fig. 2**a and 2b** can be attributed to the N–H stretching vibrations due to the presence of ammonium in struvite. Another characteristic peak at 567.25 $cm^{-1}$ and 569.5 $cm^{-1}$ of struvite samples from cow and human urine corresponds to the metal–oxygen bonding, which in this case is the Mg-O bond in struvite. Other absorbance stretches between 3500 and 2200 $cm^{-1}$ denotes the vibrations of water molecules present in struvite crystals. Both the samples had characteristic peak values in the designated range [19,20].

Fig. 3 represents the XRD pattern of struvite samples obtained from cow and human urine in the 2θ range of 10-70°. The characteristic peaks obtained are almost similar to those of standard pure struvite crystal (ICDC Standard #15–0762). In addition, precipitation of calcium phosphates such as hydroxyapatite (HA) and brushite was also observed (JCPDS:00–009-0432). On the whole, struvite recovered from cow urine had better intensity of peaks compared to human urine struvite indicating the good quality of crystals.

## 4. Conclusion

Struvite is an organic fertilizer that can be obtained from nutrient-rich wastewaters such as urine. This study presented the comparative analysis of struvite crystallization between cow and human urine. The physicochemical characteristics of urine were examined and found that nitrate concentration was peculiarly higher in cow urine. Whereas, phosphate concentration was slightly higher in human urine, while all other parameters remained almost the same. The precipitation experiments showed that phosphate recovery was better in cow urine and struvite yield was almost doubled in case of human urine. In terms of quality, cow urine had a relatively low concentration of compounds other than struvite. However, the yield was comparatively higher with human urine and hence would serve as a suitable option for pilot-scale production of struvite.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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