

Cow urine as a potential source for struvite production

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Abstract

Background Rock phosphate deposits are non-renewable and are facing a decline. Due to this, phosphate fertilizers are going to be limited in future. Struvite is a crystalline mineral substance containing equimolar amount (1:1:1) of magnesium ammonium and phosphate ions ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), a good source of phosphorus and a slow release fertilizer. In the present study it was crystallized from cow urine using brine as cheap source of magnesium. Cow urine and brine was mixed at different proportion to find out the optimum concentration for struvite crystallization. Crystallized struvite was characterized by X-ray diffraction, thermogravimetric and differential thermal analysis, Fourier transform infrared spectroscopy and scanning electron microscopy and energy dispersive spectroscopy.

Results The ratio of 1:0.5 cow urine and brine mixing gave the best quality struvite at pH 9. The analysis of struvite for phosphate, magnesium and ammonium ions showed 5.85, 3.16, and 0.56 % respectively. The fertilizer potential of struvite was evaluated on the growth of *Vigna radiata*. The best growth was observed in the pots where struvite was added at a concentration of 2 g/kg of soil.

Conclusion Struvite is a good source of phosphate and it can be recovered from livestock waste such as cow urine. Struvite can be made from a renewable source for a sustainable agricultural development. Theoretically at the yield of 40 g/L a total of 12,176 tons struvite could be made per day all over India for fertilizer use.

Keywords Brine · Cow urine · Crystallization · Fertilizer · Phosphate · Struvite

List of abbreviations

DAP	Diammonium phosphate
MgCl_2	Magnesium chloride
NaCl	Sodium chloride
FTIR	Fourier transform infrared spectroscopy
TG-DTA	Thermogravimetric and differential thermal analysis
SEM-EDAX	Scanning electron microscopy and energy dispersive spectroscopy
XRD	X-ray diffraction

Introduction

Phosphorus (chemical symbol P) is an essential nutrient element for all life forms and its consumption along with its price is increasing day by day all over the world. Rock phosphate in sedimentary deposits is the main source of phosphorus on earth. Over 75 % of phosphate rock is surface mined with the remaining recovered by underground mining. Most of this rock phosphate (80 %) is used as a raw material in the manufacture of agricultural fertilizer which supplements P for all crops. Therefore

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conventional agriculture is dependent on mined phosphate. Phosphate rock is a limited, non-renewable, and non-substitutable resource. Rock phosphate production is already facing a decline around the world as half of the P deposits on earth likely to get over in coming 60–80 years (Amanullah et al. 2010; Vance 2001). Hence it becomes important to look out for other sources of phosphorus for fertilizing our agricultural fields through sustainable development for the prolonged time. Phosphorus recycling is also of significant importance. The agricultural soil of Goa, India is deficient in phosphorus and magnesium. Therefore the Government of Goa, India is assisting farmers with 50 % subsidy on use of fertilizers containing above two elements (Government of Goa 2013).

Struvite is a crystalline mineral substance containing equimolar amount (1:1:1) of magnesium ammonium and phosphate ions ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) and is a good source of phosphorus. Apart from being a problem in sewage treatment plants (Doyle and Parsons 2002), struvite has great potential to be used as phosphate fertilizer. It can be used as slow-release fertilizer. Studies have shown that it can be equivalent or superior to other commercial phosphate fertilizers in agriculture (Ryu et al. 2012; Ghosh et al. 1996). Precipitation occurs only when the concentrations of above three ions in wastewater exceed the struvite solubility limit (>0.2 g/L) also called as supersaturation (Barak and Stafford 2006). Another condition for struvite formation is a pH has to be between 8.5–9.5 (Perera et al. 2007; Uysal et al. 2010). However selective removal of phosphorus in the form other than struvite is possible also at medium pH (Raj et al. 2013). reports have shown that phosphorous recovery Struvite precipitation methods are very promising and likewise successful on large scale (Miles and Ellis 2001; Pastor et al. 2008; Etter et al. 2011; Song et al. 2011) although the sources of the magnesium used are diverse and expensive (Burns and Moody 2002; Huang et al. 2010). Inexpensive sources of magnesium such as MgO-containing by-products (Quintana et al. 2005), seawater (Kumashiro et al. 2001), brine (Lee et al. 2003), magnesite (Gunay et al. 2008) and wood ash (Sakthivel et al. 2011) have also been used in some cases. Recovery of phosphorus in other form such as calcium phosphate and aluminum phosphate has also been tried using lime as a source of calcium (Banu et al. 2009) and alum (Do et al. 2013) as a source of aluminium respectively.

There are large amounts of phosphate available in waste streams from which struvite crystallization has been tried e.g. agriculture, sewage treatment effluent (Booker et al. 1999), industrial side streams such as semiconductor wastewater (Ryu et al. 2008), aerobically and anaerobically treated wastewater (Miles and Ellis 2001; Shu et al. 2006), landfill leachate (Di Iaconi et al. 2010), human urine (Booker et al. 1999; Tilley et al. 2008; Ganrot et al. 2007),

and animal wastewater (Burns and Moody 2002; Yetilmezsoy and Sapci-Zengin 2009, Rahman et al. 2011; Suzuki et al. 2005).

In this study we crystallized struvite in an economical way from cow urine. Brine was used as cheap source of magnesium. Furthermore the fertilizer potential of produced struvite was evaluated.

The chemical analysis of cow urine reveals that it is rich in organic molecules and minerals that has potential as fertilizer (Krishnamurthi et al. 2004) but becomes one of the nutrient sources for eutrophication when used in excess. Urine is often promoted as a liquid fertilizer but has many drawbacks (Tilley et al. 2009). Studies have shown that direct application of urine into the crop soil decreases the nitrogen fixing capacity of the soil (Di et al. 2002; Saunders 1982). Also when manure slurries are applied to the cropland to fulfill nitrogen requirement, phosphorus become over applied as its content is much higher in the manure than the crops need (Burns and Moody 2002). Hence it becomes important that these minerals are removed by some means so that the nutrient does not become an excess when urine is applied to the cropland. Struvite has been previously precipitated from anaerobically digested cow manure (Zeng and Li 2006), but it seems to be more efficient to separate cow urine from dung. Cow urine can be used to make struvite and dung can be used for anaerobic digestion to generate biogas.

The method imposes benefits such as phosphorus and nitrogen recovery thereby cutting on eutrophication. It aims at providing insight into struvite precipitation as a method to sustainably remove phosphorus from cow urine. The struvite which is obtained can be used where there is need of phosphorus and nitrogen for the cropland. Also the leftover supernatant after making struvite (having lesser phosphorus and ammonium) can be used to make ammonium sulphate (Antonini et al. 2011) or can directly be applied in local fields in required quantities.

Materials and methods

Screening of different substrates containing phosphates

The different substrates that were screened are (1) supernatant from the effluent of food waste based anaerobic digester after centrifugation at 3,000 rpm for 10 min to remove solid suspended particles. (2) Wastewater collected from an outlet of fluidized bed reactor (FBR) treating community sewage. (3) Wastewater from dairy industry. (4) Urine collected directly from Indian dairy cows during excretion using a polyethylene bucket and avoiding any contact with the floor of the cowshed. All the samples were immediately transported to the laboratory in clean

polypropylene bottles. In all samples total ammonia nitrogen pH, and total phosphorus for were analyzed in accordance with APHA standard methods (APHA 1995).

Collection of brine and its analysis

Salt pan is a good source of brine. It was collected from the crystallization pond of the saltern once the sodium chloride is precipitated out. Brine was collected from the crystallization pond of salt pans from Siridao Goa, India. This brine was analyzed for the pH, conductivity and magnesium concentration. Total ammonia nitrogen and total phosphorus were also analyzed by APHA standard methods.

Precipitation of struvite and optimization of its formation

Cow urine (pH 9) and brine were mixed at different proportions (1:0.25, 1:0.5, 1:0.75, 1:1, 1:1.5, and 1:2) in different flasks to find out the optimum struvite formation without change in the pH. After adding brine to the urine, the pH of the mixture was noted. In another set of above experiment, after addition of cow urine and brine in different ratio, the final pH was adjusted to 9 using 5 N NaOH solution and then kept on a magnetic stirrer. In one more set, pure magnesium chloride hexahydrate was added in stoichiometric ratio. After stirring for 10 min, the flasks were kept for struvite crystallization. Within 2 h white color precipitate was formed and settled down. This was then filtered using blotting paper and dried in the shade at room temperature till all the moisture was evaporated. After drying, the amount of struvite formed was calculated. The whole process was carried out at room temperature (30 ± 2 °C). The dry precipitate was further used for characterization.

Characterization

X-ray diffraction (XRD) analysis Precipitates formed under different conditions were grinded to powder using mortar and pestle. Room temperature X-ray diffraction spectra of these powder were recorded with a powder X-ray diffractometer (Mini Flex II, Rigaku, Japan) with Cu K α ($\lambda = 0.15405$ nm) radiation. The quality of the struvite obtained from different conditions was compared using the XRD patterns with that of the standard struvite XRD pattern from the International Centre for Diffraction Data (ICDD). The conditions that produced quality struvite were used to make struvite in bulk from 3 L of cow urine.

Thermogravimetric and differential thermal analysis (TG-DTA) Thermal decomposition studies of struvite were carried out on the struvite using a DTG-60 and a DTA-60 (Shimadzu, Japan) respectively. The experiments were conducted under zero air flow atmosphere ($50 \text{ cm}^3/\text{min}$).

The sample was heated in an open platinum crucible at a rate of 1.0 °C/min from 30 °C up to 300 °C.

Scanning electron microscopy and energy dispersive spectroscopy (SEM-EDAX) SEM-EDAX analysis was also performed on the powdered struvite crystals for shape, morphology and individual elemental composition in selected area using SEM (JEOL, JSM-6390) equipped with EDAX (INSTA FET, Oxford instruments) operated at 20 keV. The sample powders were deposited on a carbon tape before mounting on a sample holder and gold coated for EDAX.

Fourier transform infrared spectroscopy FTIR analysis IR spectra were recorded on Shimadzu FT-IR, Prestige-21 spectrophotometer. To obtain the spectra 1 % crystallized struvite was mixed and ground with 99 % KBr. Tablets of 10 mm diameter were prepared by pressing the powder mixture at a load of 5 tons for 2 min. The spectrum was taken in the range of $400\text{--}4,000 \text{ cm}^{-1}$ with 4 cm^{-1} resolution.

Evaluation of fertilizer potential of struvite

The effect of struvite on the growth of *Vigna radiata* (green gram or mung bean) was tested. The comparison was made with that of commercial fertilizers such as diammonium phosphate (DAP) (Jai Kisan Samrat, Zuari Industries Ltd. Zuarinagar, Goa, India) and organic manure (Stanes Dos, Stanes and company, Coimbatore, India), composition given in Table 1. Garden soil was collected from a local supplier and dried at room temperature for 15 days. It was analyzed for pH, total nitrogen and total phosphorus.

Seven sets of three pots (total 21 polypropylene pots) were prepared. Each pot had 8 cm surface diameter and 8 cm working depth. Two hundred grams of soil was taken, mixed thoroughly with the respective fertilizer and added to each pot. Three pots were used for each fertilizer. DAP fertilizer and organic manure was added at the rate of

Table 1 Composition of commercial fertilizers used in the plant growth test

Elements	Nutrient source		Unit
	DAP fertilizer	Organic manure	
N	18	1.25	%
P ₂ O ₅	46	0.58	
K ₂ O	0.0	0.81	
Ca	–	1.75	
Mg	–	0.27	
Mn	–	175	ppm
Zn	–	150	
Fe	–	1,200	
Cu	–	25	

110 kgN/ha (0.125 and 1.25 g respectively). Struvite was added in various concentrations (S1, S2, S3 and S4 corresponding to 0.8, 1.2, 1.6 and 2 g/kg respectively). Ten healthy seeds of *V. radiata* were sowed within the top 1 cm depth of soil in each pot. 40 ml of distilled water was added to each pot. One set of three pots was used as control in which no fertilizer source was added.

The experiment was carried out at room temperature of about 30 °C. All the pots were kept in the direct sunlight (D/N 12/12 h). Twenty milliliters of distilled water was added to each pot every alternate day. The germination rate was determined on day three. The length of the leaves was determined periodically in each pot. At the end of day 30, survival percentage, leaf area and total chlorophyll were determined. All the plantlets from each pot were carefully removed from the soil and washed several times with distilled water to remove all the soil particles. These were then studied for length, wet and dry weight. The dried shoots and the roots were made into powder using mortar

and pestle and were used to determine total phosphorus and total nitrogen for the shoots as well as for the roots.

Results and discussion

Composition of different waste collected, is given Table 2. The freshly collected cow urine had a pH of 6.5. The phosphorus concentration was as high as 305 mg/L. Total ammonia nitrogen content was 105 mg/L, and after maturation (pH 9) it reached to 7,732.3 mg/L. Chemical composition of cow urine depends on feeding habits, physical activities, body size and climate of resident location. The brine had a pH of 7, ammonia nitrogen was below detection, salinity was 445 parts per thousand and density was 4.26 g/L. Magnesium ions were found in a concentration of 18.53 g/L. Total P (mg/L) was highest in cow urine, 305; followed by dairy effluent, 262; effluent from food waste based anaerobic digester, 194; rice wash water, 105; and

Table 2 Chemical analysis of different samples used for struvite formation

Sr. no	Sample	pH	Total P (mg/L)	Total NH ₃ -N (mg/L)	Magnesium (g/L)	Salinity at 20 °C (‰)	Density (d 20/20) g/L	Conductivity (ms/cm)
1	Effluent from anaerobic digester	7	194	1,043	ND	ND	ND	ND
2	Wastewater	7	50	17.92	ND	ND	ND	ND
3	Rice wash water	6.5	105	ND	ND	ND	ND	ND
4	Dairy effluent	6	262	ND	ND	ND	ND	ND
5	Fresh cow urine	6.5	305	105	ND	ND	ND	ND
6	Brine	7	0.04	0	18.53	445	4.268	101
7	Matured cow urine	9	305	7,732.3	ND	ND	ND	ND

ND not determined

Fig. 1 pH variation in the cow urine when stored at room temperature

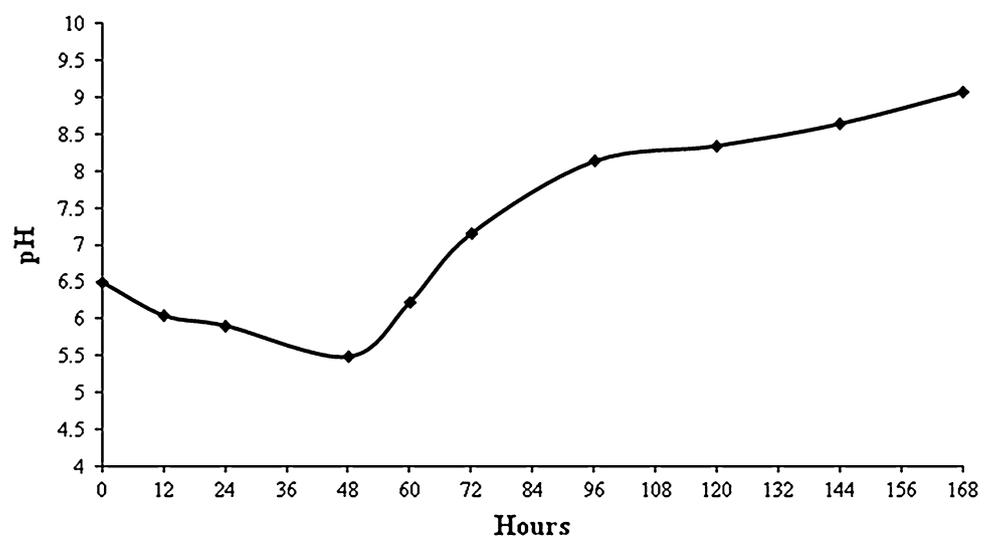




Fig. 2 Image of precipitated dried struvite taken with Nikon COOLPIX L21 digital camera

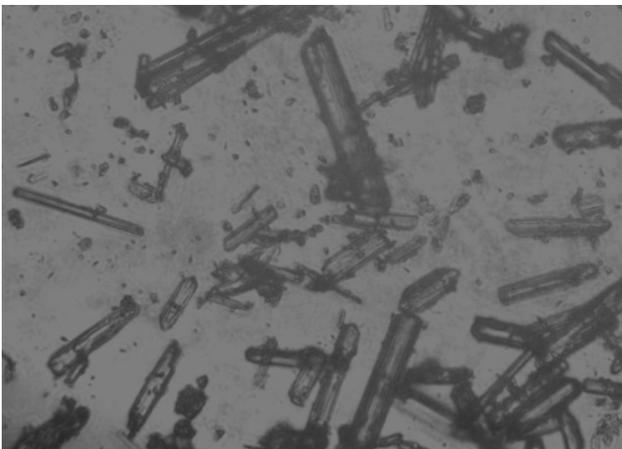


Fig. 3 Struvite crystals as seen in $\times 40$ of Nikon Eclipse TS100 phase contrast microscope. Image captured with Nikon COOLPIX L21 digital camera

sewage wastewater, 50. Decision was made to use cow urine to make struvite as it contained high concentration of phosphate and was relatively free of large suspended particles. Urine was stored at room temperature and was monitored everyday for increase in the pH up to 9 (Fig. 1).

When dried at room temperature the precipitated struvite turned into appearance of small rocky blocks (Fig. 2). This was scrapped using a needle and the particles when seen under the phase contrast microscope appeared to be as rod shaped structures (Fig. 3).

Characterization of the formed precipitate

XRD studies

Powder XRD analysis of room temperature dried struvite which was crystallized using pure magnesium chloride hexahydrate showed best results, followed by struvite

Table 3 Struvite production from cow urine using brine at different ratios of mixing

Sr no.	Urine (ml)	Brine (ml)	Weight of precipitate (g)	pH
1	50	12.5	2.40	9
2	50	25	4.28	9
3	50	37.5	4.16	9
4	50	50	3.23	8.85
5	50	62.5	3.01	8.6
6	50	75	2.29	8.5
7	50	87.5	2.14	7.5
8	50	100	2.15	7.5

crystallized using ratio 1:0.5 of cow urine to brine mixture. (Table 3); (Fig. 4) when compared to the peaks of synthetic struvite ICDD card no. 15-0762. It showed the orthorhombic crystal structure arrangement. The slight difference in the XRD spectra may be attributed to the trace amount of impurities present in the struvite precipitate. As the ratio decreased, the amount as well as the quality of struvite formed decreased. Also the pH decreases at lower ratios. The quality struvite was not obtained in lower ratios even after adjusting the pH to 9 as can be seen from Fig. 4 and Table 4. This may be due to the ion concentration present below supersaturation level due to dilution factor.

TG-DTA studies

Drying of struvite precipitate is an important step in maintaining its crystal structure size and fragility. The loss in this is dependent upon the temperature and the rate of heating. Previous studies (Frost et al. 2004) have shown the loss of mass of struvite takes place at 39.5, 57.8 and 82.6 °C resulting in decomposition of struvite crystals. In our thermal decomposition experiment on struvite crystals made using brine (Fig. 5), loss of mass was observed at 40.24 and 83.45 °C (closely resembling the previous data) with total loss in 23 and 33 % respectively of original weight. Furthermore a loss of mass was observed at 214.92 °C with total loss in 53 % of original weight. No further loss in mass was observed till 300 °C. This indicates that major loss in weight occurs between 39.5 and 83.45 °C and struvite starts dehydrating and loses its structure at 40 °C and above. Earlier studies have shown that P release from environmental sample like sludge increased with increase in temperature and is maximum at 60 °C for 3 h, (Raj et al. 2012) but degradation of the released P takes place above this temperature. Effect of temperature on crystallization of struvite from cow urine can be studied in similar way. But release of ammonia from the sample is expected at higher temperatures above 40 °C.

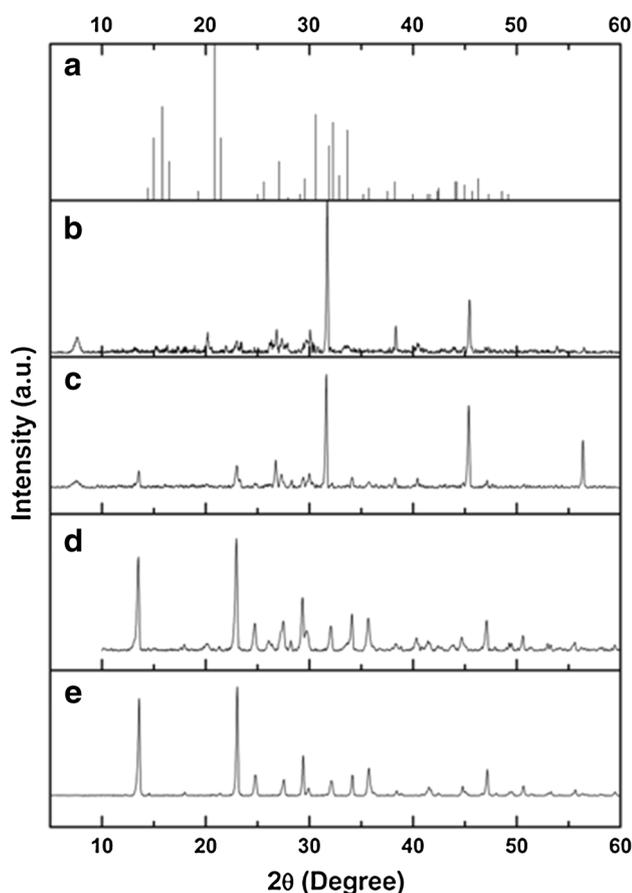


Fig. 4 Powder XRD pattern for the precipitated product obtained from cow urine **a** standard struvite ICDD Card No. 15-0762 **b** Mixing ratio 1:2, pH 7 **c** Mixing ratio 1:2 at pH adjusted to 9.0 using 1 N NaOH, and **d** Mixing ratio 1:0.5, pH 9.0 **e** using $MgCl_2$

Table 4 Struvite production from cow urine using brine at different ratios and at pH 9

Sr no.	Urine (ml)	Brine (ml)	Weight of precipitate (g)
1	50	12.5	2.40
2	50	25	4.28
3	50	37.5	4.16
4	50	50	5.17
5	50	62.5	7.12
6	50	75	5.96
7	50	87.5	8.84
8	50	100	9.23

FT-IR studies

FTIR absorption spectra are shown in Fig. 6 for struvite crystallized using brine as well as $MgCl_2$. There is no difference in the absorption pattern of both except the peak intensities are lower for the struvite crystallized using brine than that of struvite crystallized using $MgCl_2$. An

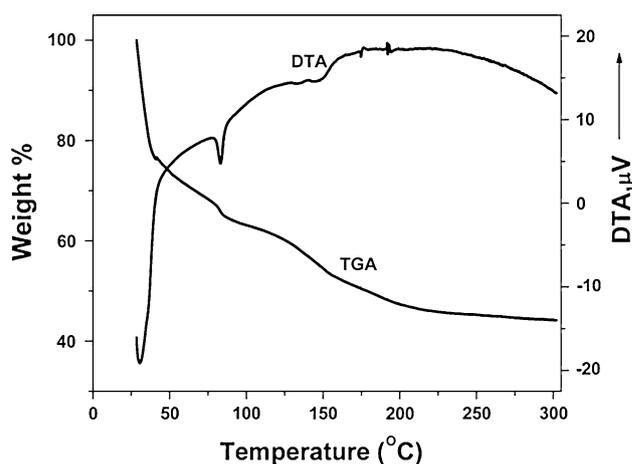


Fig. 5 TGA and DTA curve of struvite crystallized using brine

absorption peak centered at $3,558\text{ cm}^{-1}$ is due to the N–H stretching. The strong and broad peak in the range between $3,500$ and $2,750\text{ cm}^{-1}$ is due to the O–H stretching vibration motion, a characteristic of water of hydration. The weak bands seen between $2,600$ and $2,100\text{ cm}^{-1}$ are mostly due to water phosphate hydrogen bonding. The weak and broad peak at $1,641\text{ cm}^{-1}$ is due to the H–N–H or H–O–H scissoring effect. Peaks centered at $1,527$ and $1,400\text{ cm}^{-1}$ can be attributed to the N–H bending vibrations. The splitting of the peak may be due to the rotation of the ammonium ions. A low intensity but sharp peak is seen in both cases centered at $1,099\text{ cm}^{-1}$ is mainly due to the ionic phosphate (Fig. 7). Another sharp medium intensity peak centered at 846 cm^{-1} is due to the rocking of N–H bond. Weak peaks at 671 and 474 cm^{-1} are due to the metal–oxygen bond. Thus it is clear from FT-IR that there is presence of water of hydration, N–H bond NH_4^+ ion PO_4^- ion P–O bond and metal–oxygen bond.

SEM-EDAX

SEM images were taken for the powered struvite which showed the presence of irregular granular shaped particles (Figs. 8, 9). EDAX showed the composition of individual elemental composition in atomic% for both kind of crystallized struvite (Figs. 10, 11). The results are compiled in Table 5. Struvite crystallized using magnesium chloride showed P 2.31 %, Mg 11.47 % and N 3.35 %. Whereas struvite crystallized using brine showed P 2.31 %, Mg 16.72 % and N 2.35 %. The chlorine ion content was 11.32 and 19.34 % in struvite crystallized with magnesium chloride and brine respectively. This indicates that magnesium chloride may still present in struvite. Struvite crystallized from brine also contained sodium ion (Na) 9.17 % and potassium ion (K) 0.59 % for the obvious



Fig. 6 FT-IR of struvite crystallized using brine (curve a) and using $MgCl_2$ (curve b)

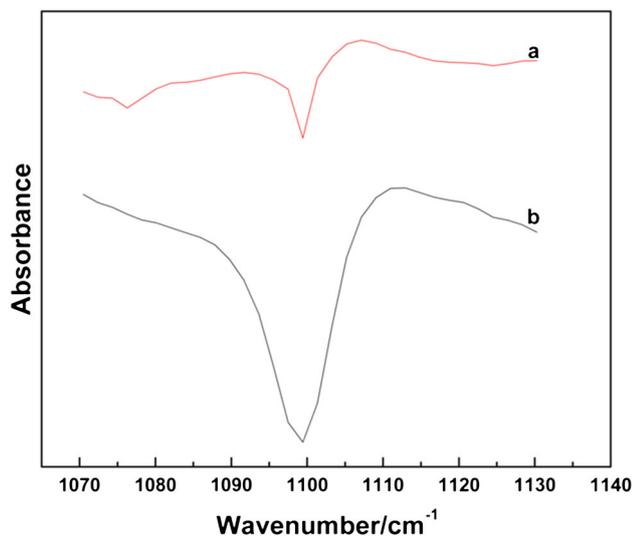
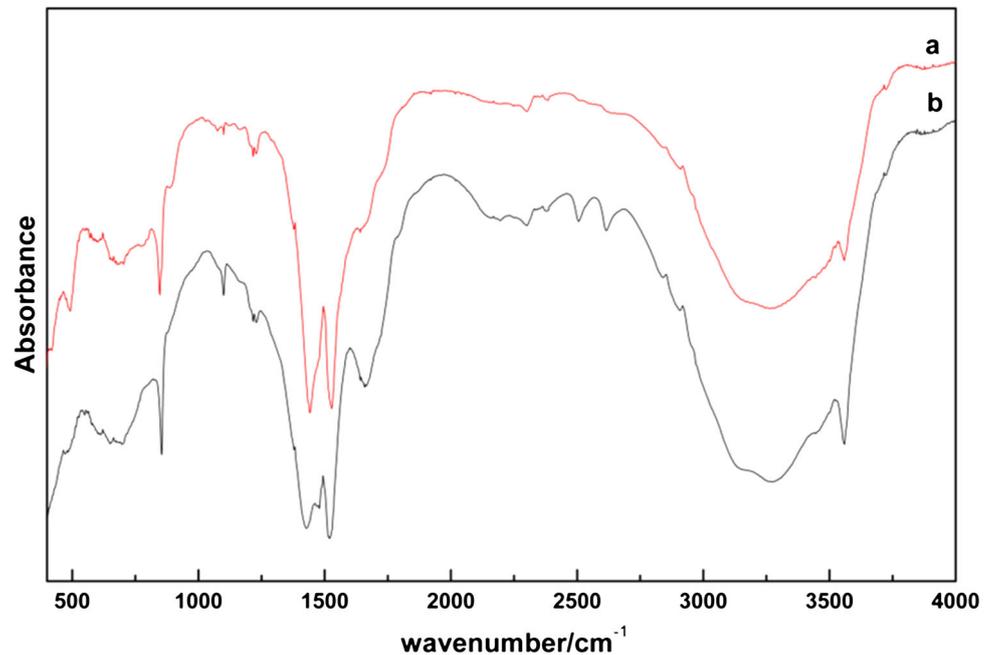


Fig. 7 Sharp peak in FT-IR absorbance of struvite crystallized using brine (curve a) and using $MgCl_2$ (curve b) centered at $1,099\text{ cm}^{-1}$

reason that the brine contains these ions in the form of NaCl and KCl and got precipitated along with the struvite. This indicates that struvite crystallized using brine contains impurities such as NaCl and KCl in small quantities. In both the cases sulfur was also present which must have originated from the cow urine itself. When to be considered as NPK fertilizer, struvite crystallized using magnesium chloride has a ratio of 10:9:0 and struvite crystallized using brine has ratio of 10:7.8:1.7. Struvite crystallized by Ryu et al. (2012), has elemental NPK ratio of 10:4.2:2.9 and can be used as fertilizer. Since magnesium is deficient in soil

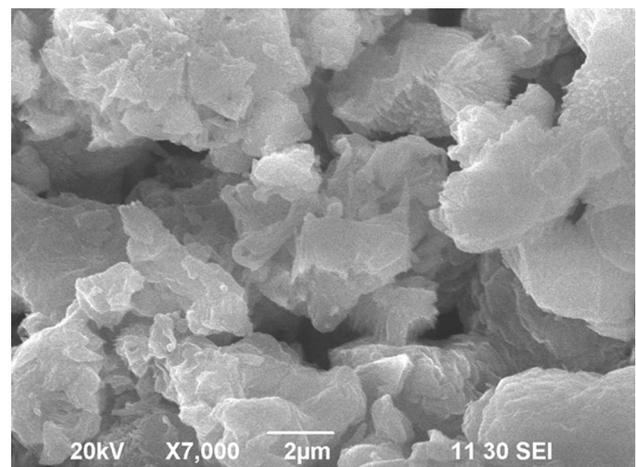


Fig. 8 SEM image of the powered struvite crystallized using magnesium chloride showing irregular granular shape particles

such as soil in Goa, use of struvite adds an advantage as farmer need not add magnesium fertilizer separately.

The analysis of struvite as per APHA standard methods for phosphate, magnesium and ammonium ions showed 5.85, 3.16, and 0.56 % respectively [theoretical values for each of them are 12.6, 9.9 and 5.7 % respectively (Sakthivel et al. 2011)].

Fertility evaluation of precipitated struvite

The obtained struvite was utilized in cultivation of *V. radiata* at different dosage and compared with that of commercial fertilizers to assess its fertility. During the

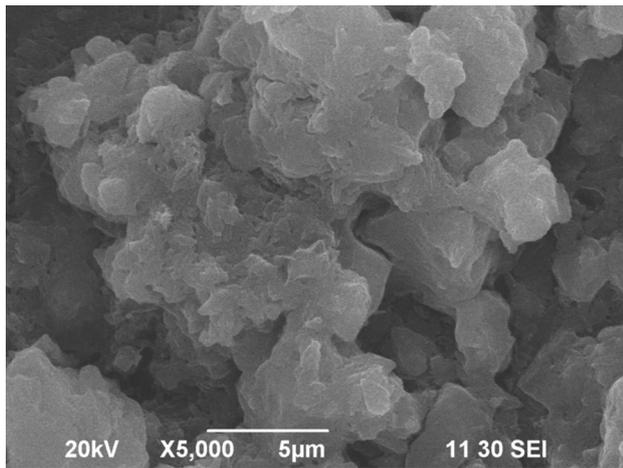


Fig. 9 SEM image of the powdered struvite crystallized using brine

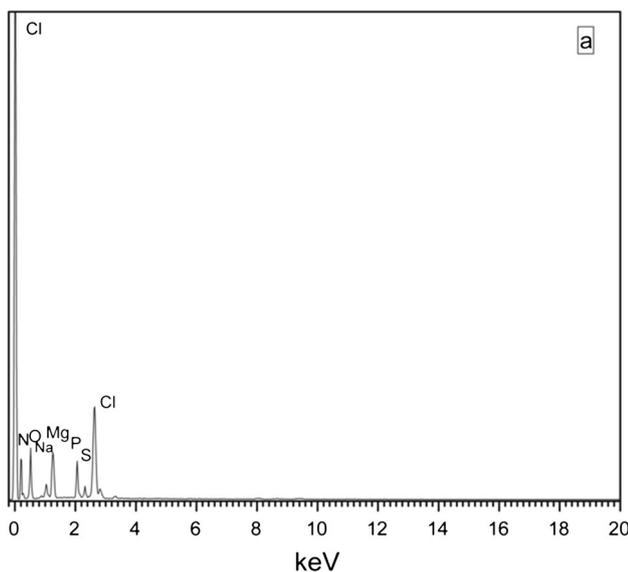


Fig. 10 EDAX of the powdered struvite crystallized using magnesium chloride

experimental period, the tallest leaf in each pot was selected and measured for its length. The tests showed that the *V. radiata* grew at different rates depending on the dosage of struvite and fertilizers as illustrated in Fig. 12. *V. radiata* in the struvite pots showed the highest growth rate. The best growth rate was observed in the pots where 2 g/kg (S4) of soil struvite was added.

Vigna radiata seeds inoculated with 1.6 and 2.0 g/kg of struvite showed a significant increase in % germination compared to control by 10 and 3.34 % (Table 6). Also the total survival at the end of day 30 was 100 % in 2.0 g/kg of struvite compared to control.

The average leaf length of *V. radiata* in DAP, organic, S1, S2, S3, S4 and control pots reached 3.8, 4.5, 4.0,

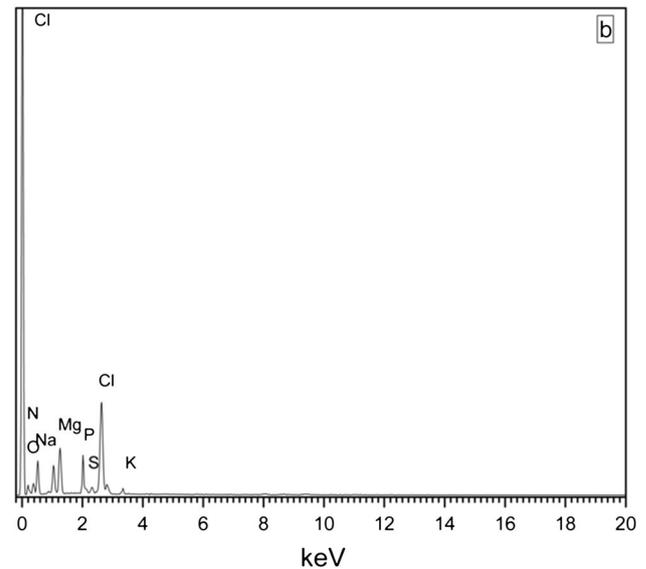


Fig. 11 EDAX of the powdered struvite crystallized using brine

Table 5 EDAX analysis of powdered struvite crystallized using magnesium chloride and brine

Element	With MgCl ₂ ·6H ₂ O (atm%)	With brine (atm%)
N	3.35	3.35
O	62.58	52.74
Na	1.37	9.17
Mg	16.72	11.47
P	2.31	2.31
S	2.35	1.03
Cl	11.32	19.34
K	–	0.59

3.7, 4.9, 5.1 and 4.6 cm respectively, as presented in Fig. 13.

As regarding the stem and root length the increase was significantly higher than the control. The stem length decreased in order of S4 > organic manure > S3 > DAP > S2 > S1 > control. Whereas the root length decreased in order of S4 > S2 > organic manure > S3 > DAP > S1 > control.

Leaf area also followed the similar order of decrease, S4 > organic manure > S3 > DAP > control > S1 > S2.

It is very much evident that the addition of 1.6 and 2 g/kg struvite significantly increased the average fresh and dry weights of stem and root of *V. radiata* in comparison with the control. The average fresh weights of stems in S4 pots ranked first in the experimental group. When above ground dry weight is considered, struvite gave superior results to that of other fertilizers.

Total chlorophyll was found to be 28.96, and 28.02 mg/g of wet weight in S4 and S3 respectively which was

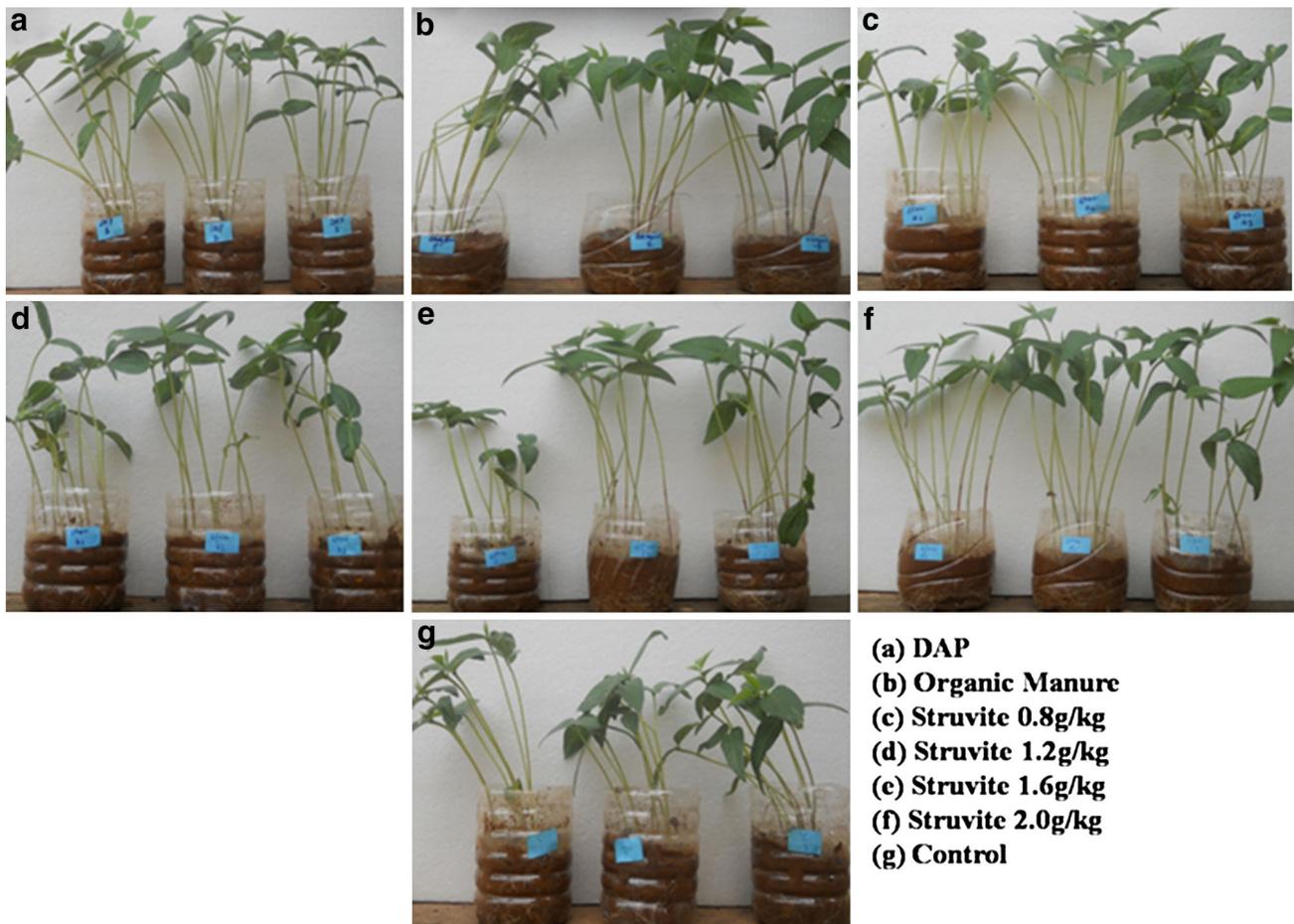


Fig. 12 *Vigna radiata* plants showing the effect of different fertilizers on its growth at 30 days after sowing

slightly higher than that of control 27.78 mg/g of wet weight.

Total phosphorus and total nitrogen were analyzed for dried stem and root. Stem total phosphorus was found to increase in order of S1 < S2 < control < DAP < S3 < organic < S4 whereas root total nitrogen was found to increase in S3 < S2 < S4 < DAP < organic manure < S1 < control.

Total nitrogen in stems was in order of organic manure < S4 < S3 < DAP < S2 < S1 < control. And in root it showed the order S4 < S3 < S2 < organic manure < DAP < control < S1.

Total struvite produced from cow urine using brine with optimum ratio was approximately 40 g/L. India's total number of dairy livestock is ranking highest in the world. In 2007 it was having a total of 199.1 and 105.3 million cattle and buffalos respectively (Government of India 2010). On average an adult dairy cow excretes about 26 kg urine per 1,000 kg body weight per day [(ASAE) 2003], which consequently becomes a major component of the

livestock waste. The manure excreted from these animals ultimately finds its way into the water bodies resulting in elevation of nutrient levels within them. If struvite is made from this waste, a large amount of phosphate can be recovered. Theoretically at the yield of 40 g/L a total of 12,176 tons struvite could be made per day all over India. Formation and optimization of struvite need to be carried out at large scale commercial level. Thorough and feasible economic evaluations need to be carried out in this regard.

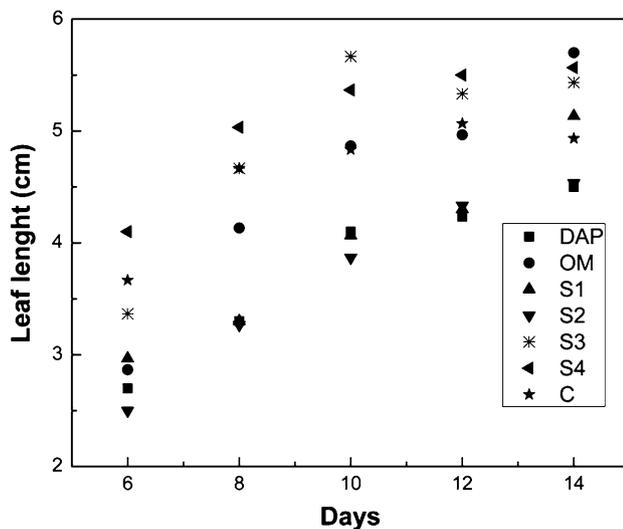
Production of struvite has an additional advantage for farmer. If a farmer is having cows, he can produce his own fertilizer containing phosphate and magnesium for agriculture rather than spending money on the purchase of commercial phosphate fertilizers.

Use of brine will further give some financial assistance to the sea salt producing community by selling the brine.

Hence new, feasible and effective ways of removing elements like phosphorus and nitrogen from such discharges are always important in nutrient pollution control of the environment.

Table 6 Analysis of plant growth experiment

	DAP	Organic manure	Struvite				Control
			(0.8 g/kg)	(1.2 g/kg)	(1.6 g/kg)	(2.0 g/kg)	
Germination rate (%)	93.33 ± 5.77	90.00 ± 0	90.00 ± 10	86.67 ± 5.77	93.33 ± 11.54	86.67 ± 15.27	83.33 ± 15.27
Total survival (%)	75.19 ± 22.67	92.59 ± 6.42	89.17 ± 10.10	70.37 ± 27.96	80.00 ± 20.00	100.00 ± 0.00	89.17 ± 10.10
Leaf area (cm ²)	8.38 ± 0.25	10.43 ± 1.94	7.57 ± 0.47	7.31 ± 0.77	9.32 ± 2.50	10.90 ± 0.390	7.73 ± 0.76
Stem length (cm)	23.77 ± 0.25	28.23 ± 2.25	19.60 ± 1.91	19.73 ± 3.33	27.60 ± 4.87	30.33 ± 1.17	19.50 ± 1.00
Root length (cm)	10.83 ± 0.76	12.17 ± 0.76	12.67 ± 2.52	10.00 ± 2.00	11.67 ± 1.53	13.00 ± 3.00	8.00 ± 1.00
Total chlorophyll (mg/g of wet wt.)	19.58 ± 3.28	24.25 ± 5.49	15.75 ± 5.67	24.17 ± 1.81	28.02 ± 2.68	28.96 ± 2.69	27.78 ± 3.64
Stem wet wt. (g)	4.12 ± 1.02	6.32 ± 1.23	2.25 ± 0.87	2.25 ± 0.20	5.04 ± 1.42	7.88 ± 1.01	3.30 ± 0.86
Stem dry wt. (g)	0.90 ± 0.16	1.52 ± 0.30	0.42 ± 0.18	0.40 ± 0.07	1.18 ± 0.46	1.87 ± 0.22	0.61 ± 0.09
Root wet wt. (g)	1.98 ± 0.14	5.25 ± 1.44	1.61 ± 0.22	0.83 ± 0.27	4.08 ± 1.81	4.06 ± 1.80	2.04 ± 0.34
Root dry wt. (g)	0.23 ± 0.04	0.86 ± 0.10	0.29 ± 0.14	0.22 ± 0.02	0.69 ± 0.35	0.72 ± 0.33	0.25 ± 0.06
Stem total phosphorus (mg/kg)	44.63 ± 10.33	66.45 ± 23.87	23.82 ± 20.48	25.09 ± 20.35	36.17 ± 2.20	61.03 ± 7.45	35.13 ± 5.21
Root total phosphorus (mg/kg)	4.94	6.54 ± 3.25	7.86 ± 0.53	1.81 ± 0.72	1.44 ± 0.54	4.88 ± 1.83	17.94 ± 5.08
Stem total nitrogen (%)	3.50 ± 0.14	2.66 ± 0.16	4.27 ± 0.08	4.20 ± 0.16	2.94 ± 0.29	2.87 ± 0.21	4.34 ± 0.16
Root total nitrogen (%)	2.87 ± 0.08	2.31 ± 0.21	3.29 ± 0.08	2.31 ± 0.08	1.75 ± 0.08	1.61 ± 0.08	2.87 ± 0.21

**Fig. 13** Length of leaves over the time

Conclusion

Struvite is a good source of phosphate and it can be recovered from livestock waste such as cow urine. Our results indicate that 1:0.5 mixing ratio of cow urine to brine gives best quality struvite. The structure and stability of struvite is affected when dried above 40 °C. The analysis of struvite for phosphate, magnesium and ammonium ions showed 5.85, 3.16,

and 0.56 % respectively. In the fertilizer potential study of struvite on *V. radiata*, 2.0 g struvite per kg of soil showed best plant growth, among the lower concentrations used. However more studies need to be carried out to ascertain the optimum amount of struvite required by different crops. Thus struvite can be made from a renewable source for a sustainable agricultural development.

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