Optimization studies on the production of struvite from human urine – waste into value

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ABSTRACT

Recovery of nutrients from wastewater streams has twin advantages of preventing eutrophication and providing value for the treatment process. Phosphate in significant quantities is available in sewage, with human urine accounting for a major portion. In this context, studies were conducted for the maximum recovery of phosphate as 'Struvite'. The significant variables that affect the struvite recovery from human urine were identified by Plackett Burman design and further optimized using a four factor central composite design. The optimal conditions for phosphate recovery were determined: pH 9.5, Mg to P ratio 1.5, precipitation time 40 min and ammonium concentration 2,000 mg L^{-1}. The maximum phosphate recovery obtained at optimal condition from synthetic urine sample was significantly higher than the real urine samples. The fertilizing ability of struvite so produced was assessed in comparison with normally used fertilizer 'Di-Ammonium Phosphate (DAP)' under identical conditions using *Ixora coccinea* L, a popular plant with medicinal values. The growth parameters of *Ixora coccinea* L were found to be significant for Struvite but could not match the performance of DAP. The twin advantages of lower cost of production particularly with the increasing demand for phosphorus and the utilization of environmentally benign waste product makes study relevant and attractive.

Keywords: Nutrient recovery, Phosphate, Struvite, Human urine, *Ixora coccinea L*, Response surface methodology

1. Introduction

Recovery of nutrients (NPK) for agricultural activities, treatment and disposal of sewage are the twin challenges confronting the society. The municipal wastewater, whose volumes are large, contains about 75% of nitrogen and about 80% of phosphorous including a significant fraction from urine excreted in the form of urea [1–2]. Urine source separation has been considered to be a sustainable substitute for the conventional sewage system [3], as it contributes about 40%–50% of the P, 75%–87% of the total N and 54%–90% of the K to municipal wastewater with only 1% of raw sewage volume [4]. On the other hand, wastewater containing phosphorus and nitrogen can lead to eutrophication in surface water [5].

Wastewater particularly the urine fraction has a potential to be a supplementary source of nutrients for food production in the context of dwindling resources of natural phosphate rock and increasing demand. To ensure the adequate supply of phosphorus, it is necessary to look for additional resources from where one can recover phosphate economically [6–8]. Current organic phosphate sources such as bone meal and animal manure are limited in resources and may not be sufficient to meet the ever-increasing demand thus making it imperative to look for easily available and conveniently process-able sources to recover the phosphate content. Several methods of nutrient recovery techniques have been used including physical (ultrafiltration) physico-chemical methods (adsorption and nanofiltration) and

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chemically aided physical methods (chemical precipitation, ion exchange, etc.). However, the economic viability of the methods is still to be established because of low fertilizer recovery [9].

Nitrogen (N) and phosphorus (P) are the essential supplements for all surviving creatures, and they play a significant role in the technical and agronomical development [10]. Human urine is a rich source of phosphorus and nitrogen and it cannot be used directly as a fertilizer. In this context, the strategy suggested by a number of studies, point to the recovery of struvite ($MgNH_4PO_4.6H_2O$) from effluent streams containing urine [11–13].

Formation of struvite precipitate has been observed [14] in wastewater and sewage treatment processes in specific locations of pipelines such as elbows, valves, aeration assemblies and pump internal components causing operational problems. In recent years, struvite recovery from wastewater treatment plants, as '*value compound*' has attracted many researchers [15–20].

Further studies have indicated the economics to be favorable if one can adopt 'integrated precipitation cum crystallization processes' for the production of struvite from varying wastewater feed stocks in large scale [14,21,22]. The primary compounds and species reported to be present in struvite include $MgHPO_4$, $MgH_2PO_4^+$, $H_2PO_4^-$, H_3PO_4, NH_3, HPO_4^{2-}, $MgOH^+$, $MgPO_4^-$, Mg^{2+}, PO_4^{3-}, NH_4^+ [23]. It is reported that struvite precipitation originates in a supersaturated solution consisting of ammonium, phosphate, and aggregates of magnesium at a controlled pH and could be improved by reducing the interference from other ions such as Na^+, etc [24–26]. The higher ammonium ion concentration not only enhances the precipitation of struvite but also provide the benefit of pH buffering to improve the yield [27].

Conversion of the nutrients to struvite by the selective removal of phosphate ions from the complex industrial liquid wastes, manure solution or municipal sewage by chemical precipitation is considered, a sustainable alternative to conventional methods [28,29]. This would result in treated effluent, free of phosphate-phosphorus and ammonia-nitrogen, leading to safe discharge besides allowing an opportunity to recover value. Most of the studies in this regard were limited to one or two parameters such as pH, temperature, etc. We believe there could be mutual interactions amongst a few parameters amongst pH, temperature, the ratio of P, N and Mg, mixing speed, precipitation time, etc. and simultaneously influence the overall yield of Struvite. Moreover, the quality and usefulness of struvite so produced particularly in the context that urine directly cannot act as a fertilizer requires to be established.

Ixora (*Ixora coccinea* L.) is popular hedging fast growing plant in subtropical regions of India, which has many beneficial uses particularly with its abounding medicinal properties and are traditionally used as hepatoprotective, chemoprotective, antimicrobial, antioxidant, antinociceptive, and anti-inflammatory activities [30–32].

In this context studies were undertaken with the objective of identifying the significant parameters using 'Response Surface Methodology' (RSM) [33,34], optimising the conditions of precipitation using 'central composite design (CCD) model', validating the condition with real samples and demonstration of the efficacy of Struvite as a fertilizer using *Ixora coccinea* L as a model plant.

2. Materials and methods

2.1. Materials

Synthetic urine components magnesium chloride (99%), potassium dihydrogen phosphate (99.5%), creatinine (99%), sodium citrate (99%), ammonium chloride (99.5%), potassium chloride (99.5), urea (99.5%) were purchased from Sisco Research laboratories Pvt., Ltd., Mumbai, India. Tryptic soy broth was purchased from Hi Media Laboratories Pvt Ltd, (Mumbai, India). Diammonium phosphate was obtained from Agricultural Technology Information Centre (ATIC), Kattupakkam, Kancheepuram District, Tamilnadu.

2.2. Synthetic urine

Synthetic urine solution was prepared following the standard method [35]. AR grade chemicals have been used throughout the experiments. Typical composition of one liter solution used for the experiments, consisted of 0.65 g magnesium chloride, 2.8 g potassium dihydrogen phosphate, 0.02 g of sodium oxalate, 1.1 g creatinine, 0.65 g of sodium citrate, 1.0 g ammonium chloride, 1.62 g potassium chloride, 2.3 g sodium sulphate, 0.65 g calcium chloride, 4.62 g sodium chloride, 25 g urea and 10 g tryptic soy broth added together in one liter of distilled water. The content of the mineral components in synthetic urine correspond to mean concentration found in 24 h period in normal human urine. The natural urine sample was collected from three different persons over a day and mixed well (Table 1), which used as standard sample for compare the phosphate recovery from synthetic urine sample. The real urine sample consists primarily of water (91%–96%), with organic solutes including urea, creatinine, uric acid, and trace amounts of enzymes, carbohydrates, hormones, fatty acids, and inorganic ions such as sodium (Na^+), potassium (K^+), chloride (Cl^-), magnesium (Mg^{2+}), calcium (Ca^{2+}), ammonium (NH_4^+), sulfates (SO_4^{2-}), and phosphates. The pH of urine is normally around 6.2 with a range of 5.5–7.0. The specific gravity of urine may range from 1.002 to 1.037. Synthetic urine solution compositions were modified appropriately to suit the current experimental design.

Table 1
Real human urine composition

Composition	Values (g L^{-1})
$CaCl_2.2H_2O$	0.52 ± 0.01
$MgCl_2.6H_2O$	2.58 ± 0.62
NaCl	2.62 ± 0.01
Na_2SO_4	1.90 ± 0.01
$Na_3C_6H_5O_7.2H_2O$	0.47 ± 0.06
$Na_2C_2O_4$	0.01 ± 0.03
KH_2PO_4	4.24 ± 0.09
KCl	1.62 ± 0.22
Urea	12.35 ± 0.18
$C_4H_7N_3O$ (creatinine)	0.95 ± 0.13

2.3. Struvite precipitation

Jar-test apparatus equipped with six beakers with a working volume 0.5 L each was used for optimization studies. The stock solutions of synthetic urine were filled in the beakers, and the experiments were carried out as per the experimental design. For each sample, the pre-determined amount of known concentration of MgO solution was added and later desired pH was adjusted using NaOH solution. The beaker was kept at room temperature for about an hour to ensure complete formation of struvite (precipitate) and the contents were filtered with 40 μm Whatman filter paper. The filter paper with the precipitate was dried at 110°C in a hot air oven until attaining concordant weights. The efficiency of the precipitation was assessed by analyzing the residual phosphate (PO_4^{3-}) content in the filtrate by the spectroscopic method using ammonium molybdate.

2.4. Statistical design of experiment

Plackett Burman Design (PBD) model was used to design the experiments and Minitab software package (Minitab Inc., USA) was used for analyzing the experimental responses in order identify the factors which impact the outcome namely the extent of phosphate removal. This statistical model considers mutual interaction amongst the factors that impact phosphate recovery. A set of 12 experimental runs were carried out using nine process variables (Table 2). The factors considered are: pH (X_1), (Mg/P) Ratio (X_2), precipitation time (X_3), stirring speed (X_4), temperature (X_5), seeding crystal size (X_6), reactor volume (X_7), ammonium concentration (X_8), sodium concentration (X_9) at two levels ''+1'' for high level and ''–1'' for low level. Potassium concentrations (X_{10}), calcium concentration (X_{11}) were considered as dummy variables. All experiments were performed, and phosphate recovery (%) was taken as the response. The factors with confidence level higher than 90% were considered sufficiently significant for phosphate recovery. Four independent variables namely, pH, Mg/P ratio, precipitation time and ammonium concentration were selected based on the two-level screening by the

PBD method. These variables were further optimized by Central Composite Design (CCD) model to obtain maximum phosphate recovery. As per the experimental design matrix, thirty different experimental sets were carried out in the predetermined range of values: pH (8–11) (A_1), Mg/P ratio (1–2) (A_2), precipitation time (20–60 min) (A_3) and ammonium concentration (1,000–3,000 mg l^{-1}) (A_4) as shown in (Table 3). Statistical analyzes including the analysis of variance (ANOVA) and the multiple regressions by Design Expert 7.1.6 statistical software (Stat-Ease, Inc., Minneapolis, USA) were carried out.

2.5. Struvite analysis

The phase purity of the recovered struvite was confirmed by XRD-powder diffraction pattern (D/max-RB, Rigaku, Japan with CuKα), FT-IR spectrum was recorded with KBr discs containing 2 wt% of crystal in the wave number range of 4,000–500 cm^{-1} with a 4 cm^{-1} resolution. Morphology of struvite crystal was studied using SEM with SEM-EDS (S-3000, Hitachi Japan). TGA/DTA of struvite was analyzed using Thermo Gravimetric Analysis (DTG-60H, Shimadzu, Japan) to get the temperature profile at 20ºC min^{-1} under nitrogen environment.

2.6. Mini Ixora plant growth analysis

Mini Ixora (*Ixora coccinea* L) plant growth was studied in the controlled pot experimental setup by collecting air dried (12 d) soil from SRMIST, Kattankulathur, India. The effect of struvite on the growth of ornamental and medicinal plant Mini Ixora (*Ixora coccinea* L) was tested for one season, in August. The average and minimum temperature in the period were 28.5°C and 18.7°C respectively, and maximum and minimum relative humidity were 91.3% and 68.3% respectively. The soil characteristics both physical and chemical were evaluated as per the standard protocol (Agricultural technology information centre (ATIC) Kattupakkam, Kancheepuram District, Tamil nadu, India). The soil texture was sandy loamy with a pH of about 6.2, electrical conductivity 0.51 ds m^{-1}, nitrogen 51 ppm,

Table 2
Plackett -Burman experimental design for screening of process parameters for phosphate recovery

Run order	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}	Phosphate recovery (%)
1	8	1	20	150	20	1,000	1,000	1,000	2,000	2,500	200	78
2	11	1	60	150	50	100	100	1,000	2,000	500	200	72
3	11	1	60	150	20	1,000	1,000	3,000	500	500	50	80
4	8	1	60	50	50	1,000	100	3,000	2,000	2,500	50	68
5	11	2	60	50	20	100	1,000	1,000	2,000	2,500	50	58
6	11	1	20	50	50	100	1,000	3,000	500	2,500	200	90
7	8	2	60	50	50	1,000	1,000	1,000	500	500	200	59
8	11	2	20	50	20	1,000	100	3,000	2,000	500	200	78
9	8	2	60	150	20	100	100	3,000	500	2,500	200	64
10	8	2	20	150	50	100	1,000	3,000	2,000	500	50	68
11	8	1	20	50	20	100	100	1,000	500	500	50	68
12	11	2	20	150	50	1,000	100	1,000	500	2,500	50	83

Table 3
Central composite design (in actual units) for phosphate recovery with observed and predicted responses

Standard order	A_1	A_2	A_3	A_4	Phosphate recovery (%)	
					Experimental	Predicted
1	08	1	20	1000	59	59
2	11	1	20	1000	62	62
3	08	2	20	1000	60	59
4	11	2	20	1000	65	63
5	08	1	60	1000	61	62
6	11	1	60	1000	67	66
7	08	2	60	1000	60	62
8	11	2	60	1000	69	67
9	08	1	20	3000	60	64
10	11	1	20	3000	69	67
11	08	2	20	3000	60	61
12	11	2	20	3000	65	65
13	08	1	60	3000	61	63
14	11	1	60	3000	64	67
15	08	2	60	3000	59	61
16	11	2	60	3000	66	66
17	6.5	1.5	40	2000	52	47
18	12.5	1.5	40	2000	52	55
19	9.5	0.5	40	2000	76	74
20	9.5	2.5	40	2000	71	72
21	9.5	1.5	0	2000	63	64
22	9.5	1.5	80	2000	71	68
23	9.5	1.5	40	0	58	61
24	9.5	1.5	40	4000	69	65
25	9.5	1.5	40	2000	89	90
26	9.5	1.5	40	2000	89	89
27	9.5	1.5	40	2000	89	88
28	9.5	1.5	40	2000	89	89
29	9.5	1.5	40	2000	89	89
30	9.5	1.5	40	2000	89	89
31	08	1	20	1000	59	59

phosphorus 5.1 ppm, and potassium 80.5 ppm. The optimal fertilizer dosage was fixed based on the soil characteristics. Cuttings of the species *Ixora coccinea* (5 cm tall) acquired from succulent producer and collector were utilized as a plant substance. The trial configuration used was the randomized block design, with three treatments, each one containing seven replications. Three sets of seven pots (21 polypropylene pots of 20 cm diameter and 20 cm depth) were prepared. 1 kg of soil was taken in each of the pots. Soil was blended with struvite for seven pots and blended with DAP for other seven pots. Seven pots were filled with the soil without any blending to serve as the control. The treatment details were: T1 – control; T2 – Struvite; T3 – DAP. 100 mL of water was poured to each pot every day. The pots were kept under sunlight. The growth and flowing time were monitored. At the end of 30 d, the growth parameters (shoot length, root length and the number of flowers) were analyzed statistically.

3. Results and discussion

3.1. Optimization of the process condition for struvite precipitation

Initially, eleven factors (corresponding to nine parameters of the process and two dummy factors) were studied in the PBD experiments in twelve different trials. The results given in (Table 2) indicate the highest phosphate removal in Trial-6 and the least in Trial-5. The response data were subjected to regression analysis to assess the *p*-value and hence the confidence level. The *p*-value corresponding to 90% confidence level has been fixed as the bench mark to identify the significant parameters from the relatively non-significant ones given in Table 4. The perusal of the responses along with the statistical determinants indicates precipitation time, pH, (Mg/P) ratio and ammonium concentrations to be the critical parameters influencing the yield of the precipitate. Further, we conclude that stirring speed (rpm), seeding crystal size (μm), sodium concentration (mg L⁻¹), potassium concentration (mg L⁻¹) and reactor volume (mL) are not as significant based on the *p*-values. Fig. 1 illustrates the Pareto chart for the above experiments and the parameters were screened out which were less than the benchmark confidence level of 90%. Previous study indicated that the Mg molar ratio, pH level, aeration rate, reaction time and temperature significantly influencing the struvite recovery [36].

Further experiments were conducted using central composite experimental design (CCD) to identify the optimal conditions for obtaining the maximum yield of Struvite. The variables considered for the study were pH (A_1), Mg/P ratio (A_2), precipitation time (A_3) and ammonium concentration (A_4). All the other parameters were kept constant such as stirring speed, temperature, seeding crystal size, reactor volume, sodium concentration, potassium concentrations, and calcium concentration. These values were later subjected to multiple linear regression analysis and the corresponding ANOVA chart reflecting the interaction parameters is presented in (Table 5) along with the '*P*' value (phosphate recovery). The regression Eq. (3) gives correlation between the significant variables for the phosphate recovery.

$$Y_1 = 89.00 + 1.96A_1 - 0.38A_2 + 0.96A_3 + 0.96A_4 + 0.31A_1A_2 + 0.19A_1A_3 + 0.06A_1A_4 + 0.06A_2A_3 - 0.56A_2A_4 - 0.94A_3A_4 - 9.43A_1^2 - 4.05A_2^2 - 5.68A_3^2 - 6.55A_4^2 \quad (1)$$

The ANOVA results signify that the linear and square terms in second-order polynomial model are highly significant ($p \leq 0.005$) and adequate to denote the correlation for phosphate recovery. Results show that A_1, A_1A_1, A_2A_2, A_3A_3, and A_4A_4 had a significant effect on the phosphate recovery. A correlation factor of 0.92 between the experimental and predicted values indicate reasonable agreement.

3.2. Interaction effect between the process factors and phosphate recovery

The results obtained based on the CCD were presented as 3D response surface plots. The phosphate recovery with reference to pH and Mg/P ratio (Fig. 2(a)), pH and precipitation

time (Fig. 2(b)) pH and ammonium concentration (Fig. 2(c)) was shown in (Fig. 2). Fig. 3 indicates the phosphate recovery with reference to precipitation time and (Mg/P) (Fig. 3(a)), ammonium concentration and Mg/P (Fig. 3(b)) and ammonium concentration and precipitation time (Fig. 3(c)).

Fig. 2(a) which presents the interactions between pH and Mg/P ratio on phosphate recovery shows that the *P* recovery increases with a rise in pH from 8 to 9.5 at constant precipitation time and ammonium concentration. However, the further increase in pH leads to the reduction in phosphate recovery. Recovery of about 74% obtained at pH 9.5 agrees with the literature [37]. Increase in the recovery of P with pH can be attributed to the decrease in the solubility of struvite with pH [38]. However, beyond pH 9.5, the formation of magnesium phosphate appears to decrease the yield of struvite [39].
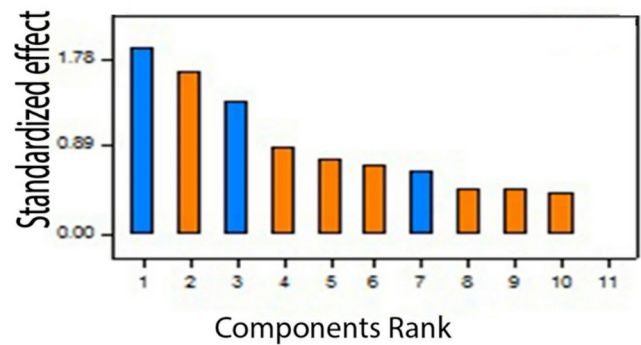

Fig. 1. Pareto chart for significance of process parameter on phosphate recovery.

Table 4
Statistical analysis of Plackett–Burman experimental design results on phosphate recovery

Terms	Coefficient	F-value	p-value	Confidence level (%)
Constant	72.17	10.15	0.0413	
Ph	4.67	20.81	0.0197	98.0
Mg:P ratio	−3.83	14.04	0.0332	96.6
Precipitation time (min)	−5.33	27.19	0.0137	98.1
Stirring speed (rpm)	2.00	3.82	0.1455	85.5
Seeding crystal size (μm)	2.17	4.49	0.1244	87.6
Ammonium concentration (mg L^{-1})	2.50	5.97	0.0922	90.8
Sodium concentration (mg L^{-1})	−1.83	3.21	0.1710	82.9
Potassium concentration (mg L^{-1})	1.33	1.70	0.2834	71.7

Table 5
Analysis of variance (ANOVA) for effect of variable on phosphate recovery (R^2:0.96)

Factors	Sum of squares	Degrees of freedom	Mean square	F-value	p-value
Model	3,820.28	14	272.88	30.76	<0.0001
A_1	92.04	1	92.04	10.37	0.0057
A_2	3.38	1	3.38	0.38	0.5466
A_3	22.04	1	22.04	2.48	0.1358
A_4	22.04	1	22.04	2.48	0.1358
A_1A_2	0.56	1	1.56	0.18	0.6807
A_1A_3	0.56	1	0.56	0.063	0.8046
A_1A_4	0.063	1	0.063	0.0007	0.9342
A_2A_3	0.063	1	0.063	0.0007	0.9342
A_2A_4	5.06	1	5.06	0.57	0.4617
A_3A_4	14.06	1	14.06	1.59	0.2273
A_1A_1	2437.57	1	2437.57	274.74	<0.0001
A_2A_2	450.36	1	450.36	50.76	<0.0001
A_3A_3	884	1	884	99.64	<0.0001
A_4A_4	1177.50	1	1177.5	132.72	<0.0001
Residual error	133.08	15	8.87		
Lack-of-fit	133.08	10	13.31		
Pure error	0.000	5	0.000		
Total	3953.37	29			

A_1: pH; A_2: Mg:P ratio; A_3: precipitation time; A_4: ammonium concentration.
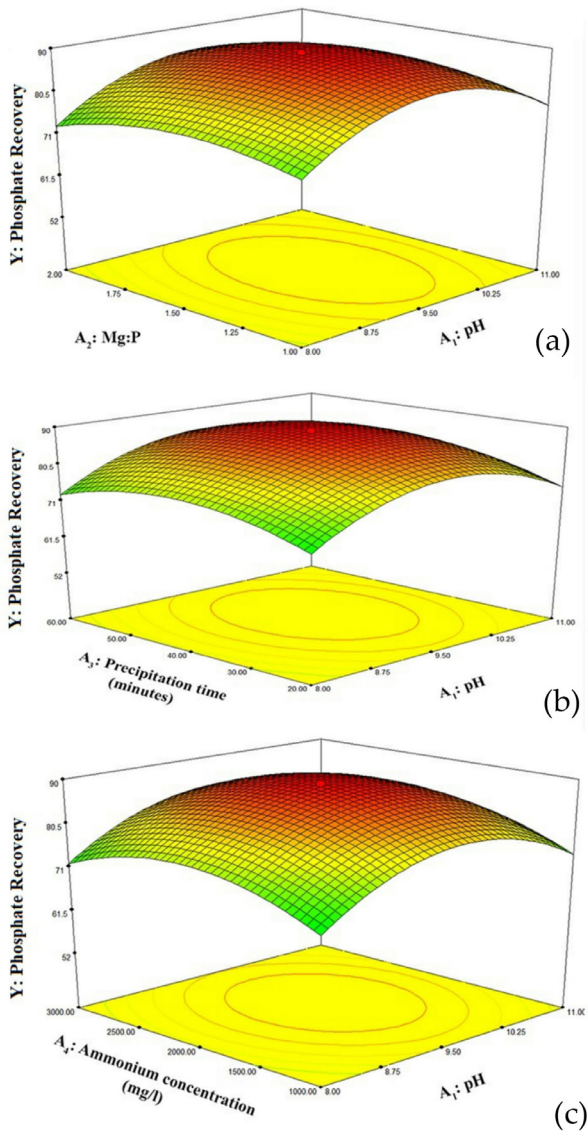
Fig. 2. ((a)–(c)) Response surface for phosphate removal efficiency as a function of (a) interactions between pH and Mg:P; (b) interactions between pH and precipitation time; (c) interactions between pH and ammonium concentration.
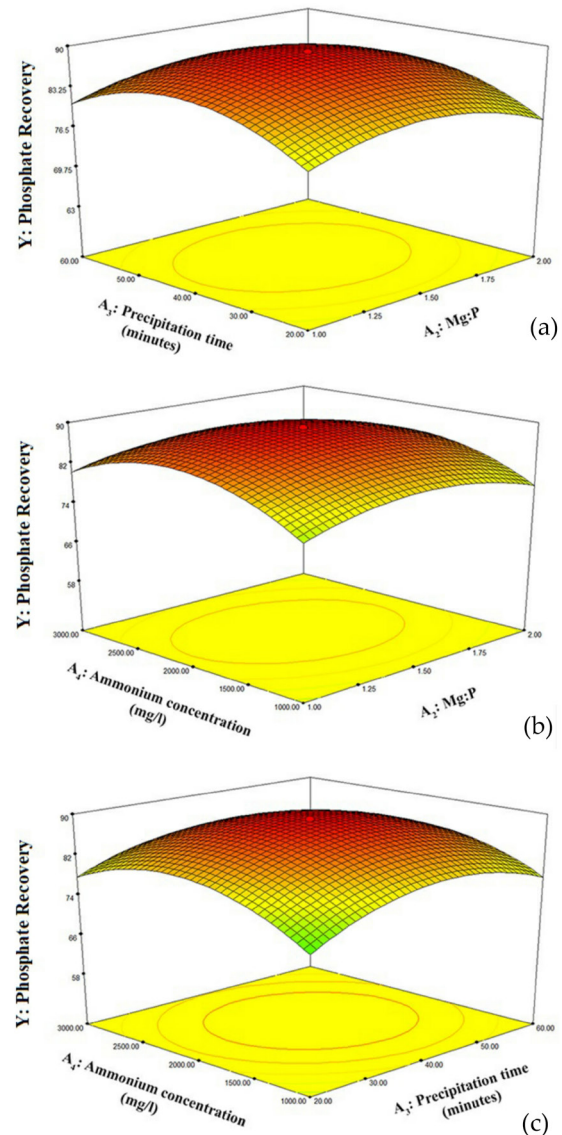

Fig. 3. ((a)–(c)) Response surface phosphate removal efficiency as a function of (a) interactions between Mg: P and precipitation time; (b) interactions between Mg: P and ammonium concentration; (c) interactions between precipitation time A_3 and ammonium concentration.

A similar trend was observed for Mg/P ratio as the precipitation increased up to a ratio of 1.5 recording a maximum level of ~89% '*P*' precipitation. Further increase of Mg/P ratio resulted in a significant decline in the yield.

Fig. 2(b) displays the combined effect of pH and precipitation time on the response, while the other two variables are kept a constant level. It was seen that the phosphate recovery initially increases with precipitation period till ~40 min. Further increase in the period does not lead to any significant increase in phosphate recovery suggesting that the maximum phosphorous recovery can be obtained at around 40 min at 9.5 pH and 2,000 mg L^{-1} ammonium concentration. The response surface plot of the interactive effect of pH and ammonium concentration as shown in Fig. 2(c) indicates that the phosphorous recovery increases with simultaneous increase in pH till 9.5 and ammonium

concentration till 2,000 mg L^{-1} respectively, beyond which the yield shows a declining trend.

Fig. 3(a) illustrates the interactive effect of Mg/P ratio and precipitation time on phosphate recovery. At short precipitation times, the phosphate removal efficiency was not significant. The precipitation time of 40 min was found to be sufficient for the formation struvite flocs leading to settling. When the time was less the precipitation was not complete probably due to unavailability of necessary settling time. After 40 min there was no considerable increase in the phosphate recovery percentage.

Fig. 3(b) is about the effects of Mg/P ratio and ammonium concentration on the optimal yield of ~79% phosphorous recovery at 1.5 ratio of Mg/P and 2,000 (mg L^{-1}) of ammonium concentration. It is evident that excess Mg/P ratio (>1.5)

and ammonium concentration (>2,000 mg L^{-1}) reduce the struvite crystal formation thereby resulting in the reduced recovery of phosphate. The interaction between precipitation time and ammonium concentration are depicted in Fig. 3(c). These results showed that an optimum yield of ~75% recovery was observed near the central value of precipitation time (40 min) and ammonium concentration (2,000mg l^{-1}) in the selected region. The preceding observations lead to the following conclusions:

(i) Maximum yield of ~89% phosphate recovery can be obtained at pH 9.5, ammonium concentration of 2,000 mg L^{-1}, Mg/P ratio of 1.5 and a precipitation time of 40 min. Similar findings have reported that ~92.6% phosphate recovery can be obtained at pH 9.5, reaction time 34.76 min and 25.23°C temperature [40]. (ii) pH higher than 9.5 favors the formation of magnesium phosphate thereby reducing the amount of struvite formation. (iii) Increase in ammonium concentration beyond 2,000 mg l^{-1} leads to reduced struvite formation probably because excess ammonium ions hinder the formation of struvite. Validation experiment was performed with real human urine sample to recover ~79% of phosphate is given in Table 6. The above result was find phosphate recovery obtained from synthetic sample was comparatively greater than the real human urine sample. Previous literature shown 99.39% phosphate removal was obtained at optimum conditions of 500 mg·L^{-1} [PO$_4^{-3}$] concentration, [PO$_4^{-3}$]:[Ca^{+2}] molar ratio of 1:1.6, and influent pH of 10 [41].

Table 6
Phosphate recovery % for real human urine

Sample	Phosphate recovery (%)			
	Trial 1	Trial 2	Trial 3	Mean
Human urine	77.2	80.5	79.6	79.1

3.3. Struvite purity and crystal size

The XRD pattern of the sample analyzed using Match XRD software is presented in Fig. 4. The phase purity of the sample was found to be 87%, and the density is 1,701 kg/m^3. The space group analysis of the sample assessed as orthorhombic (a = 6.9950 Å, b = 6.1420 Å, and c = 11.2180 Å) is in good agreement with the findings [42–44]. SEM-EDS analyzes the morphology of 9.5 μm crystals obtained from different trials were assessed and the pictures are shown in Fig. 5. The mixed shape of crystals, a combination of rod, brick and rectangular shapes, formed during precipitation and crystallization process can be seen. These observations were in agreement with the earlier work of the morphology of struvite crystals formed from wastewater [45,46]. Chemical composition indicated the presence of Mg, P, N and O on the synthesized struvite crystals with Mg/P ratio as 1.19 which is in good agreement with specified chemical composition.

The FT-IR spectrum of synthesized struvite crystals shown in Fig. 6 shows the presence of water of hydration (OH stretch and a broadband around 3,200 cm^{-1}). The broadband around 3,200 cm^{-1} can also include NH stretching vibrations. The absorption occurring at 2,924 cm^{-1} and doublet at 2,880 cm^{-1} was due to the NH$_4^+$ ions. The absorptions occurring at 2,394, 1,630, and 1,436 cm^{-1} had been attributed to NH bending. The absorption 1,009 cm^{-1} indicates ionic phosphate and 494 and 572 cm^{-1} was due to metal-oxygen bond. Drying of struvite precipitate is a significant stage in sustaining its fragility and crystal size. Figs. 7((a)–(c)) shows the TGA/DTA curve of the dried struvite sample. TGA of the struvite sample indicated only the loss of moisture around 110°C. A loss of 40% mass was detected at 220°C and there was no additional loss of mass till 300°C. Thus, thermal analysis confirmed the usage of struvite as fertilizer in fields without any structural change.
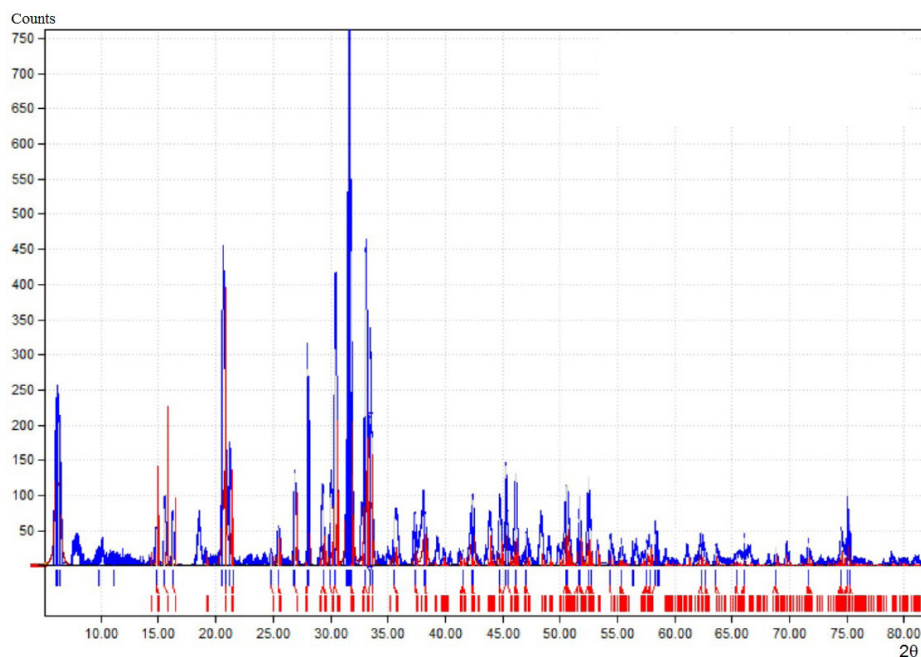

Fig. 4. XRD analysis of struvite. (Blue line – experimental pattern, Red line – calculated pattern).
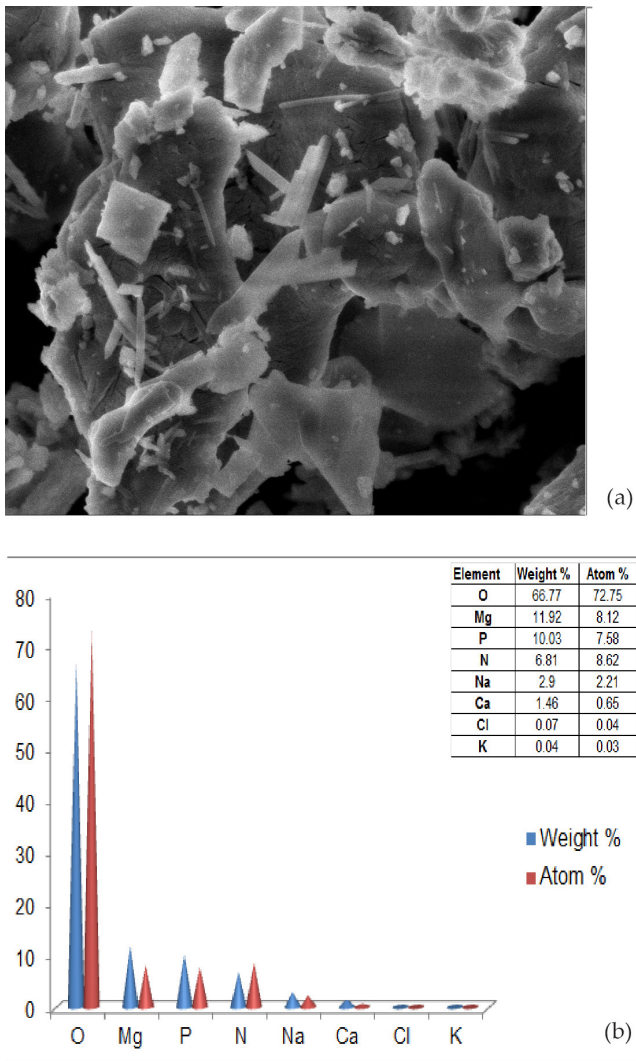
Fig. 5. (a) SEM with (b) EDS analysis of struvite.

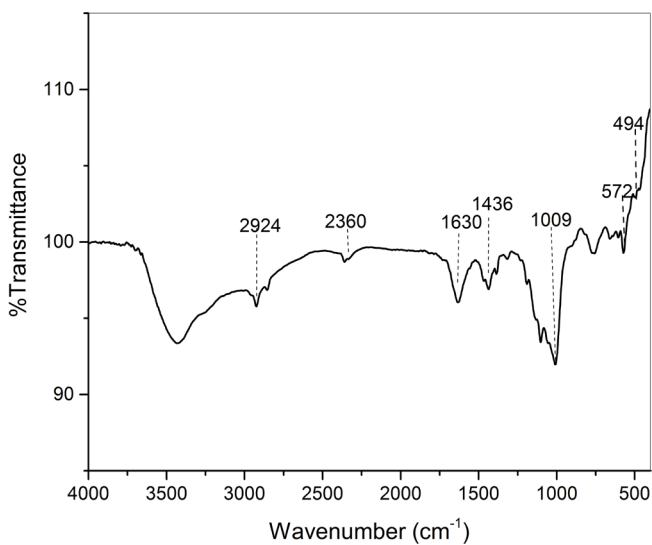| Element	Weight %	Atom %
O	66.77	72.75
Mg	11.92	8.12
P	10.03	7.58
N	6.81	8.62
Na	2.9	2.21
Ca	1.46	0.65
Cl	0.07	0.04
K	0.04	0.03

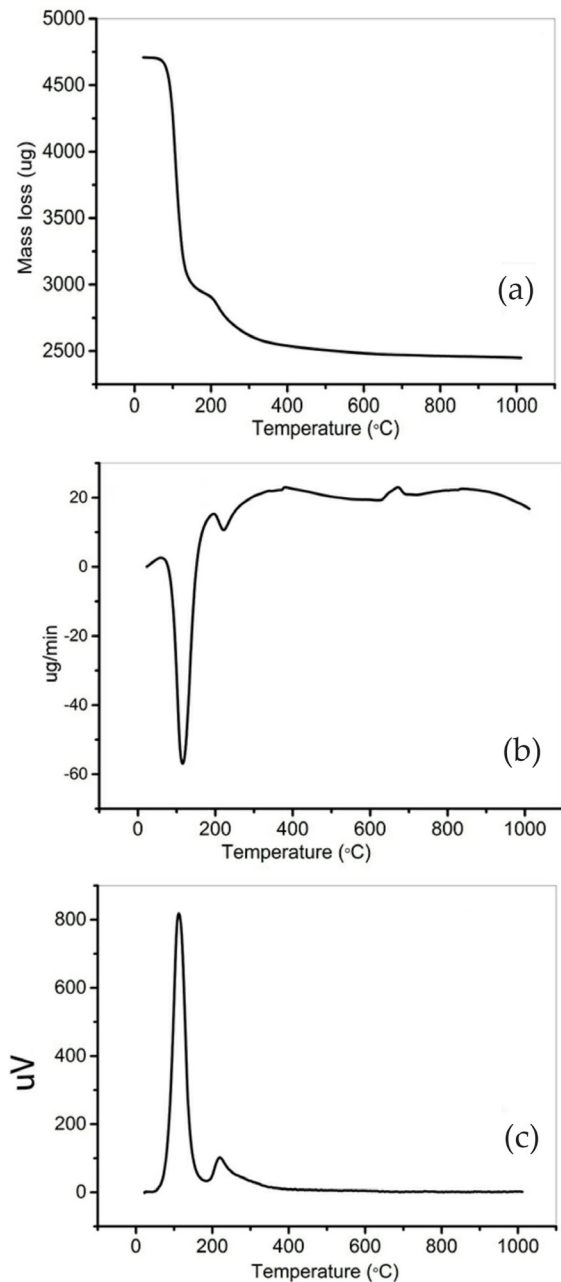Fig. 6. FTIR spectrum analysis of struvite.

Fig. 7. Thermo gravimetric (TGA) analysis of struvite (a) Thermogravimetric Analysis of struvite (TGA), (b) Differential thermogravimetry of struvite (DTG) and (c) Differential thermal analysis of struvite (DTA).

3.4. Statistical analysis studies on growth of mini Ixora (Ixora coccinea L)

Mass production of *Ixora coccinea L*, a high P demand plant is of commercial market demand because of its medicinal and horticulturist value [47,48].Experimental results to assess the efficacy of struvite using *Ixora coccinea L* were analyzed by ANOVA to test the effect with and without fertilizer on plant growth by random sampling. The growth parameters considered were the length of the root, length of the shoot and number of flowers at the constant period of 30 d.

Average data for each replication was calculated, and then mean and standard deviation (SD) of the replications were determined using analysis of variance. Fisher's protected least significance difference (LSD) test at the 5% level was used to compare treatment means. The effect of struvite and DAP on the growth parameters (shoot length, root length and the number of flowers) of Ixora is shown in Fig. 8. Fertilization treatment of struvite significantly increased the shoot length, root length and number of flowers by 15.6%, 20.7%, and 30.3% compared with the control. Interpretation of treatment effect on shoot length, root length and number of flowers was shown in (Table 7).

It was evident that struvite treated soil enhanced the overall plant growth compared with the control and it is similar to DAP treated soil. It was observed that early budding occurred in the DAP and struvite supplemented soil resulting in more number of flowers. The analysis of variance (ANOVA) for the growth parameters is depicted in Table 8. It was seen
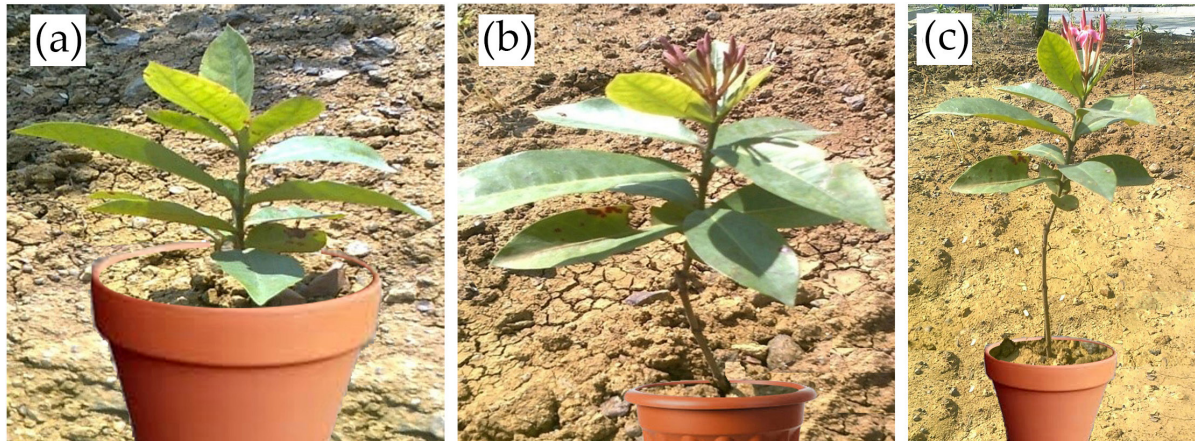

Fig. 8. *Ixora coccinea* L plant pots at different applications after 15 days growth (a) Control, (b) Struvite, (c) DAP

Table 7
Effect of fertilizers and formulation on *Ixora coccinea* L –shoot length root length and number of flowers

Growth parameters	Treatments	Replications							Total	Mean
		R1	R2	R3	R4	R5	R6	R7		
Shoot length	T1	30.20	29.60	28.80	27.50	27.20	26.90	29.10	199.30	28.47
	T2	33.22	32.56	32.83	32.73	33.18	32.82	33.17	230.51	32.93
	T3	35.21	34.51	36.12	36.65	36.83	39.05	34.50	252.88	36.13
Root length	T1	09.60	10.00	10.60	09.10	08.80	08.50	10.10	66.70	09.53
	T2	12.00	12.20	11.45	11.56	11.09	10.97	11.11	80.37	11.48
	T3	14.76	14.03	13.28	15.02	14.08	14.91	13.00	99.09	14.16
Number of flowers	T1	16.00	18.00	16.00	17.00	14.00	16.00	18.00	115.00	16.00
	T2	21.00	20.00	21.00	21.00	21.00	20.00	21.00	145.00	21.00
	T3	24.00	23.00	26.00	27.00	26.00	25.00	23.00	174.00	25.00

T1 – Control; T2 – Struvite; T3 – DAP; R1, R2, R3, R4, R5, R6 and R7 – replications.

Table 8
ANOVA for Shoot length, root length & number of leaves of *Ixora coccinea* L

Growth parameters	Source of variance	Degrees of freedom	Sum of square	Mean square	*F*-value
Shoot length	Replication	6.00	1.54	0.26	0.13
	Treatments	2.00	206.94	103.47	51.56
	Error	12.00	24.08	2.01	–
Root length	Replication	6.00	1.94	0.32	0.58
	Treatments	2.00	75.53	37.76	67.58
	Error	12.00	6.71	0.56	–
Number of flowers	Replication	6.00	4.67	0.78	0.40
	Treatments	2.00	248.67	124.33	63.94
	Error	12.00	23.33	1.94	–

that the *F*-value from the statistical analysis was less than 0.05 and hence the null hypothesis (H_0) could be rejected.

With regards to root length, shoot length and number of flowers the degree of freedom was 3.89 (5%) and 6.93 (1%) between the treatments and 3.00 (5%) and 4.80 (1%) between the replications. From the results, it was clear that T3 (DAP) and T2 (struvite) were independently and significantly higher than T1 (control).

4. Conclusions

Chemical and physical parameters of production of Struvite were optimized with synthetic urine first and subsequently validated with natural urine. The optimum conditions were found to be pH 9.5, Mg/P ratio1.5, ammonium concentration 2,000 ppm with 40 min precipitation time. The fertilizer value of produced struvite was found to be good even though in absolute terms its performance is below that of synthetic DAP. Our studies indicate a strong case for segregating urine at source and process nearby to avoid transportation challenges. Further studies are required to scale up the process and for recycling the spent stream so as to still minimize the nutrient dispersed to the environment. As the product is generated from environmentally benign waste, possibly at a lower cost the production looks attractive for field application.

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