Research Article

Received: 4 December 2023 Revised: 21 April 2024 Published online in Wiley Online Library: 8 May 2024

(wileyonlinelibrary.com) DOI 10.1002/jctb.7661

Nutrient recovery from manure digestate by using waste magnesite powder and bone meal as sustainable substitutes for struvite precipitation

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Abstract

BACKGROUND: Struvite ($MgNH_4PO_4.6H_2O$) precipitation is a sustainable approach that can offer simultaneous removal/recovery of nutrients from biogas plant effluents. However, most biogas plant effluents contain a higher molar concentration of nitrogen (N) than magnesium (Mg) and phosphorus (P). Therefore, the external addition of Mg^{2+} and phosphate (PO_4^{3-}) salts is needed to maximize the recovery. In this study, Mg-rich waste magnesite powder and P-rich bone meal were used as sustainable additives. The Box–Behnken design was applied to determine optimum conditions of process parameters (pH, Mg:N and P:N molar ratios) to maximize ammonium-nitrogen (NH_4-N), PO_4-P and Mg^{2+}recoveries.

RESULTS: NH_4-N, PO_4-P and Mg^{2+} recoveries were in the ranges 78.5%–96.9%, 69.2%–96.3% and 75.1%–99.9%, respectively. The actual and predicted values showed significant consistency, indicating that the model is satisfactory. Under optimum conditions ($pH = 9.0$, $Mg:N = 2.2$, $P:N = 1.8$), $97.8 \pm 0.1\%$ NH_4-N, $96.6 \pm 0.31\%$ PO_4-P and $84.4 \pm 0.9\%$ Mg^{2+} recovery were attained. The X-ray diffraction results confirmed the sole presence of struvite crystals. Scanning electron microscopy images showed irregular prismatic orthorhombic crystals and amorphous material depositions on precipitates of ~25 μm crystal size. The product was 49% struvite with 15.2% P content. The heavy metal content was lower than regulatory limits.

CONCLUSION: Even though waste material and industrial by-products have been used as additives in this process, high NH_4-N and PO_4-P recoveries were recorded under optimum conditions. These results are promising and illustrate a powerful example of industrial symbiosis, and the precipitate containing struvite can serve as a valuable product.

Keywords: nutrient recovery; struvite; bone meal; waste magnesite powder; optimization

INTRODUCTION

The uncontrolled discharge of wastes with high nitrogen (N) and phosphorus (P) content causes severe environmental problems such as the eutrophication of water bodies, which may end up in harmful algal blooms, producing toxins that are risky for human health and the environment.[1,2] In fact, P is the limiting nutrient for algae growth in most freshwater bodies for example, lakes and rivers.[3] Therefore, even a moderate level anthropogenic discharge of P to such water bodies may cause a significant shift in the ecosystem, leading to a steadily increasing deterioration of water quality.[3] Therefore, it is crucial to take preventive actions that limit P discharge into surface waters. However, N and P are vital for preserving life as they are the building blocks of DNA,[4] and play a crucial role in food production and agriculture. There is a huge industry demand for ammonia (NH_3) and ~70% of produced NH_3 is used for fertilizer production.[5] Given that >70% of NH_3 is produced via natural-gas-based steam reforming, its production is highly emission- and energy-intensive.[5] Unfortunately, there is no better picture for P; it is commonly extracted from phosphate rock mines, and yet phosphate rocks are nonrenewable.[1,6] Further, the majority of the phosphate rock reserves are located in Morocco with lesser amounts (in order of abundance) in Iraq, China, Algeria, Syria, Jordan, South Africa, USA and Russia.[7] This uneven spatial distribution of such a vital resource is a concern for many countries, including Turkey. Therefore, over the past decade, there has been a lot of focus on recycling and recovering N and P through efficient resource management.[8] To this end, it is critical to focus our efforts on highly concentrated and widely available streams such as manure-fed biogas plant effluents.[9-11]

Phosphorus recovery can be achieved by a variety of methods, such as adsorption,[12] metal ion precipitation[13] and reverse

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osmosis.[14] However, these methods produce dense sludge, treatment of which is expensive, and thus may only temporarily solve the problem without providing a sustainable solution. Therefore, there is a need for a sustainable and economically viable nutrient recovery process. Struvite [magnesium ammonium phosphate (MAP), $MgNH_4PO_4.6H_2O$] precipitation is a promising nutrient recovery approach that has been commonly applied to a variety of streams such as anaerobically digested poultry manure,[11] urine,[15] leachate[16] and swine manure.[17] Furthermore, with this process, simultaneous N and P recovery is possible, and the product can be used as fertilizer.

Struvite is a white, insoluble crystalline material. Precipitation of this compound takes place when the levels of NH_4^+, Mg^{2+} and PO_4^{3-} are above the solubility product threshold under alkaline conditions.[16,18] Struvite precipitation takes place according to the reaction [Eqn (1)] where $n = 0, 1,$ or 2[19]:

$$Mg^{2+} + H_nPO_4^{n-3} + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4.6H_2O\downarrow + nH^+ \quad (1)$$

In order to achieve efficient recovery of N and P by struvite precipitation from anaerobically digested wastes, it is necessary to add significant quantities of Mg^{2+} and PO_4-P rich chemicals.[16] This is due to the relatively higher abundance of N ions than other struvite-forming ions (Mg and P) in such waste streams. The external addition of such ions in the form of pure chemicals such as magnesium oxide (MgO) or phosphoric acid (H_3PO_4) is costly and risks financial sustainability.[20] Therefore, sustainable replacements of pure chemicals are being explored to develop an economically viable and environmentally friendly struvite precipitation process. However, foreign ions—other than Mg^{2+}, P and N—may be present in the system during the precipitation of struvite, due to the wide variety of wastewater sources or additives that are used in the process. Calcium (Ca^{2+}; the most common), potassium (K^+), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), copper (Cu^{2+}), zinc (Zn^{2+}) and aluminium (Al^{3+}) are typical foreign ions found in wastewater streams.[21] These ions may impact the rate of struvite formation reaction, the effectiveness of recovery, the morphology and the purity of the final product.[21,22] Depending on the relative abundance of the foreign ions, solids other than struvite such as K-struvite, hydroxyapatite, calcium carbonate and brucite may coprecipitate and lower the recovery of the target nutrients. Therefore, the final product quality must be analyzed, especially when unconventional additives are used for struvite precipitation. Seawater[23,24] and bittern[25] are some substitutes that have been previously used as Mg^{2+} sources and nutrient recovery efficiencies were comparable to efficiencies attained with pure chemicals. Another option is to use waste magnesite powder (WMP), which is a byproduct of the manufacturing process of converting magnesite ($MgCO_3$) into MgO.[26] The estimated worldwide deposits of $MgCO_3$ are ≈3420 million tons, with Turkey accounting for >160 million tons of this total.[26,27] During the processing of $MgCO_3$, ~13–25% of WMP is produced, and because WMP is composed of very fine particles (~60 μm particle size), its disposal is problematic.[26] In addition, there is currently no recognized application or use for this waste material in Turkey.[26,27] Likewise, alternative P sources have been explored to replace pure additives. A good example is the use of bone meal (BM) as a P source in the struvite precipitation process.[28,29] BM is a by-product of the meat industry that is produced by cooking and removing fat from mammal corpses and then drying and crushing them.[30] Contrary to the majority of naturally occurring phosphate ores, BM is devoid of heavy metals; hence, the obtained struvite product may even be more suitable as fertilizer.[31] More than 3.5 million tons BM are produced annually in the European Union.[32] In the case of Turkey, estimated BM production equals 400 000 tons per year based on the annual number of slaughtered cattle.[33,34] Only around 37% (~150 000 tons) of this total have a beneficial use as chicken feed.[33] Therefore, both BM and WMP have long-term potential as sustainable P and Mg^{2+} sources for struvite precipitation. Previously, WMP and BM have been used separately to replace pure chemical additives in the struvite precipitation process. Yet, to the best of the authors' knowledge, this is the first study that simultaneously investigates the addition of BM and WMP for struvite precipitation from biogas plant effluents.

This study aims to offer a sustainable process for struvite precipitation that provides a powerful example of 'industrial symbiosis'. In this industrial symbiosis model, the meat, magnesite processing and biogas industries are linked to achieving nutrient recovery simultaneous with waste management. The proposed concept enables a circular economy example because the value-added product, struvite, can be employed as a slow-release fertilizer. In the experimental study, we used Box–Behnken Design (BBD) to define the optimum levels of significant process parameters to simultaneously maximize N, P and Mg^{2+} recoveries. The obtained value-added product was further analyzed through X-ray diffraction (XRD) and scanning electron microscopy (SEM), and the purity was measured.

MATERIALS AND METHODS

Preparation of the biogas plant sample

Digestate was obtained from a full-scale mesophilic anaerobic digester fed with cattle manure located in Polatli, Turkey. The sample was centrifuged at 11 000×*g* for 15 min. The original sample with a total solids (TS) content of 16% was diluted to a TS of 9% to enable continuous mixing. The initial PO_4-P concentration of the digestate sample was quite low (~0.3 mmol L^{-1}), and thus the dissolution of P from the solid phase was the only way to recover the highest amount of nutrients.[11] Therefore, the sample was subjected to an acidic dissolution process to increase PO_4-P concentration and maximize P recovery. Acidic dissolution was accomplished in three steps[10]: (i) acid addition, (ii) mixing and (iii) centrifugation. Briefly, sulfuric acid (H_2SO_4) of 6.5 N was added until pH was decreased to 2.0 ± 0.2. The mixture was continuously mixed overnight using a stirrer (VELP Scientifica Srl, Usmate, Italy). Finally, the sample was centrifuged at 11 000×*g* for 15 min to collect the supernatant. This liquid solution is called P-enriched digestate and was kept at 4 °C until use after characterization (Table 1).

Preparation of WMP and BM solutions

The BM was collected from DSA Agri-food Products, Kirikkale, Turkey. WMP was obtained from KÜMAŞ Magnesite Inc., Kütahya, Turkey. Characterizations of these raw materials are presented in Table 1. Like biogas plant effluent, an acidic dissolution process was applied to both raw materials for proper solubilization of Mg^{2+} and PO_4-P before experimental runs. The method was modified from Siciliano and De Rosa.[35] Briefly, 60 g BM was dissolved in 150 mL 3 N H_2SO_4. In the case of WMP, 90 g solid WMP was dissolved into 100 mL 3 N H_2SO_4; H_2SO_4 was used to prevent the dissolution of Ca^{2+} ions.[35] The mixtures were mixed for 2 h and

Table 1. Characteristics of P-enriched digestate, raw WMP and raw BM

Parameters	P-enriched digestate	WMP	BM
PO_4-P (mg L^{-1})	1100 ± 110 (35.5 ± 4 mmol L^{-1})	-	-
NH_4-N (mg L^{-1})	1950 ± 180 (139 ± 13 mmol L^{-1})	-	-
K (mg g^{-1})	2.0 ± 0.1 (51.2 ± 2 mmol L^{-1})	0.367 ± 0.02	2.5 ± 0.1
Mg (mg g^{-1})	1.14 ± 0.05 (46.9 ± 2 mmol L^{-1})	270 ± 10	3.4 ± 0.1
Fe (mg g^{-1})	1.06 ± 0.01 (18.9 ± 0.002 mmol L^{-1})	14.6 ± 0.2	n.d.
Na (mg g^{-1})	0.90 ± 0.01 (39.1 ± 0.04 mmol L^{-1})	0.597 ± 0.01	6.2 ± 0.2
Ca (mg g^{-1})	0.49 ± 0.01 (12.2 ± 0.05 mmol L^{-1})	6.6 ± 0.1	170 ± 10
P (mg g^{-1})	-	n.d.	74 ± 2
Zn (mg g^{-1})	0.033 ± 0.002 (0.5 ± 0.03 mmol L^{-1})	0.021 ± 0.001	n.d.
Al (mg g^{-1})	0.013 ± 0.001 (0.5 ± 0.04 mmol L^{-1})	0.720 ± 0.04	n.d.
Cu (mg kg^{-1})	2.1 ± 0.1 (33 ± 1.6 μmol L^{-1})	15.1 ± 0.3	n.d.
Cr (mg kg^{-1})	1.5 ± 0.1 (0.5 ± 1.9 μmol L^{-1})	286 ± 7	n.d.
Ni (mg kg^{-1})	0.80 ± 0.03 (13.6 ± 0.5 μmol L^{-1})	668 ± 14	n.d.
Pb (mg kg^{-1})	0.052 ± 0.002 (0.02 ± 0.01 μmol L^{-1})	11.5 ± 0.04	n.d.
Cd (mg kg^{-1})	0.014 ± 0.001 (0.12 ± 0.009 μmol L^{-1})	0.67 ± 0.04	n.d.

(-) indicates a parameter that was not measured.
WMP, waste magnesite powder; BM, bone meal; n.d., not detected.

centrifuged at 4000×*g* for 15 min. The supernatant solutions obtained after centrifugation were used as liquid Mg^{2+} and P sources in the experiments. The WMP solution contained 88 g L^{-1} Mg^{2+} (3.6 mol L^{-1}), and the BM solution contained 18 g L^{-1} PO_4-P (0.6 mol L^{-1}) and 0.4 g L^{-1} NH_4-N (28 mmol L^{-1}).

Experimental design and optimization

A response surface methodology (RSM) is a statistical and mathematical approach utilized to mathematically model and analyze engineering problems, and effectively minimizes the required number of experiments for analysis.[36] Its main objective is to optimize the response surface, which is influenced by different process parameters via measuring the correlation between adjustable input parameters and the resulting response surfaces.[36] BBD was selected as RSM in this study because it can assess multiple factors with the smallest number of experimental runs possible.[37] Most importantly, interactions between factors can be investigated via BBD.[37] In the formation of struvite, pH is a key parameter, and any change in the pH of the solution may affect struvite precipitation.[38] Low pH values hinder struvite formation, and at high pH values, co-precipitates may be produced along with struvite, which may cause a decline in NH_4-N recovery efficiency.[20,39] Additionally, the struvite precipitation process is highly affected by the concentrations of Mg^{2+}, P and N.[39] Struvite precipitation occurs when molar concentrations of Mg^{+2}, NH_4^+ and PO_4^{-3} are equivalent, making their availability crucial.[40,41] Although molar amounts of the struvite-forming ions should be equal, the foreign ions like Ca^{2+}, Na^+ and Al^{3+} present in the digestate, BM and/or WMP may react with Mg^{+2} and PO_4^{-3} causing a decline in the ions available to form struvite.[40,41] Accordingly, the optimum molar ratios of the struvite-forming ions should be evaluated by considering the type of wastewater used. For these reasons, in this study, the BBD matrix was created using three operational factors: pH (A), Mg:N molar ratio (B) and P:N (C). Each factor was tested at three levels (Table 2): −1 denotes the low level, +1 represents the high level, and 0 shows the midpoint to evaluate experimental error.[42] Researchers have reported a range of values for the optimal pH for struvite, ranging from 8.0 to 10.7.[43] Because the purity of the struvite decreases after pH 9, the pH (A) range was selected as 8–9 in this study.[44] At this pH range other Mg^{2+} and PO_4-P -containing compounds can form and lower their availability for struvite reaction.[45] This is why the amount of PO_4-P and Mg^{2+} were kept higher than the theoretical value required to obtain high recoveries.[45] Therefore, to maximize NH_4-N recovery, Mg:N and P:N molar ratios were set to >1. The ranges of the factors were 1.5–2.3 for Mg:N (B) and 1.2–2 for P:N (C). The performance responses were selected as NH_4-N, PO_4-P and Mg^{2+} recoveries. Recovery was calculated according to levels after the addition of sustainable substitutes.

For quality control, experiments were run in triplicate, thus a total of 45 experiments were carried out. Through data processing a second-order polynomial reaction related to nutrient recovery was obtained [Eqn (2)]:

$$\hat{Y}_{NR/PR/MR} = \beta 0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 A^2 + \beta_5 B^2 + \beta_6 C^2 \\ + + \beta_7 AB + \beta_8 AC + \beta_9 BC \qquad (2)$$

where $\hat{Y}_{NR}$ is the predicted response for NH_4-N recovery $\hat{Y}_{RP}$ is the predicted response for PO_4-P recovery, $\hat{Y}_{MR}$ is the predicted response for Mg^{2+} recovery, β_0 is the intercept, β_1, β_2, β_3 are linear coefficients, β_4, β_5, β_6 are squared coefficients, β_7, β_8, β_9 are interaction coefficients, and A, B, C are independent variables.

Struvite precipitation

The batch-type tests were conducted in four sequential phases: (i) addition of reagents, (ii) pH adjustment, (iii) settling, and (iv) filtration.[10,46] Each reactor contained 40 mL P-enriched digestate sample. To set the desired molar ratio of Mg:N:P inside the reactor, the required volumes of WMP and BM solutions were calculated based on their initial concentrations in the reactor. Then, WMP and BM solutions were added to the reactors, and the target pH was set by adding 10 N NaOH. The solution was mixed using a magnetic stirrer (VELP Scientifica Srl). The pH of the solution was measured continuously until a steady pH at the desired level was observed. After the pH value was stabilized (with a variation

Table 2. Box–Behnken experimental design

Factors	Levels		
	−1	0	+1
pH	8.0	8.5	9.0
Mg:N (molar ratio)	1.5	1.9	2.3
P:N (molar ratio)	1.2	1.6	2.0

of ±0.1), the equilibrium state was reached. After equilibrium, the reactors were kept mixing at 200 rpm for 30 mins. All of the experiments were performed at room temperature (~20 °C). The reactors were then settled for 1 h to allow the separation of crystallized precipitate from the bulk liquid. Finally, the reactor contents were filtered through a folded coarse filter (ISOLAB, product code 1.107.40.140) to separate the product from the liquid. The filtrate was subjected to Mg^{2+}, NH_4-N and PO_4-P, measurements. The remaining part on the filter, that is, the product was dried at a temperature-controlled room (35 ± 1 °C) for 24 h and its weight was recorded. The product was manually separated from the filter paper and subjected to XRD, SEM and elemental analyses.[21]

Analytical methods

All samples were filtered using 0.45-μm filters to remove any suspended particles before analyses. The amino acid colorimetric method (method 8178; Hach, Ames, IA, USA) and the Nessler colorimetric method (method 8038; Hach) were used to quantify the PO_4-P and NH_4-N concentrations, respectively. A portable pH meter was used to measure the pH (Starter300; Ohaus, Parsippany, NJ, USA). A spectrophotometer was used for colorimetric methods (DR 2800; Hach). All metals and ions except Mg^{2+} were measured with inductively coupled plasma mass spectrometry (ICP-MS) (DRC II; Perkin Elmer, Waltham, MA, USA) in METU-Central Laboratory, Turkey. Mg^{2+} concentrations were determined using atomic absorption spectroscopy (Aanalyst 400; PerkinElmer), following the protocols outlined in the Standard Methods.

The XRD tests were carried out to explain the structural behavior of the powder samples, to verify that the precipitate contains struvite. All of the samples were examined using a Ultima IV X-ray diffractometer (Rigaku, Tokyo, Japan) at METU Central Laboratory. During XRD, the scan range was set to 5–70°, and the duration time/scan speed was 1 deg min^{-1}. The morphologies of the precipitates were analyzed with field emission SEM (Quanta 400F; FEI, Hillsboro, OR, USA) at METU Central Laboratory.

Elemental analysis [carbon (C), hydrogen (H), N, sulfur (S)] was conducted with an elemental analyzer CHNS-932; LECO Corp., St Joseph, MI, USA) at METU Central Laboratory. Extracted P (2% Citric Acid Soluble) in the effluent was analyzed using ICP-OES (TS EN 15959) at Çınar Environmental Laboratory Co. Other macro- and microelements were analyzed with ICP-MS (TS EN ISO 17294) at Çınar Environmental Laboratory Co. when METU Central Laboratory was not in operation. Unwanted particles may precipitate concurrently during struvite crystallization, influencing the struvite crystal development, owing to the complexity of composition of the digestate, WMP and BM. Because struvite is the desired chemical, the product purity is determined by the proportion of struvite in the solid precipitate. The purity may impact the effectiveness of the product for end-use applications and the market price. Theoretically, the elemental composition of pure struvite is 9.9% Mg, 5.7% N and 12.6% P.[47] Because the only precipitate that contains N is struvite, purity was calculated as given in Eqn (3).[47]

$$\text{Purity}\,(\%) = \frac{n_{\text{NH4−N}}}{5.7} \times 100 \tag{3}$$

Where $n_{\text{NH4-N}}$ is the molar ratio of N in the product and 5.7 is the theoretical molar ratio of N.

RESULTS AND DISCUSSION

RSM for the optimization of struvite crystallization process

BBD was used for optimization of the process parameters to maximize NH_4-N, PO_4-P and Mg^{2+} recoveries. BBD provided 15 different experiments; within these, there were 12 different designs and three repetitions of the center point. Second-order regression equations related to the NH_4-N recovery (NR), PO_4-P recovery (PR) and Mg^{2+} (MR) are described as:

$$\begin{aligned}\hat{Y}_{\text{NR}} = {} & -420 + 61.2\,\text{pH} + 99.5\,\text{Mg}:\text{N} + 158.7\,\text{P}:\text{N} \\ & - 2.07\,\text{pH}^*\text{pH} - 25.11\,\text{Mg}:\text{N}^*\text{Mg}:\text{N} \\ & - 26.55\,\text{P}:\text{N}^*\text{P}:\text{N} - 2.70\,\text{pH}^*\text{Mg}:\text{N} - 10.86\,\text{pH}^*\text{P}:\text{N} \\ & + 16.94\,\text{Mg}:\text{N}^*\text{P}:\text{N}\end{aligned} \tag{4}$$

$$\begin{aligned}\hat{Y}_{\text{PR}} = {} & -1451 + 339.0\,\text{pH} - 37.0\,\text{Mg}:\text{N} + 142.9\,\text{P}:\text{N} \\ & - 19.24\,\text{pH}^*\text{pH} + 0.05\,\text{Mg}:\text{N}^*\text{Mg}:\text{N} \\ & - 38.55\,\text{P}:\text{N}^*\text{P}:\text{N} + 3.08\,\text{pH}^*\text{Mg}:\text{N} - 7.97\,\text{pH}^*\text{P}:\text{N} \\ & + 16.45\,\text{Mg}:\text{N}^*\text{P}:\text{N}\end{aligned} \tag{5}$$

$$\begin{aligned}\hat{Y}_{\text{MR}} = {} & 1177 - 220.9\,\text{pH} - 32.0\,\text{Mg}:\text{N} - 142.2\,\text{P}:\text{N} \\ & + 11.08\,\text{pH}^*\text{pH} - 6.86\,\text{Mg}:\text{N}^*\text{Mg}:\text{N} \\ & - 10.21\,\text{P}:\text{N}^*\text{P}:\text{N} + 1.94\,\text{pH}^*\text{Mg}:\text{N} + 17.95\,\text{pH}^*\text{P}:\text{N} \\ & + 18.52\,\text{Mg}:\text{N}^*\text{P}:\text{N}\end{aligned} \tag{6}$$

Experimental results demonstrated that NH_4-N recoveries ranged between 78.5 ± 0.5% and 96.9 ± 0.6%, PO_4-P recoveries between 69.2 ± 5.0 and 96.3 ± 1.3%, and Mg^{2+} recoveries between 99.9 ± 0.1 and 75.1 ± 0.3% (Table 3). The residual concentrations of NH_4-N, PO_4-P and Mg^{2+} corresponding to each run are given in Table 3. The actual and predicted values plots showed significant consistency ($R^2 = 0.8404$ for NR, $R^2 = 0.8739$ for PR and 0.9187 for MR) (Fig. 1). The model had a high correlation and the calculated R^2 values demonstrated that the model fitted the data with sufficient accuracy.[48] The deviations of the model and the experiments may be a result of the impurities present in the additives.

Table 3. Box–Behnken design, experimental and predicted results for NH_4_N recovery, residual PO_4-P concentration, and residual concentrations of NH_4-N, PO_4-P and Mg^{2+}

	Factors			Responses (%)			Residual (mmol L^{-1})		
Run	pH	Mg:N	P:N	NH_4-N Recovery	PO_4-P Recovery	Mg^{2+} Recovery	NH_4-N	PO_4-P	Mg^{2+}
1	8.0	1.5	1.6	82.9 ± 0.4	81.7 ± 1.1	97.9 ± 0.3	17.1	30.3	3.2
2	9.0	1.5	1.6	85.3 ± 0.4	84.5 ± 3.0	99.9 ± 0.1	15.2	26.9	0.07
3	8.0	2.3	1.6	96.6 ± 0.6	87.7 ± 2.1	89.1 ± 0.2	3.7	23.0	29.0
4	9.0	2.3	1.6	96.9 ± 0.6	92.9 ± 1.6	92.7 ± 0.5	3.6	14.2	19.5
5	8.0	1.9	1.2	80.2 ± 0.4	84.9 ± 0.4	96.0 ± 0.1	11.3	18.4	40.2
6	9.0	1.9	1.2	90.0 ± 0.3	94.1 ± 0.8	85.9 ± 0.4	5.32	8.1	30.8
7	8.0	1.9	2	94.7 ± 0.3	70.2 ± 2.4	95.7 ± 0.1	5.1	60.0	8.0
8	9.0	1.9	2	95.8 ± 0.1	73.0 ± 0.3	99.9 ± 0.1	4.4	53.3	0.04
9	8.5	1.5	1.2	83.3 ± 0.7	83.6 ± 1.1	92.1 ± 0.6	19.5	23.1	14.1
10	8.5	2.3	1.2	78.5 ± 0.4	96.3 ± 1.3	75.1 ± 0.3	23.4	5.6	62.7
11	8.5	1.5	2	89.5 ± 0.4	69.2 ± 5.0	99.9 ± 0.1	10.8	63.7	0.05
12	8.5	2.3	2	95.4 ± 0.3	92.3 ± 1.0	94.8 ± 0.8	4.4	14.4	10.1
13	8.5	1.9	1.6	92.1 ± 0.5	89.7 ± 0.5	94.2 ± 0.6	8.6	17.7	15.3
14	8.5	1.9	1.6	96.3 ± 0.2	93.8 ± 0.7	92.8 ± 0.2	4.4	15.4	12.2
15	8.5	1.9	1.6	96.4 ± 0.3	91.1 ± 0.7	92.5 ± 0.3	4.3	14.0	16.0

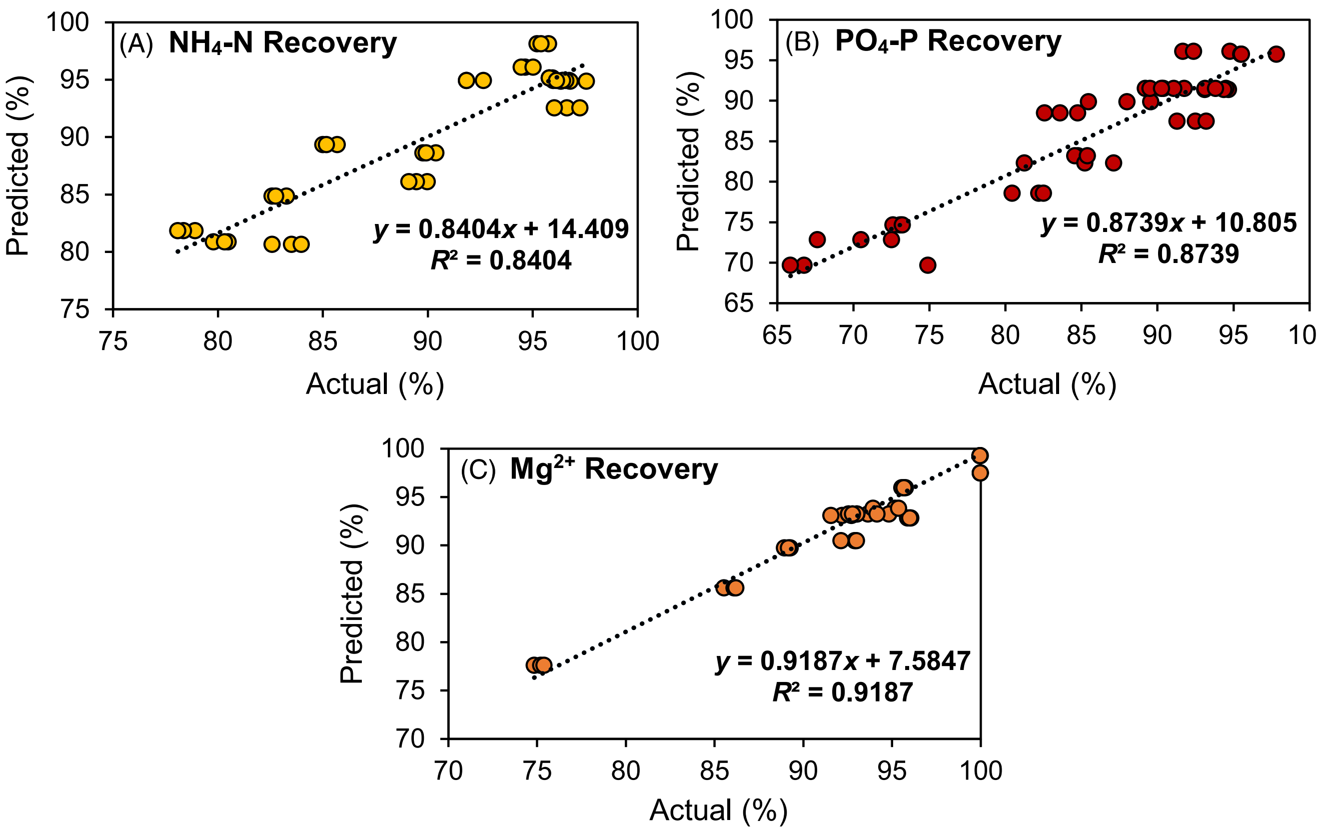

Figure 1. Scatter diagram of predicted *versus* experimental response values for the (A) NH_4-N (B) PO_4-P and (C) Mg^{2+} recovery (%).

Even though substitutes such as WMP and BM that are heterogeneous in nature have been used in this study, in nine of 15 experimental runs, NH_4-N recoveries were >90%, with a maximum of 97%. This is significantly higher than our previous findings with manure digestate even though pure chemicals ($MgCl_2.6H_2O$ and H_3PO_4) were used as additives.[11] In a similar work where poultry manure digestate was subjected to an acidic dissolution process, NH_4-N recoveries were limited to 60–65% whereas all PO_4-P was recovered when the Mg:N:P ratio ranged from 1:1:1 to 1.5:1:1 at pH 8.5.[11] The NH_4-N recoveries attained in the present study are also higher than the maximum NH_4-N removal efficiency reported with landfill leachate, where authors investigated the effect of alternative additives, namely, low-cost MgO and waste H_3PO_4 in struvite precipitation.[16] The maximum NH_4-N removal in that study was 82% with a 3:1:1 Mg:P:N molar ratio at pH 9, which is lower than the maximum recovery attained in our study; however, the residual PO_4-P concentration of 56 mg L^{-1} (1.8 mmol L^{-1}) reached in this previous report was lower than the residual PO_4-P concentrations in our study (Table 3).[16] P can precipitate in varying forms and thus its recovery is significantly impacted by the nature of the feed solution. In another study where BM was used as the P source and saltwater bittern was used as the Mg^{2+} source in the struvite precipitation experiments, the feed was again selected as leachate.[49] At a Mg:P:N molar ratio of 1.3:1:1.3:1 at pH 9 the recoveries of NH_4-N, PO_4-P and Mg^{2+} were 96%, 99.6% and 92%, respectively, which were consistent with the findings reported in this research.[49] Clearly, the use of alternative additives such as BM and WMP for the struvite precipitation process is a viable option even for nutrient recovery from such complex materials as manure digestate and leachate.

The precision and significance of derived model parameters were examined using the analysis of variance (ANOVA). ANOVA results for the response surface quadratic model of the responses are given in Table 4. The regression analysis of NH_4-N recovery indicated that all three factors (pH, Mg:N and P:N) had significant effects ($P < 0.05$) on NH_4-N recovery. Among them, the P:N molar ratio was the most significant factor (*F*-value of 84.8), followed by the Mg:N molar ratio ($F = 31.3$) and pH ($F = 8.3$). Clearly, the amount of added P has a significant role in N recovery because large amounts of Ca^{2+} and Mg^{2+} that may come from BM and/or WMP can compete against struvite ($MgNH_4PO_4$) for PO_4^{-3} to produce $Mg_3(PO_4)_2$ and $Ca_3(PO_4)_2$.[50] This competition would decrease available PO_4^{-3} for struvite precipitation and may lower NH_4-N recovery.[50] Because the selected pH range (8–9) was within the optimal range of struvite precipitation, it had a relatively less significant effect. Consistent with this, the quadratic effect of pH was insignificant ($P > 0.05$) whereas the quadratic effects of Mg:N and P:N showed a significant effect ($P < 0.05$) on NH_4-N recovery. Of the interaction effects, only pH × Mg:N was insignificant (Table 4).

The regression analysis of the PO_4-P recovery indicated that all three factors (pH, Mg:N and P:N) had a significant effect ($P < 0.05$) on the PO_4-P recovery. Similar to NH_4-N recovery, the P:N molar ratio was the most significant factor followed by Mg:N and pH. Regarding their quadratic effects, pH × pH and P:N × P:N showed statistically significant impacts ($P < 0.05$) on the PO_4-P recovery whereas the quadratic effect of Mg:N × Mg:N was insignificant. Except Mg:N × P:N, the interaction effects were insignificant ($P > 0.05$).

In comparison to the others, Mg^{2+} recovery provided the greatest correlation between the experimental and model results ($R^2 = 0.9187$, $F = 43.93$; Fig. 1). Similar to PO_4-P and NH_4-N recoveries regarding Mg^{2+} recovery, the order of significance was P:N, Mg:N and pH. In fact, regarding Mg^{2+} recovery the impact of pH was insignificant ($P > 0.05$). Even though pH × Mg:N interaction was insignificant, pH × P:N interaction was significant which implies that pH level changes the availability of P that may react with Mg^{2+}, increasing its precipitation.

Response surface analysis

The interaction effects of variables can be visualized on response surface plots while the other factors are held constant. 3D response surface plots are given in Fig. 2 for the NH_4-N, PO_4-P and Mg^{2+} recoveries. From the surface plots of NH_4-N in Fig. 2(A), on the one hand, it was indicated that increasing the P:N ratio from 1.2 to 2 and raising Mg:N ratio from 1.5 to 2.3 resulted in the maximum NH_4-N recovery. On the other hand, an increase in the Mg:N ratio from 1.9 to 2.3 resulted in a lower NH_4-N recovery than that with a 1.2 P:N ratio. This shows that when P is fixed, increasing Mg^{2+} concentration helps NH_4-N recovery but to a certain limit, beyond which it is no more beneficial in terms of NH_4-N recovery. As Mg:N ratio increased with the addition of WMP, there could be an enhancement in the production of amorphous Mg^{2+} and Ca^{2+} phosphates, which could result in a reduction in the recovery of NH_4-N.[23] Figure 2(B) shows the interaction effect of pH × P:N on NH_4-N recovery. A response surface plot's slope indicates how significantly an input variable influences a response variable. Thus, P:N is more influential on NH_4-N recovery rather than pH change. Because the slope in Fig. 2(A) is greater than that in Fig. 2(B),(C), it is clear that the interaction impact of Mg:N × P:N is more significant than the others on NH_4-N recovery (Fig. 2). Also, these results are consistent with the ANOVA outputs given in Table 4.

The significant effect of P:N on NH_4-N recovery may be explained by the fact that increasing P:N enables particle size increase of the precipitates; thus, a higher amount of struvite is produced at the same reaction time.[51] Besides, an increase of pH from 8 to 9 caused an increase in the NH_4-N recovery, which may be a result of a decrease in the H^+ concentration and, thus, increasing HPO_4^{-2} concentration. This could improve struvite production and accelerate the recovery of NH_4-N.[50] Recently, where BBD was applied to maximize NH_4-N recovery during struvite precipitation Zhou and others[51] changed pH between 9 and 10 and it was reported that pH × P:N significantly affected the recovery of NH_4-N. Even though their pH range was wider, their results are consistent with our findings.

The interaction effects of process variables on the PO_4-P recovery are given in Fig. 2(D–F). Considering the slope of the graphs, the P:N molar ratio was the most significant variable, and the findings match the ANOVA outputs (Table 4). A higher P:N molar ratio in the range of 1.2:1 and 2:1 resulted in high residual PO_4-P concentration (Table 3), indicating low PO_4-P recovery. This may indicate that beyond a certain concentration ratio, the P is in excess of those other ions that it may precipitate with. For example, when the P:N ratio was higher than the Mg:N ratio, the recoveries were lower. However, for a given P:N ratio, PO_4-P recovery increases along with an increase in the Mg:N ratio at varying pH levels [Fig. 2(F)]. Similar to this, Zin et al.[52] stated that the molar ratio of Mg^{2+} to PO_4-P should be greater to accomplish >90% PO_4-P removal.

Three-dimensional surface plots for Mg^{2+} recovery are given in Fig. 2(G–I). Figure 2(G) shows that Mg:N and P:N molar ratio has an opposite effect on Mg^{2+} recovery. For example, the highest recovery was achieved at the lowest Mg:N ratio of 1.5 and the highest P:N molar ratio of 2.0, and vice versa the lowest recovery was attained at the Mg:N ratio of 2.3 and P:N of 1.2. In their study, Siciliano and De Rosa[35] also showed that when the amount of Mg was increased, Mg^{2+} recovery decreased from 99% to 81%. A high P:N ratio resulted in high Mg^{2+} recovery; a possible explanation may be the precipitate of Mg^{2+} with excess PO_4^{3-} in forms other than struvite, such as $Mg_3(PO_4)_2$.[52]

Verification of optimum conditions

The process was optimized to determine a particular experimental condition at which the NH_4-N, PO_4-P and Mg^{2+} recovery

Table 4. ANOVA results for the NH_4-N, PO_4-P and Mg^{2+} recoveries

Source	DF	Adj SS	Adj MS	*F*-value	*P*-value
NH_4-N recovery (%)					
Model	9	1540.00	171.11	20.47	0.000
Linear	3	1040.11	346.70	41.48	0.000
pH	1	69.68	69.68	8.34	0.007
Mg:N	1	261.72	261.72	31.32	0.000
P:N	1	708.70	708.70	84.80	0.000
Square	3	351.63	117.21	14.02	0.000
pH*pH	1	2.98	2.98	0.36	0.554
Mg:N*Mg:N	1	178.74	178.73	21.39	0.000
P:N*P:N	1	199.83	199.83	23.91	0.000
2-way interaction	3	148.27	49.42	5.91	0.002
pH*Mg:N	1	3.50	3.50	0.42	0.522
pH*P:N	1	56.64	56.64	6.78	0.013
Mg:N*P:N	1	88.13	88.13	10.54	0.003
$R^2 = 0.8404$		$R^2_{(adj)} = 0.7993$		$R^2_{(pred)} = 0.7266$	
PO_4-P recovery (%)					
Model	9	2949.26	327.7	26.94	0.000
Linear	3	2193.18	731.06	60.11	0.000
pH	1	149.75	149.75	12.31	0.001
Mg:N	1	942.64	942.64	77.51	0.000
P:N	1	1100.79	1100.79	90.5 M1	0.000
Square	3	637.89	212.63	17.48	0.000
pH*pH	1	256.26	256.26	21.07	0.000
Mg:N*Mg:N	1	0	0	0	0.994
P:N*P:N	1	421.43	421.43	34.65	0.000
2-way interaction	3	118.19	39.4	3.24	0.034
pH*Mg:N	1	4.55	4.55	0.37	0.545
pH*P:N	1	30.5	30.5	2.51	0.122
Mg:N*P:N	1	83.14	83.14	6.84	0.013
$R^2 = 0.8739$		$R^2_{(adj)} = 0.8414$		$R^2_{(pred)} = 0.7802$	
Mg^{2+} recovery (%)					
Model	9	1587.91	176.435	43.93	0.000
Linear	3	1187.55	395.849	98.57	0.000
pH	1	0.01	0.009	0	0.963
Mg:N	1	549.56	549.565	136.84	0.000
P:N	1	637.97	637.973	158.85	0.000
Square	3	138.61	46.202	11.5	0.000
pH*pH	1	85.05	85.053	21.18	0.000
Mg:N*Mg:N	1	13.35	13.353	3.32	0.077
P:N*P:N	1	29.54	29.54	7.36	0.010
2-way interaction	3	261.76	87.252	21.73	0.000
pH*Mg:N	1	1.81	1.806	0.45	0.507
pH*P:N	1	154.59	154.593	38.49	0.000
Mg:N*P:N	1	105.36	105.359	26.23	0.000
$R^2 = 0.9187$		$R^2_{(adj)} = 0.8978$		$R^2_{(pred)} = 0.8569$	

efficiencies are the highest. By using response optimizer tool, optimum conditions were obtained as pH 9.0, Mg:N molar ratio 2.2 and P:N molar ratio 1.8 with corresponding responses of 97.4% [95% prediction interval (PI): 90.95–100] NH_4-N recovery, 90.2% (95% PI: 82.44–98.03) PO_4-P recovery and 96.8% (95% PI: 92.30–100) Mg^{2+} recovery. The tests were conducted under the model-provided optimal conditions to assess the dissimilarity between the experimental value and the optimum value estimated by the model. The experimental results were as follows: 97.8 ± 0.1% NH_4-N recovery, 96.6 ± 0.31% PO_4-P recovery and 84.4 ± 0.9% Mg^{2+} recovery. The experimental findings and predicted response values agree with a dissimilarity of 0.4%, 6.9% and 14.3% for the NH_4-N, PO_4-P and Mg^{2+} recoveries, respectively. Because the predicted value was quite close to the experimental result, the model helps estimate the NH_4-N recovery under different conditions. For PO_4-P recovery, the result was within PI. However, there was a considerable discrepancy between the predicted and experimental results for Mg^{2+}. The residual concentrations of the ions were 2.1 ± 0.07, 5.8 ± 0.53 and 33.3 ± 1.95 mmol L^{-1} for the NH_4-N, PO_4-P and Mg^{2+} ions,

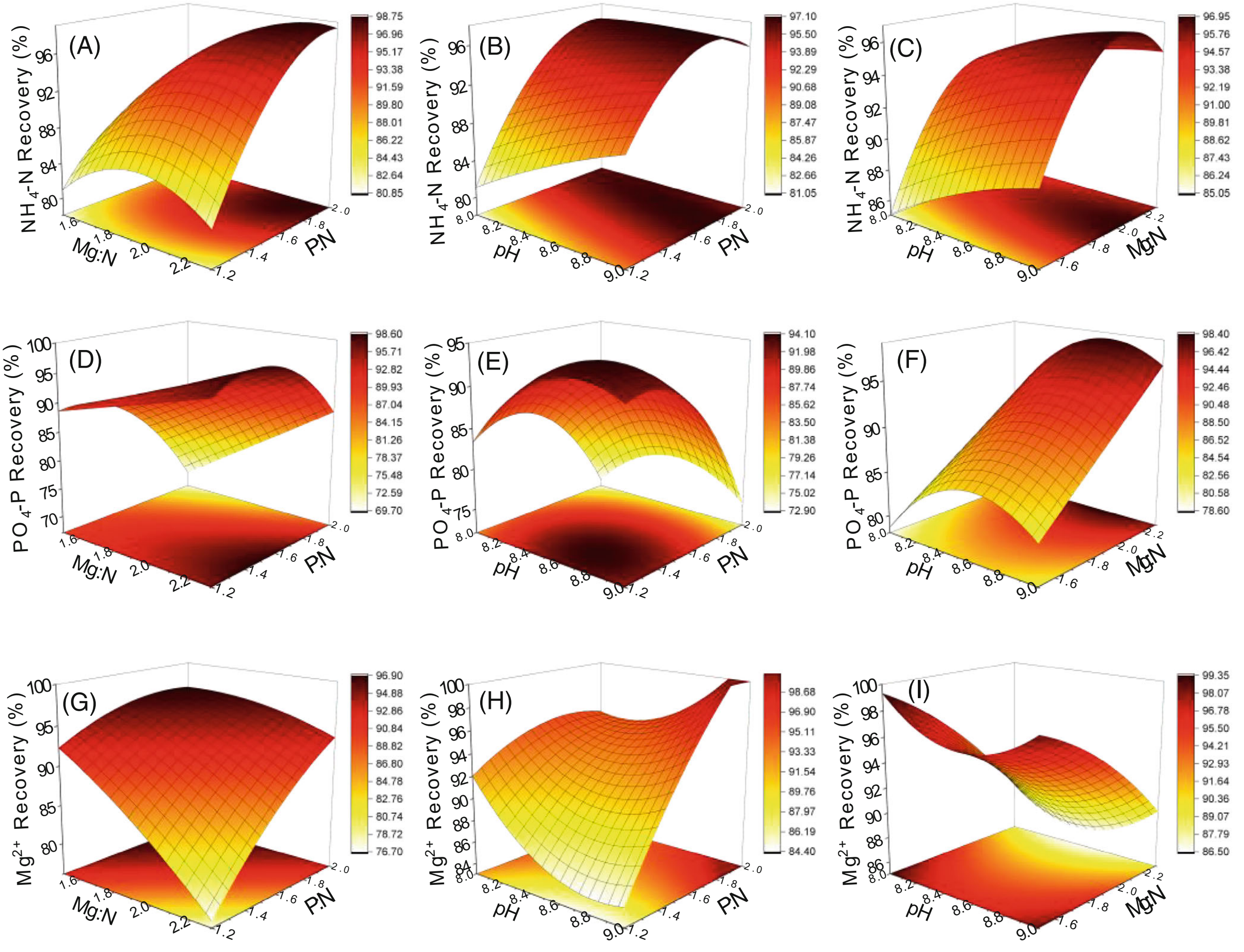

Figure 2. 3D surface and contour plots for NH_4-N (A–C), PO_4-P (D–F) and Mg^{2+} (G–I) showing the interaction of pH (8.0–9.0), Mg:N (1.5–2.3) and P:N (1.2–2.0) by fixing one factor at a time (pH 8.5, Mg:N 1.9 or P:N 1.6).

respectively. This indicates that NH_4-N and PO_4-P limit the precipitation, and excess Mg^{2+} remains in the solution. Nevertheless, our study demonstrates that the constructed model effectively identifies the optimal conditions for nutrient recovery through the incorporation of WMP and BM as additives.

Product purity and characterization

The dried precipitates from 15 runs of BBD experiments, as well as the precipitate from the verification experiment, were all subjected to XRD analysis to determine if the obtained precipitates were struvite. The XRD patterns of the products are given in Fig. 3. Although WMP and highly heterogenous BM were used in this study intensity and positions of the XRD patterns match only with the reference struvite pattern (JCPDS file no.15–0762); hence it was confirmed that all of the samples contained only struvite crystals. Figure 3 shows that the mineralized products were preferentially oriented along the [010] direction because the products had significantly strong (020) and (040) diffractions resulting from the use of BM and WMP compared to the standard card of the struvite (Fig. 3).[53] Other studies have also shown the occurrence of struvite crystals exhibiting similar oriented growth.[54,55]

The XRD pattern of the product formed at the optimal conditions (pH 9.0, Mg:N 2.2, P:N 1.8) in the verification step is shown in Fig. 4. This product was also subjected to SEM analysis to assess the structure and morphology of the product (Fig. 4). Similar to others, the XRD pattern of the precipitate obtained at the optimal conditions matched with struvite, and there was no sign of any other crystalline compounds (Fig. 4). SEM images showed that the precipitates have irregular prismatic orthorhombic crystals. The structure was consistent with the literature, where rectangular platelet, prismatic, needle, and pyramidal shaped crystals have been observed in different studies.[40,50] The SEM images of the product distinctly reveal well-defined crystals, accompanied by surface depositions of some impurities. The crystal size of the struvite has been reported between 10 and 40 μm,[35] and the crystal size of the product attained under optimum conditions is ≈25 μm, which is consistent with the literature. The molar ratio of the ions, crystal growth conditions such as mixing, and temperature can all be used to explain the various morphologies and sizes of struvite.[40]

In order to assess the product quality, the elemental composition of the dried product was examined (Table 5). The mass of the product obtained at optimum condition was 0.12 ± 0.01 g product per mL digestate sample. Because other precipitates

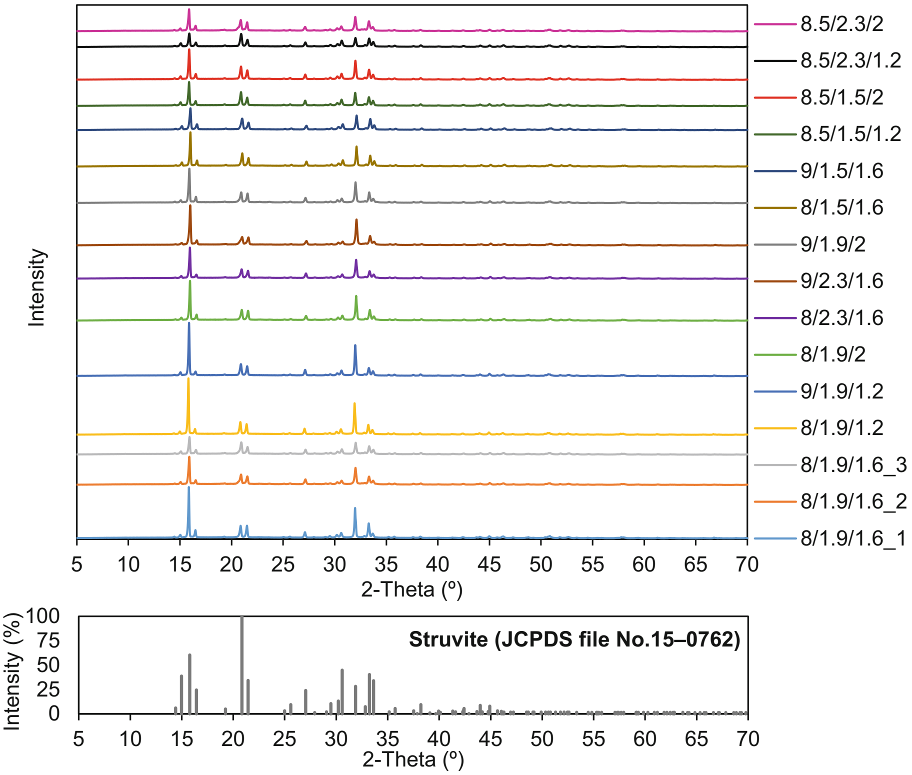

Figure 3. X-ray diffraction results of the precipitates obtained from experimental runs compared with the peaks of reference struvite (JCPDS file no.15–0762) (conditions are given as pH/Mg:N/P:N).

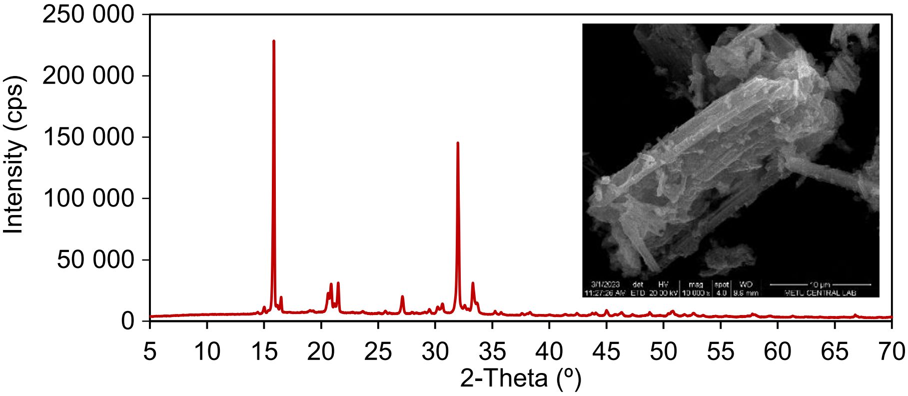

Figure 4. X-ray diffraction spectra and scanning electron microscopy images at ×6000 magnification of the product under optimum condition (pH 9.0, Mg:N 2.2, P:N 1.8).

may be present in the product, purity is an important parameter to consider especially as it is a factor that will play a role in the economic viability of the process. The impurities present in the BM and WMP may cause co-precipitates that decrease the purity of the product. The highest impurity was Na due to NaOH addition. Thus, the possibility of using aeration for pH increase should be evaluated in future studies.[56] The obtained product was composed of 49% struvite. This level of purity was similar to that in a study where authors reported a purity range of 44–48% for the precipitates that were obtained from pig slurry with dosing of $MgCl_2.6H_2O$ as Mg source.[57] In that study authors reported that the obtained struvite was appropriate for use as an agricultural fertilizer.[57] In our work, the product P level was 15.25%, which is consistent with the typical P content of struvite (11–26%).[58] Moreover, the heavy metal composition of the product was lower compared to Turkey's national regulations.[46] These findings suggest that the product may have potential as a fertilizer,[57] even though sustainable low-cost substitutes were utilized in the crystallization process. Turkey is >90% dependent on other countries in terms of fertilizer production;[59] thus these results will help in the creation of a high-value, P-rich product that can be utilized to diversify the current fertilizer supply system. Certainly, fertilizer assays

Table 5. Elemental composition of the product

Macro-elements		Micro-elements	
Element	%	Element	%
P	15.25	Al	0.083
Mg	6.7	Mn	0.066
H	4.7	Zn	0.04
Na	4.27	Ni	0.006
C	4.05	B	0.002
N	2.8	Ba	0.001
K	1.42	Co	0.001
S	1.39	Ti	0.001
Fe	1.22	V	0.001
Ca	0.875	Cr	0.001
		Cu	0.0004
		As	0.0002
		Li	0.0001
		Cd	0.00002
		Se	0.00002
		Pb	0.000001

must be carried out to examine the potential of the product to be used as fertilizer and this is out of the scope of this current work.

CONCLUSION

In this study, we explored the utilization of BM and WMP as sustainable alternatives to pure P and Mg^{2+} sources for struvite precipitation from cattle manure digestate. The objective was to assess the potential of nutrient recovery through this approach. BBD was applied to determine the optimum conditions for important process parameters namely, pH, Mg:N and P:N molar ratios. A model was developed to predict the recovery performance and ANOVA revealed that the model had been satisfactorily fitted to the experimental data. Additionally, 3D surface plots provided a visual insight into the different factors' combined effects on the responses selected as NH_4-N, PO_4-P and Mg^{2+} recovery. Among the parameters, the P:N molar ratio was the most significant factor for all responses. During the verification experiments, 97.8 ± 0.1% NH_4-N recovery, 96.6 ± 0.31% PO_4-P recovery and 84.4 ± 0.9% Mg^{2+} recovery were attained under the optimum conditions (pH 9.0, Mg:N 2.2, P:N 1.8). In the verification experiment, product quality was analyzed through purity measurement, XRD, and SEM. Even though waste material (WMP) and industrial by-product (BM) were used as additives in this process, almost complete NH_4-N and PO_4-P recoveries were recorded under optimum conditions. However, residual Mg^{2+} concentration was higher compared to most digestate effluents, which may need further attention. The product's levels of P and heavy metals were satisfactory and this suggests a possible agricultural application of this value-added product as a fertilizer.

BM and WMP have a significant potential to be used partially or entirely as additives for the industrial recovery of nutrients because they are waste or by-product materials. These results are promising and illustrate a powerful example of industrial symbiosis between the meat, magnesite and biogas industries. The findings of this experimental study will stimulate more efforts to create sustainable strategies for resource recovery.

AUTHOR CONTRIBUTIONS

FEK: conceptualization, data curation, laboratory measurements, data analyses, writing – original draft. IE: conceptualization, methodology, data analyses, writing – original draft. YDY: conceptualization, investigation, funding acquisition, project administration, supervision, writing – review & editing. All authors read and approved the final manuscript.

ACKNOWLEDGEMENTS

This work was supported by the Royal Academy of Engineering Newton Fund Transforming Systems Through Partnerships Program (grant no: TSP1283), the Scientific and Technological Research Council of Turkey (TUBITAK) (grant no: 22AG019) and the Science Academy through 2022 BAGEP. We thank METU Central Laboratory for metal, XRD, and SEM analysis, Polres for providing the digestate sample, and our Newton Fund project partners: Sütaş Dairy Products Inc., GTE Sustainability and Energy Consultancy, and Cranfield University.

CONFLICT OF INTEREST

The authors declare no competing interests.

DATA AVAILABILITY STATEMENT

The data used in this manuscript is included in the text.

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