



Phosphate recovery from swine wastewater by struvite precipitation and process optimization using response surface methodology

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ABSTRACT

This study investigated the recovery of phosphate (P) as struvite from swine wastewater. In this study, the influence of pH, Mg:P molar ratio, Ca and CO_3^{2-} was studied. The optimum pH for achieving high P recovery efficiency was found as 9.5. The purity of struvite precipitates is decreased from 84.5% to 69.7%. At Mg:P molar ratio of 3:1, the maximum P recovery efficiency achieved was 95%. The presence of Ca ions in swine wastewater inhibited the formation of struvite. The existence of CO_3^{2-} is also preventing the recovery of P as struvite. Moreover, optimization and interaction between the factors were performed using Box-Behnken design of response surface methodology. A model was developed, and optimized conditions for achieving high P recovery efficiency was found as pH is 9.5, Mg:P molar ratio is 3.21, Ca: Mg molar ratio is 1.93, CO_3^{2-} :P molar ratio is 3.49. An economic evaluation showed that the cost to recover P as struvite was 2.06 \$/m³.

Keywords: Phosphate recovery; Struvite; Calcium; Carbonate; Response surface methodology

1. Introduction

Phosphorous is one of the most significant nutrients essential for all living beings and also plays an essential role in the development of agricultural and industrial sectors [1,2]. However, the existing phosphate (P) reserves are limited worldwide [2,3] and will be depleted within 100 years [4–6]. Phosphate rock is a significant raw material for several chemical industries such as the fertilizer industry, feed, and food additives manufacturing industry [7]. Among these industries, fertilizer industry alone consumes 79% of the rock phosphate and also the demand for fertilizers is raising day by day due to the need for providing food to the rapidly growing population with a finite availability of cultivable land [8,9]. On the other hand, due to human activities, it (phosphate) is entering into the environment by different pathways (e.g., discharging of wastewater rich in P) and responsible for the eutrophication of freshwater bod-

ies [10,11]. Therefore, recovery of P from wastewater had great importance [12,13] and also helpful for sustainable utilization of resources.

Several physico-chemical and biological techniques such as adsorption [14], metal ion precipitation [15,16], and enhanced biological phosphorous removal [17] are available to recover P from wastewater. Among all those technologies recovery of P in the form of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) had a more significant advantage [18,19] and also it can be used as a fertilizer. The solubility of struvite fertilizer is less, when compared to conventional fertilizer, which makes it more advantageous to use as a fertilizer [20,21]. Moreover, excessive utilization of conventional fertilizers results in accumulation of heavy metals in soil [22,23], thus altering the natural phosphorous cycle. To overcome the above-mentioned difficulty, it is desirable to use struvite as a fertilizer. Therefore, recovery of P from wastewater as struvite is considered as a promising approach [24].

Different types of wastewater are entering into the environment by various activities [25,26] such as municipal wastewater [27], agro-industry wastes [28], swine waste-

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water [14] and urine [29]. Among all these wastewater, swine wastewater consists of abundant nitrogen (N) and P, if this wastewater is discharged without proper treatment leads to pollution such as eutrophication of water bodies and depletion of dissolved oxygen content in water bodies [14]. Therefore, to avoid such problems, stringent standards have to be implemented for reducing the concentration of P and N entering into the environment [30]. Thus, recovery of P from swine wastewater not only helpful for sustainable utilization of P resources but also beneficial for reducing the eutrophication of water resources.

Generally, swine wastewater is rich in P and ammonium [31,32], but it contains a minimal quantity of magnesium (Mg). Therefore, to achieve a high recovery of P from swine wastewater as struvite, the addition of Mg source is required. Different salts such as seawater [33], brucite [34], $MgCl_2$ [35] and magnesite [36] were used as a source of Mg. Huang et al. [14] reported that 98% of phosphate was recovered from swine wastewater by struvite precipitation using bittern as a source of Mg. Xiao et al. [37] used dolomite neutralization supernatant of waste sulfuric acid as a Mg source to recover P by struvite precipitation approach and achieved 95% recovery. Huang et al. [10] studied the recovery of P from swine wastewater using Mg alloy, and 96% of P recovery was achieved. Furthermore, the addition of Mg source to the wastewater will be done according to different Mg: P molar ratio. Therefore, finding an optimum quantity of Mg (where P recovery is maximum) required is necessary. Moreover, the presence of other ions such as Fe^{3+} , K^+ , Zn^{2+} , and Cu^{2+} also influences the recovery of P as struvite [6,38]. Calcium (Ca) and carbonate (CO_3^{2-}) ions are most often found in all wastewater.

Thus, in the current study, magnesium oxide (MgO) was used as a source of Mg to recover P from swine wastewater as struvite. The effect of pH on the recovery of P as struvite was investigated. Influence of ions such as Ca, Mg and CO_3^{2-} on the P recovery as struvite was studied. Characterization of formed precipitates was done using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). To find interactions among various parameters and as well as to optimize the factors influencing the process, response surface methodology (RSM) was used in the present study. Economic assessment of the entire process was calculated.

2. Materials and methods

2.1. Swine wastewater

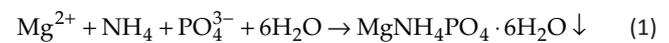
Swine wastewater was collected from small scale swine farm located at karukkangattur, Erode district in Tamilnadu, India. The collected wastewater was stored in a refrigerator at 4°C to prevent further degradation. Before the use, the wastewater was filtered using 0.45 μm filter paper for removing suspended solids. Initial characteristics of collected swine wastewater and characterization were done according to standard methods [39]. Table 1 shows the initial characteristics of collected swine wastewater.

As shown in Table 1, it is observed that the swine wastewater used in the present study is rich in NH_4^+ and PO_4^{3-} concentration and also has a small quantity of Mg^{2+} . NH_4^+ to PO_4^{3-} molar ratio was found as 1.94, which is more than the

Table 1
Initial characteristics of swine wastewater

Parameters	Values
pH	8.23
Alkalinity	2076 mg/L as $CaCO_3$
Mg^{2+}	282 mg/L
$P-PO_4^{3-}$	594 mg/L
NH_4^+	1152 mg/L
Ca^{2+}	400 mg/L
COD	2880 mg/L

required stoichiometric molar ratio in struvite precipitation by Eq. (1) [40].



Therefore, phosphate in the wastewater can be recovered as struvite, if a sufficient quantity of Mg^{2+} is added into the system. Hence, the addition of Mg^{2+} was done according to Mg:P ratio of 2 to 4 using MgO salt. The occurrence of Ca^{2+} and CO_3^{2-} in the wastewater also interferes the recovery of P by struvite precipitation.

2.2. Chemicals

MgO was used as a crystallization reagent to enhance phosphate recovery from swine wastewater. Along with these, other chemicals such as NaOH (1 N) and H_2SO_4 (1 M) were used to adjust the pH of the wastewater. All the chemicals used in this study were of analytical grade.

2.3. Experimental procedure

In this current study, the experiments were carried out in three different stages, and the operational method for each step is given below. The overall schematic diagram of P recovery carried out in the present study as struvite is shown in Fig. 1.

2.3.1. Recovery of P as struvite using MgO as a Mg source

To achieve high recovery efficiency of P as struvite, MgO is used as a source of Mg. The experiments were carried out in a 1000 ml reactor containing 500 ml of swine wastewater and placed on a magnetic stirrer. Then, MgO was added to the swine wastewater according to different Mg:P molar ratios (2, 3 and 4). Later, the solution was mixed thoroughly at a stirring speed of 500 rpm. Furthermore, the solution pH was adjusted to the required value (8 to 11) using 1 N NaOH solution and allowed to react for 30 min. Finally, the solution was allowed to precipitate for 30 min, from which 10 ml of supernatant was collected and filtered through 0.45 μm filter paper for further analysis.

2.3.2. Effect of Ca on P recovery as struvite

To study the influence of Ca on P recovery as struvite, initially 500 ml of swine wastewater was taken in 1000 ml

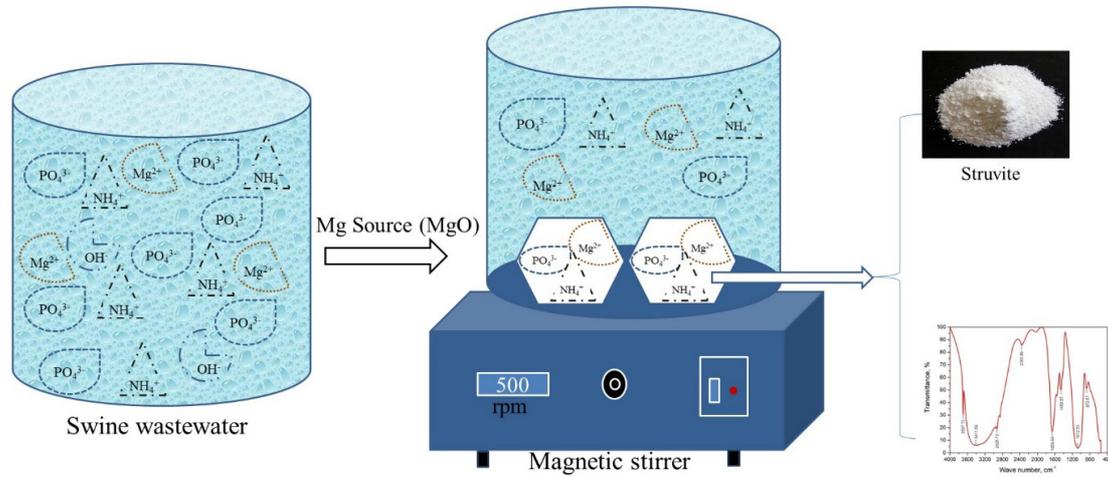


Fig. 1. Schematic representation of process.

reactor and placed over a magnetic stirrer. Then, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was added to the swine wastewater according to Ca:Mg molar ratio of 1, 1.5, 2, 2.5, 3 and 3.5. During the experiment, pH of the swine wastewater was adjusted to 9.5 and then it was allowed to react for 30 min. Once the reaction is completed, the solution was permitted for 30 min to precipitate. Finally, 10 ml of supernatant was collected and filtered through a $0.45 \mu\text{m}$ filter paper for further analysis.

2.3.3. Effect of CO_3^{2-} on P recovery as struvite

To investigate the influence of CO_3^{2-} on P recovery as struvite, 500 ml of swine wastewater was taken in 1000 ml reactor. Then, Na_2CO_3 was added to the swine wastewater at various CO_3^{2-} :P molar ratios (1 to 3.5). The pH of the swine wastewater was maintained at 9.5 and then kept above the magnetic stirrer. Then, the swine wastewater allowed to react for 30 min after that it was permitted to precipitate for a period of 30 min. Finally, 10 ml of supernatant was collected and filtered through a $0.45 \mu\text{m}$ filter paper for further analysis.

2.4. Optimization of process parameters by RSM

Several complex reactions will occur within the swine wastewater; it is necessary to optimize the parameters which will influence the recovery of P as struvite. RSM is one of the techniques, which is used for optimizing and also to find interaction among various individual parameters [41,42]. RSM consists of both mathematical and statistical methods, which are used to develop a mathematical relationship between the dependent variable (i.e., response) and independent variables (i.e., factors).

2.4.1. Experimental design

All the independent variables such as pH, Mg: P molar ratio, Ca: Mg molar ratio and CO_3^{2-} :P molar ratio, which influences the P recovery efficiency are considered in three levels ranging from -1 to +1. Then, the optimization was

Table 2
Parameters and levels

Parameters	Levels		
	-1	0	+1
pH (X_1)	8	9.5	11
Mg:P molar ratio (X_2)	2	3	4
Ca:Mg molar ratio (X_3)	1	2.25	3.5
CO_3^{2-} :P molar ratio (X_4)	1	2.25	3.5

carried out using Box-Behnken design (BBD) of RSM. The independent variables considered while developing a model are pH (X_1), Mg: P molar ratio (X_2), Ca: Mg molar ratio (X_3) and CO_3^{2-} :P molar ratio (X_4). The parameters and levels of each parameter are shown in Table 2.

2.4.2. Development of model and statistical analysis of data

The data collected after the BBD experiments were analysed using Design expert 11.0. The experimental data is fitted with second order polynomial equation and is given below.

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \quad (2)$$

where Y is the dependent variable (i.e., P recovery efficiency), b_0 is the constant, b_i is the coefficient of independent variable X_i , b_{ii} is the coefficient of quadratic variable X_i^2 , b_{ij} is the coefficient of interaction variable X_i and X_j . The quality of the developed model can be assessed by performing an analysis of variance (ANOVA). From the analysis, if the probability of variable is found as > 95%, then it is considered as a significant variable; otherwise, it is not considered as a significant variable.

2.5. Analysis

The pH of the solution was determined using a pH meter (Metrohm, 827 pH lab). Phosphate concentration was

measured according to vanadomolybdophosphoric acid method using UV visible spectrophotometer (Perkin-Elmer, Lambda 35) at 470 nm wavelength.

Phosphate recovery was calculated by Eq. (3).

$$\text{Recovery, (\%)} = \frac{(P_i - P_e)}{P_i} * 100 \quad (3)$$

where P_i is the initial phosphate concentration, (mg/L) and P_e is the final phosphate concentration, (mg/L).

The purity of the struvite precipitates was determined by dissolving 0.5 g of precipitates in 0.5% of nitric acid solution and made it up to 100 ml by adding ultra-pure water. Therefore, purity was calculated using the below Eq. (4).

$$\text{Purity (\%)} = \frac{\text{Mass of struvite in precipitates}}{\text{Total mass of precipitates}} * 100 \quad (4)$$

2.6. Characterization of formed struvite precipitates

Fourier transform infrared spectroscopy (FTIR-2000, PerkinElmer) was used to characterize functional groups, bonding types and nature of compounds that are present in struvite precipitates. It will collect the spectral data between 4000 cm^{-1} to 400 cm^{-1} . FTIR data provides information about its functionality based on band location and intensity. X-ray diffractometer (D-Max/Ultima III, Rigaku) was used to know the nature of formed precipitates.

3. Results and discussions

3.1. Effect of pH on recovery of P

pH is one of the most critical factors controlling the recovery of P as struvite [10]. Furthermore, pH of the system influence the species of constituent ions of struvite (Mg^{2+} , PO_4^{3-} and NH_4^+). Therefore, to study the impact of pH on P recovery and purity of struvite, the experiments were carried out at a pH range of 8 to 11 and the results are shown in Fig. 2.

From Fig. 2, it is revealed that the recovery efficiency of P increased from 72% to 91% with an increase in pH from 8 to 9.5 respectively. However, at a pH > 9.5, recovery of P is slightly decreased with a further rise in pH. Similarly, the purity of struvite is also dropped from 84.5% to 69.7% with an increase in pH from 8 to 11. Therefore, optimum pH was considered as 9.5 and is used to carry out further studies.

According to Eq. (1), the essential ions for the formation of struvite are Mg^{2+} , PO_4^{3-} and NH_4^+ but the species formed by these ions will vary with respect to pH of the system [14]. Generally, PO_4^{3-} exist in different forms such as HPO_4^{2-} and H_2PO_4^- depending upon the pH of the system. For example, if the pH of the system is ranged from 5 to 6.5, the predominant phosphate species present in the solution was H_2PO_4^- [43]. Whereas pH ranged from 7 to 9, the dominant species in the solution was HPO_4^{2-} [2]. In the present study, the pH of the system is in between 8 to 9.5, due to the presence of HPO_4^{2-} species and as well as lower concentration of H^+ favours the struvite precipitation reaction which helps to achieve higher P recovery efficiency and at the same time helpful for achieving high purity of struvite. However, at a pH > 10, Mg^{2+} present in the wastewater reacts with OH^-

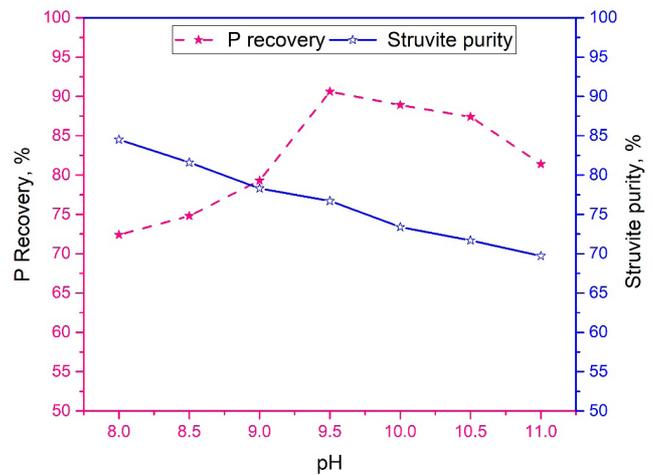


Fig. 2. Variation of P recovery efficiency and purity of struvite at different pH. (Experimental condition: stirring speed = 500 rpm, reaction time = 30 min).

and forms $\text{Mg}(\text{OH})_2$ [44]. Thus, the availability of Mg^{2+} for struvite formation is reduced and also amount of $\text{Mg}(\text{OH})_2$ formation increases with an increase in pH [14].



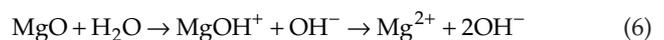
Hence, reduction in the P recovery as struvite is observed, which also responsible for the decrease in purity of the struvite. These observations are consistent with the studies reported by Song et al. [1] and Hao et al. [45].

3.2. Effect of Mg^{2+} on recovery of P

To study the effect of Mg^{2+} on recovery of P as struvite, the experiments were conducted at various Mg:P molar ratios of 2, 3 and 4. The variation of P recovery with different molar ratios is shown in Fig. 3.

From Fig. 3 it is observed that the P recovery increased with an increase in the molar ratio at different pH values. At a pH 8, the raise in P recovery is significant; whereas at a pH of 9.5 to 10.5, there is no much significant raise in P recovery. For pHs 9.5, 10 and 10.5, the maximum P recovery achieved is 95% at a molar ratio of 4. Since, there is no much difference in P recovery observed at higher pH (9.5, 10 and 10.5) and also for molar ratio of 3 and 4, therefore optimum molar ratio was considered as 3. Shen et al. [32] reported that to achieve 90% of the P recovery, the Mg: P ratio required should be higher than 2.4.

The reaction mechanism for removing phosphates using MgO is given below. When MgO is added to the solution, immediately hydrolysis takes place at the surface of MgO.



Which results in release of Mg^{2+} and OH^- ions into the solution and the solution surrounding the MgO is super-saturated with $\text{Mg}(\text{OH})_2$ ($K_{sp} = 10^{-11.1}$). Therefore, OH^- and Mg^{2+} concentration increases at the surface [46,47]. Thus, the availability of Mg^{2+} to interact with P is greater at higher

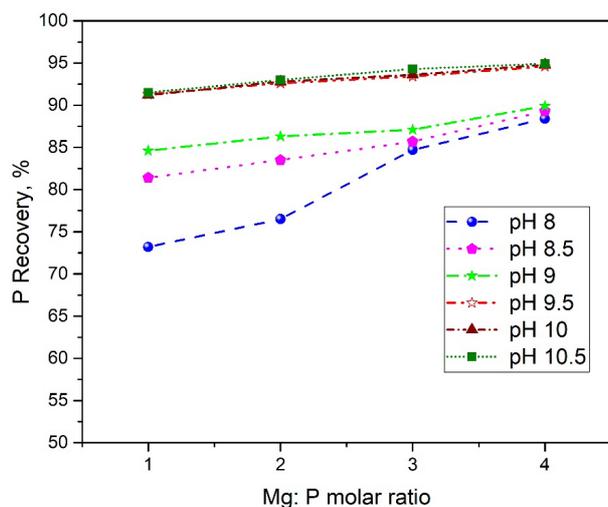


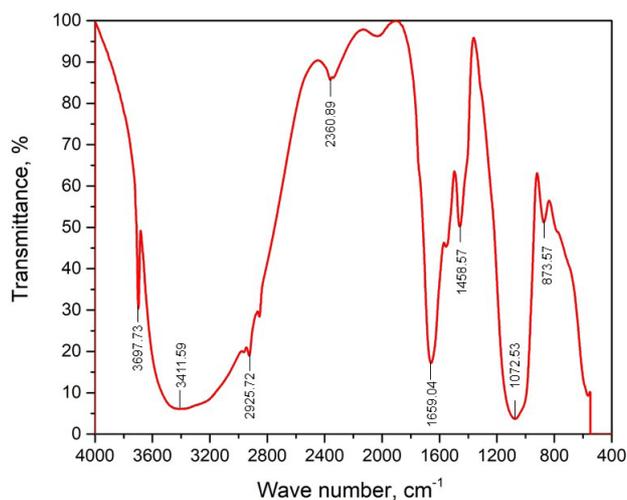
Fig. 3. Influence of Mg on recovery of P at different pH values. (Experimental condition: stirring speed = 500 rpm, reaction time = 30 min).

molar ratios than at lower molar ratios. The possible magnesium phosphate species at higher molar ratios are $MgNH_4PO_4 \cdot 6H_2O$ ($K_{sp} = 10^{-13.16}$), $MgHPO_4 \cdot 3H_2O$ and $Mg_3(PO_4)_2$ ($K_{sp} = 10^{-25.2}$), which enhances the recovery of P [48]. Similarly, at higher pH (>9.5) recovery is more than at lower pH, this is due to the presence of high Ca^{2+} (from Table 1) in the system, which reacts with PO_4^{3-} and forms $Ca_3(PO_4)_2$. The accumulation of $Ca_3(PO_4)_2$ in the system is also responsible for achieving higher recovery. Therefore, for achieving high recovery of P as struvite at lower pH, increase in Mg:P is the best strategy thereby formation of $Ca_3(PO_4)_2$ can be avoided. These observations are similar to the results reported by Song et al. [1].

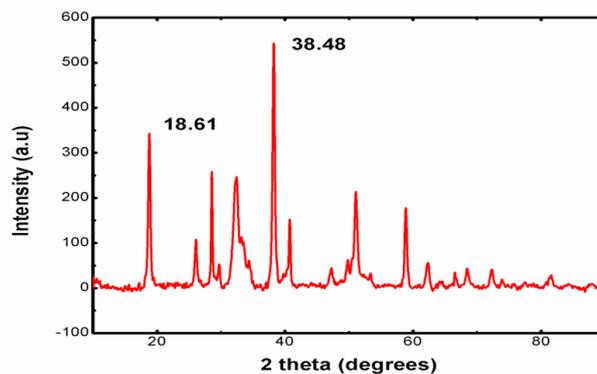
To further corroborate the results, precipitates obtained at pH 9.5 and at Mg: P molar ratio of 3:1 are characterised using FTIR and XRD. Fig. 4a and b show the FTIR and XRD pattern of formed precipitates respectively.

From Fig. 4a it is observed that the peaks correspond to water of crystallization are: 3411.59 cm^{-1} , 2360.89 cm^{-1} , 1659.04 cm^{-1} , and 873.57 cm^{-1} . Whereas the peaks due to metal-oxygen bond (i.e., deformation of OH linked to Mg^{2+}) is observed at 873.57 cm^{-1} . Similarly, peaks at 873.57 cm^{-1} , 1072.53 cm^{-1} are due to the symmetric and asymmetric stretching vibration of PO_4^{3-} molecules respectively. The peaks observed at 2925.72 cm^{-1} , 1659.04 cm^{-1} , 3697.73 cm^{-1} , 1458.57 cm^{-1} are due to symmetric stretching, symmetric bending, asymmetric stretching, and asymmetric bending vibrations of NH_4^+ molecules in precipitate respectively. Therefore, the presence of metal-oxygen, PO_4^{3-} , NH_4^+ and water molecules confirms the formed precipitates are struvite.

From Fig. 4b it is observed that peaks were compared with standard struvite and confirmed that precipitates were monoclinic struvite by verifying standard peaks. Two significant peaks with higher values of intensity at around 550 and 350 corresponding to 38.48 and 18.61 were found respectively. Similar peaks were reported by Chauhan and Joshi [49].



(a)



(b)

Fig. 4. (a) FTIR spectra and (b) XRD pattern of obtained precipitates.

3.3. Effect of Ca^{2+} on recovery of P

The presence of Ca^{2+} in the swine wastewater influence the recovery of P as struvite. Therefore, to study the impact of Ca^{2+} on recovery of P as struvite, Ca:Mg molar ratio was maintained at 1, 1.5, 2, 2.5, 3 and 3.5 respectively. The recovery efficiency of Mg, P and Ca are found at different molar ratios and are shown in Fig. 5.

From Fig. 5 it is observed that the recovery efficiency of P and Ca is increasing with an increase in Ca:Mg molar ratio. However, Mg recovery was decreasing as Ca:Mg ratio is rising. At Ca:Mg molar ratio of 3.5, almost 96% of P, and 93% of Ca is recovered, whereas 91% of Mg is remained in the solution. Which indicates that the Ca and phosphate present in the system are reacting with each other and forms calcium phosphate species. The different possible calcium phosphate species are tricalcium phosphate [$Ca_3(PO_4)_2$], octacalcium phosphate [$Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$], dicalcium phosphate [$CaHPO_4$], dicalcium phosphate dihydrate [$CaHPO_4 \cdot 2H_2O$] and hydroxyapatite [$Ca_5(PO_4)_3 \cdot OH$], also the formation of species mentioned above depends on pH of the system [50]. When the solution pH < 7, the formation of $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$ takes place in the system;

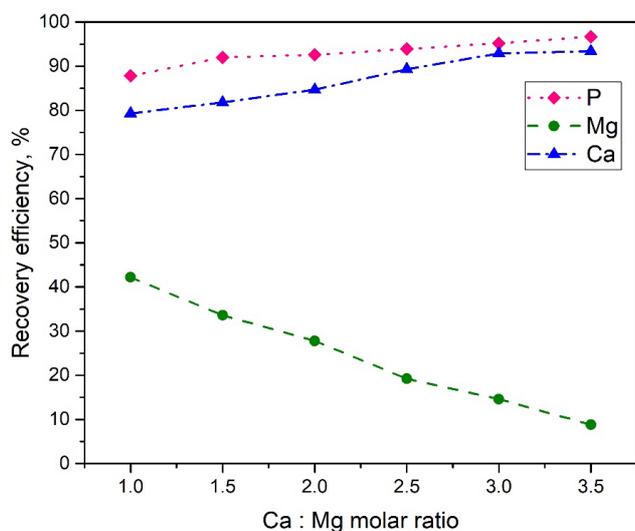
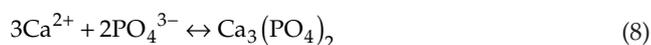
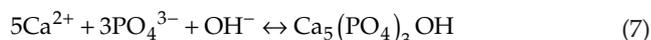


Fig. 5. Effect of Ca: Mg molar ratio on recovery of P, Mg and Ca. (Experimental Condition: pH = 9.5, reaction time = 30 min, stirring speed = 500 rpm).

however $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_5(\text{PO}_4)_3\text{-OH}$ formation occurs, when the solution pH is 9–11 [48]. Since the experiment is conducted at pH of 9.5 in this study, the formed calcium species are tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{-OH}$) and the reactions are given below.



This may be the reason for achieving high P and Ca recovery efficiency, which inhibits the formation of struvite as well as the purity of struvite precipitate. Therefore, to obtain pure struvite precipitates, the Ca:Mg ratio in the system must be controlled. Le Corre et al. [51] reported that the existence of Ca significantly influence the growth of struvite precipitates. Yan and Shih [38] observed that the presence of Ca inhibited the struvite formation.

3.4. Effect of CO_3^{2-} on recovery of P

To study the effect of CO_3^{2-} on recovery of P, the experiments were conducted at different CO_3^{2-} :P ratios ranging from 1 to 3.5, and corresponding recovery efficiency of P and Mg was found and are shown in Fig. 6. Since the experiments are conducted at a pH of 9.5, at that pH both CO_3^{2-} and HCO_3^- exist in the solution. Even though, both ions (CO_3^{2-} and HCO_3^-) exist, it is considered as CO_3^{2-} .

From Fig. 6 it is observed that as CO_3^{2-} :P molar ratio increasing, P recovery decreasing and Mg recovery increasing. Which indicates that reaction of P with other ions is declining whereas Mg is reacting with other ions and forms precipitate. At a ratio of 3.5, 84% of P is recovered whereas Mg recovery is 87%. Therefore, P recovery is effected by the increasing concentration of carbonate in solution. Another reason is that Mg^{2+} has more affinity towards CO_3^{2-} when compared to PO_4^{3-} , which results in the formation of MgCO_3

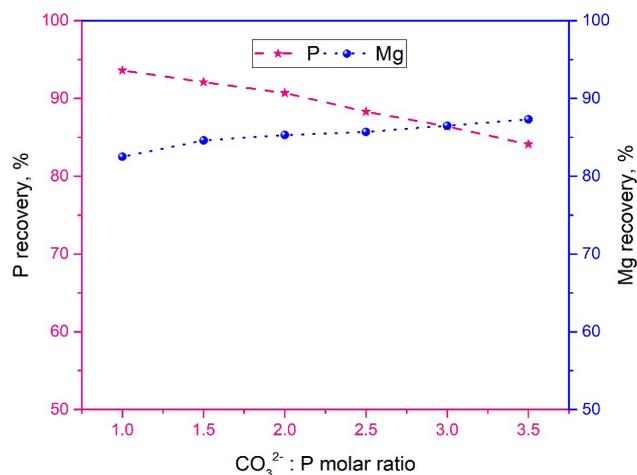


Fig. 6. Influence of CO_3^{2-} : P molar ratio on P and Mg recovery efficiency. (Experimental Condition: pH = 9.5, reaction time = 30 min, stirring speed = 500 rpm).

and MgHCO_3^+ precipitates. Thus, the activity of Mg^{2+} to interact with PO_4^{3-} and NH_4^+ was further reduced. Kabdaşlı et al. [52] reported that the existence of CO_3^{2-} increased the induction time of struvite formation. Ca present in the solution (from Table 1) react with carbonate ions, led to the formation of calcium carbonate. Hence, formed calcium carbonate hinder the struvite formation, thereby purity of the struvite would be diminished [53].

3.5. Optimization of P recovery efficiency by RSM

In this study, the optimization of factors was carried using BBD technique of RSM. The BBD matrix and corresponding response (i.e., P recovery efficiency) values are shown in Table 3.

Response values are fitted with the quadratic model given in Eq. (9), where all influencing parameters are provided in code values.

$$Y = 83.10 + 14.71X_1 + 11.40X_2 + 8.65X_3 + 19.44X_4 + 6.13X_1X_2 + 2.22X_1X_3 - 9.47X_1X_4 - 1.07X_2X_3 - 8.36X_2X_4 - 10.21X_3X_4 - 20.61X_1^2 - 7.74X_2^2 - 3.38X_3^2 - 12.18X_4^2 \quad (9)$$

where Y is the P recovery efficiency (%), X_1 is pH, X_2 is Mg:P molar ratio, X_3 is Ca: Mg molar ratio, X_4 is CO_3^{2-} : P molar ratio.

3.5.1. Analysis of variance for model

To assess the quality of the developed model ANOVA is used. The details of ANOVA for the established model are given in Table 4.

From Table 4 it is observed that F value and P value (probability) for a developed model is 32.54 and <0.0001 respectively, which indicates that the developed model is significant. The correlation coefficient (R^2) for the developed model was found as 0.9702, which represents the model predicted values and actual (experiment) values are consistent with each other. The adequate precision value for the

Table 3
Box- Behnken matrix and corresponding response

Run	Factor 1 X_1 :pH	Factor 2 X_2 :Mg: P	Factor 3 X_3 :Ca: Mg	Factor 4 X_4 :CO ₃ ²⁻ : P	Response 1 P Recovery efficiency (%)
1	9.5	3	2.25	2.25	83.1
2	8	3	2.25	3.5	60.13
3	8	3	1	2.25	40.53
4	9.5	3	2.25	2.25	83.1
5	9.5	2	2.25	3.5	76.67
6	9.5	3	1	3.5	88.48
7	8	3	2.25	1	3.37
8	11	3	2.25	1	50.88
9	9.5	3	3.5	1	71.4
10	9.5	4	2.25	1	70.56
11	9.5	3	1	1	25.6
12	8	2	2.25	2.25	40.23
13	9.5	2	3.5	2.25	65.2
14	11	3	3.5	2.25	86.29
15	9.5	3	3.5	3.5	93.45
16	11	3	1	2.25	68.24
17	8	4	2.25	2.25	46.11
18	9.5	4	2.25	3.5	90.2
19	11	3	2.25	3.5	69.78
20	9.5	4	1	2.25	72.37
21	9.5	3	2.25	2.25	83.1
22	11	2	2.25	2.25	55.51
23	9.5	4	3.5	2.25	83.12
24	9.5	3	2.25	2.25	83.1
25	9.5	2	2.25	1	23.61
26	9.5	2	1	2.25	50.19
27	11	4	2.25	2.25	85.91
28	9.5	3	2.25	2.25	83.1
29	8	3	3.5	2.25	49.71

Table 4
ANOVA for quadratic model

Source	Sum of Squares	Mean Square	F-value	p-value	Significant
Model	14113.73	1008.12	32.54	< 0.0001	Significant
X_1 -pH	2596.90	2596.90	83.82	< 0.0001**	
X_2 -Mg: P	1560.89	1560.89	50.38	< 0.0001**	
X_3 -Ca: Mg	897.18	897.18	28.96	< 0.0001**	
X_4 -CO ₃ ²⁻ : P	4535.35	4535.35	146.40	< 0.0001**	
$X_1 X_2$	150.31	150.31	4.85	0.0449*	
$X_1 X_3$	19.67	19.67	0.6349	0.4389	
$X_1 X_4$	358.34	358.34	11.57	0.0043*	
$X_2 X_3$	4.54	4.54	0.1464	0.7077	
$X_2 X_4$	279.22	279.22	9.01	0.0095*	
$X_3 X_4$	416.77	416.77	13.45	0.0025*	
X_1^2	2755.61	2755.61	88.95	< 0.0001**	
X_2^2	388.34	388.34	12.54	0.0033*	
X_3^2	73.89	73.89	2.38	0.1448	
X_4^2	962.48	962.48	31.07	< 0.0001**	

$R^2 = 0.9702$, Adequate precision = 21.0549

**Significant at 99% confidence level

*Significant at 95% confidence level

model was 21.0549 (desired adequate precision > 4), which represents an adequate signal for the model. P values < 0.01 are considered as highly significant whereas P value < 0.05 are considered as significant variables. All the independent variables (pH (X_1), Mg: P molar ratio (X_2), Ca: Mg molar ratio (X_3) and CO_3^{2-} :P molar ratio (X_4)) were showed high significant effect on the response value. Whereas the interaction terms pH \times Mg: P molar ratio ($X_1 \times X_2$), pH \times CO_3^{2-} :P molar ratio ($X_1 \times X_4$), Mg: P molar ratio \times CO_3^{2-} :P molar ratio ($X_2 \times X_4$), Ca: Mg molar ratio \times CO_3^{2-} :P molar ratio ($X_3 \times X_4$) are showed a significant effect on the response value.

3.5.2. Determination of optimal conditions using RSM

According to the model, optimized conditions for achieving maximum recovery efficiency (90.84%) are: pH is 9.5, Mg:P molar ratio is 3.21, Ca:Mg molar ratio is 1.93, CO_3^{2-} :P molar ratio is 3.49. To validate the model developed

recovery efficiency, an experiment is conducted at the same optimized condition and the recovery efficiency was found as 88.62%. There is no significant variation between the model predicted value and experiment value was found. Therefore it is concluded that the developed model can be used for finding recovery efficiency at different conditions.

3.5.3. Response surface analysis

Response surfaces showing the interaction between variable parameters and their effect on P recovery efficiency are shown in Figs. 7a–d.

Fig. 7a shows the influence of interaction between pH and Mg:P molar ratio on P recovery efficiency. It is observed that lower pH (< 9.2) values along with lower Mg:P molar ratio resulted in decreasing the P recovery efficiency. However, higher pH value ($9.2 < \text{pH} < 10$) with higher Mg: P molar ratio results in higher P recover efficiency (shown in

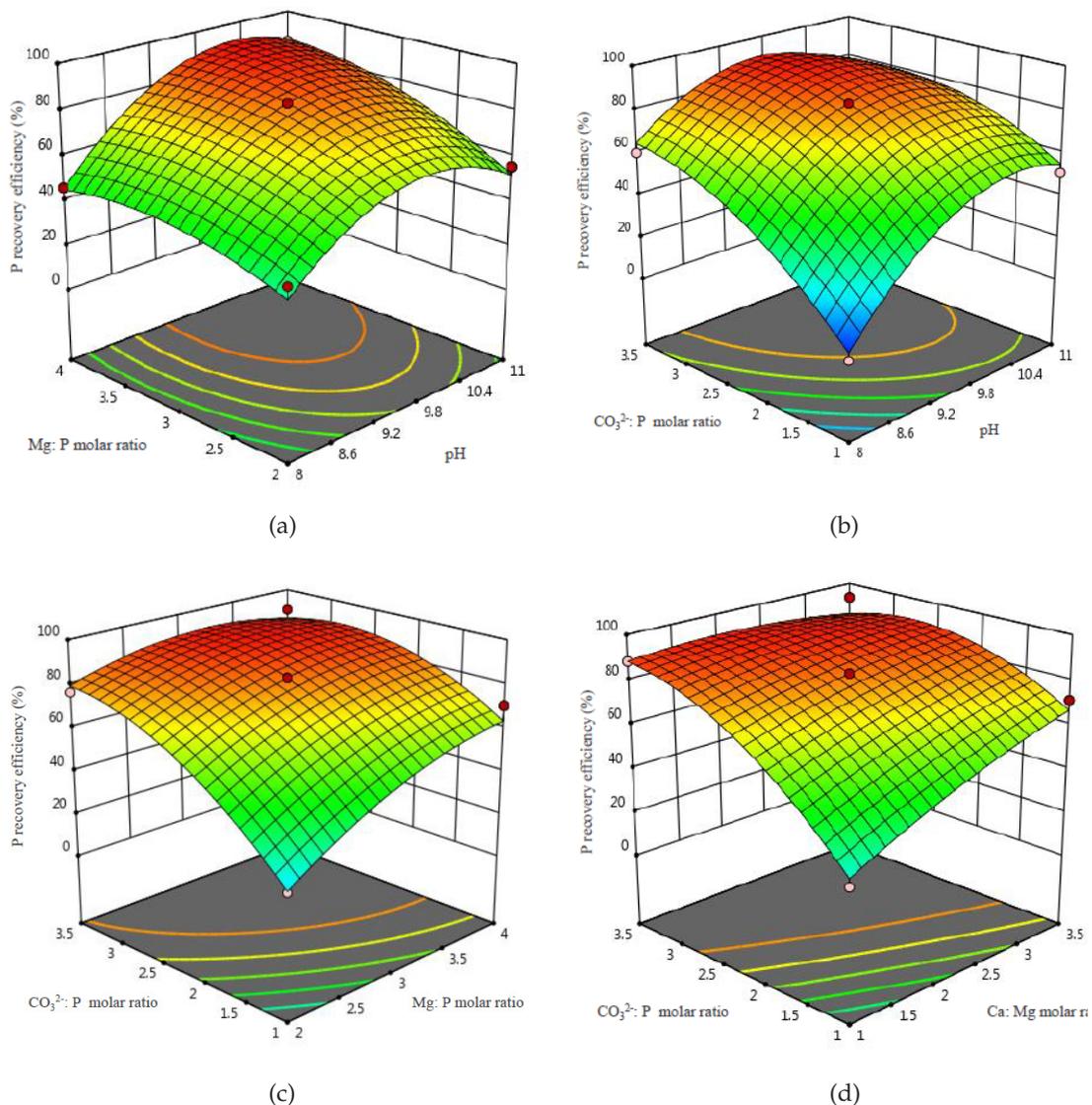


Fig. 7. Effect of interaction terms on recovery efficiency (a) pH \times Mg:P molar ratio (b) pH \times CO_3^{2-} :P molar ratio (c) Mg:P molar ratio \times CO_3^{2-} :P molar ratio (d) Ca:Mg molar ratio \times CO_3^{2-} :P molar ratio.

red colour). Similarly, at a pH beyond 10, further increase in Mg:P molar ratio increased the P recovery efficiency. At greater Mg:P molar ratio, the availability of Mg in the solution is high. Therefore it reacts with P and forms $Mg_3(PO_4)_2$, resulted in higher P recovery efficiency.

Fig. 7b shows the effect of interaction between pH and CO_3^{2-} :P molar ratio on P recovery efficiency. It is found from Fig. 7b that, when CO_3^{2-} :P molar ratio is high and at lower pH, P recovery efficiency is low. Lower pH with lower CO_3^{2-} :P molar ratio results in decreasing the P recovery efficiency.

The interaction effect of CO_3^{2-} :P molar ratio with Mg:P molar ratio and Ca:Mg molar ratio is shown in Fig. 7c and d. It is observed from Fig. 7c and d that CO_3^{2-} :P molar ratio showed similar behaviour with both Mg:P and Ca:Mg molar ratios. At a fixed high CO_3^{2-} :P molar ratio, the required P recovery efficiency can be achieved by adding a slight quantity of Mg and Ca. Similarly, at low CO_3^{2-} :P molar ratio, addition of higher quantity of Mg and Ca are required to achieve desired P recovery efficiency.

3.6. Economic evaluation

The economic estimation for recovery of P from swine wastewater as struvite using present study was carried out. The optimal conditions used while performing the cost analysis are: MgO used is 3 g/L, pH 9.5, NaOH was used to adjust the pH to 9.5 and reaction time of 30 min. The cost for chemicals and energy is considered but the price for manpower and equipment is not considered while performing a cost analysis. In this cost analysis, the value of the recovered products is also not included. The market rate of the chemicals, energy details and the cost required to recover P by the present study is given in Table 5.

From Table 5 it is observed that the cost required to recover P by this process is 2.06 \$/m³. The cost of the present study is high due to the consumption of NaOH in the process. Huang et al. [14] reported that the cost required to recover P by struvite crystallization was 2.58 \$/m³, where bittern was used as Mg source. Thus, the present study cost to recover P is 20% less when compared to the cost reported by Huang et al. [14]. Therefore, the recovery of P by the current study is considered as an alternative for sustainable utilization P resources.

4. Conclusions

In the present study, P was recovered as struvite from swine wastewater using MgO as a source of Mg. The pH of the wastewater affected the P recovery as struvite and

Table 5

The market rate of chemicals/energy and the cost evaluation to recover P from swine wastewater using MgO

Chemical/energy	Market price	Cost by the present study (\$/m ³)
MgO	0.46 (\$/Kg)	1.48
NaOH	0.35 (\$/Kg)	0.37
Energy used	0.07 (\$/KW-h)	0.21
Total cost		2.06

purity of the formed struvite. The maximum P recovery was attained at a pH of 9.5. The increase in Mg:P molar ratio increases P recovery and the optimum Mg:P molar ratio was taken as 3:1 due to economical consideration. The presence of Ca in solution affected the P recovery as struvite. Similarly, increase of CO_3^{2-} concentration in solution also decreased the recovery of P as struvite. A model was developed using BBD technique of RSM to optimize and as well as to find the interaction between factors on P recovery as struvite. RSM results indicated that the interaction terms, pH x Mg: P molar ratio, pH x CO_3^{2-} :P molar ratio, Mg:P molar ratio x CO_3^{2-} :P molar ratio, Ca:Mg molar ratio x CO_3^{2-} :P molar ratio showed significant effect on P recovery. The economic evaluation revealed that the proposed method is economically feasible and cost effective.

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