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Optimization and kinetics of nutrient removal from wastewater by chemical precipitation of struvite

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ABSTRACT

Nutrient removal by the precipitation of struvite from synthetic municipal wastewater was tested. Response surface methodology with the Box–Behnken experimental design was employed to determine the optimal phosphorus removal efficiency with the influencing process variables of pH, temperature, magnesium to phosphorus molar ratio, mixing speed (rpm), and organic contents. Under the values of pH, temperature, Mg to P ratio, mixing, and organic content of 9.86, 26.5°C, 1.64, 80 rpm, and 1,020 mg sugar/l, respectively, optimum phosphorus (PO_4-P) removal efficiency of 90.1% was obtained. Results of analysis of variance indicated that the quadratic model predicts the responses adequately with the five factors that coded the process variables. The effects the factors have on the amount of PO_4-P removal were ranked (with their relative scores) in the descending order of pH (11.8), Mg:P ratio (6.2), organic content (2.4), mixing speed (1.1), and temperature (0.5), where the ranking quantifications were according to the respective coefficients of the factors in the quadratic model equation. Removal of nitrogen (NH_4-N) was limited by equal molar amount of PO_4-P removed and thus the remaining NH_4-N must be subsequently treated using usual nitrogen removal processes.

Keywords: Struvite; Municipal wastewater; RSM; Box–Behnken design; Precipitation kinetics

1. Introduction

Nutrients contained in wastewater can deteriorate the ecosystem of the water body that receives the wastewater discharge [1]. Harmful algal blooms and declines in wildlife and wildlife habitat are often the results of excess nitrogen and phosphorus in the water body concerned. To protect water quality and the ecosystem, stringent effluent standards require proper and efficient removal of nutrients from all wastewaters discharged to the water body. Among the methods of nutrient removal, struvite precipitation is of interest because with struvite, nitrogen and phosphorus can be removed from a waste stream in a form that phosphorus and nitrogen are recoverable. In addition to meeting the theme of ecosystem protection and sustainable development, this recovery of phosphorus also suits the urgent need of phosphorus recycling because of the short supply of natural resource of phosphorus [2,3].

The compound commonly known as struvite has the composition of magnesium ammonium phosphate hexahydrate. Struvite is a crystalline solid that is

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formed according to the general and simplified reaction:

$$
\begin{aligned}
&Mg^{2+} + NH_4^+ + H_nPO_4^{n-3} \\
&\quad + 6H_2O \leftrightarrows MgNH_4PO_4.6H_2O + (n)H^+
\end{aligned}
\tag{1}
$$

Precipitation of struvite from wastewater has multiple benefits of nutrient (phosphorus and nitrogen) removal and recovery. Struvite usually precipitates as stable white orthorhombic crystals with an N:P:Mg molar ratio of 1:1:1. The compositions of nitrogen, phosphorus, and magnesium make struvite a potentially marketable product for the fertilizer industry. The advantages of nutrient recovery as struvite include the by-production of fertilizer [4], reduction of the overall loading to wastewater treatment plant [5], reduction of inhibitory effect of nitrogenous compounds to biological treatment system [6], and concomitant reduction of heavy metal in wastewater [7].

Struvite as a phosphorus and nitrogen recovery method for real wastewater has received frequent experimental studies. At the foresight of the aforementioned urgency of natural phosphorus shortage, large increase in the number of researches of both theoretical and applicability themes on struvite formation was reported in recent years. All the research efforts should improve the full-scale applications of the struvite method, which in the past had not been extensive due mostly to economical consideration [8]. Precipitation of struvite can be influenced by physical and chemical attributes of the wastewater system. Such influencing factors include supersaturation ratio, pH, Mg:P ratio, degree of mixing, temperature, and seeding conditions [8–10]. The effects these factors have on struvite precipitation must be adjusted or controlled to achieve a suitable combination that is beneficial to the operation of a treatment plant for nutrient removal. Response surface methodology (RSM) is used extensively for optimization of the operating conditions and for predictive model building for chemical and biochemical processes. RSM with the Box–Behnken design (BBD) is a useful tool for the design of experimental operation conditions to guide experimenters to the optimum response. In addition to capturing the optimum, the kinetics dictated by the operating factors may serve further guidelines in practical process operations, in which efficiency and economics are of foremost importance.

Studies of struvite recovery of phosphorus have mainly been conducted on wastewaters that are highly concentrated with nutrients, such as digester liquor or animal excreta wastes [2,5]. Special recommendation of the struvite method is made for wastewater treatment plants with enhanced biological phosphorus removal (EBPR) [11], in which polyphosphates released from phosphorus rich sludge must be recovered. The struvite recovery method is considered suitable for these highly concentrated wastewaters (CWW) because these CWW contain ammonium, phosphorus, and magnesium compositions that make struvite recovery economical. Furthermore, prevention of spontaneous struvite deposition at undesirable location along CWW flow-line is also a major requirement. Overall, struvite for phosphorus removal from raw municipal wastewater (RMW) has not been a major focus due to the inconvenience of low P and N concentration in RMW. For example, phosphorus discharged or wasted from animal wastes is approximately five times that of RMW [12].

From every angle of technical and scientific development, the mere P and N concentration consideration must not preclude the equal chances of recovering phosphorus from RMW by the struvite method. The purposes of this study, therefore, were to determine the optimal operating conditions and the kinetics of struvite precipitation from RMW. By completing these objectives, rationale about the practical feasibility of removing and recovering nutrients from RMW can be obtained. Test findings will enable the establishment of operational technique for the process of struvite precipitation from raw wastewater, and thus achieving the overall goal of improving nutrient recovery from municipal wastewater.

2. Materials and methods

2.1. Experiments

The test wastewater was synthesized with compositions similar to those contained in pretreated RMW [13]. The synthetic wastewater contained 10 mg/l (0.323 mM) of phosphorus (PO_4-P) and 40 mg/l (2.86 mM) of total nitrogen (inorganic). P and N were prepared with technical grade potassium dihydrogen phosphate (KH_2PO_4) and ammonium chloride (NH_4Cl) dissolved in distilled water. Organic content was simulated with food sugar, which is considered to have minimum reaction with struvite, if any. Proteins, which may have been broken down to inorganic ammonium before nitrification, and fats, which may be present in small amount in pretreated municipal wastewater, were not included. The precipitating agent was magnesium chloride ($MgCl_2.6H_2O$, technical grade). With the inorganic compositions in the main wastewater or $MgCl_2$ additions, common cations and anions were included, except Ca^{2+} and $SO_4{}^{2-}$. Complications with phosphorus precipitation due to other components that may exist in some particular real wastewaters were not explored in this study.

The effects of five factors (variables) on the precipitation of phosphorous as struvite were tested. The varying factors were pH, magnesium to phosphorus molar ratio (Mg:P), organic content (S), stirring speed (G), and temperature (T). These factors were made-up with the following chemicals or equipment: (1) initial pH was adjusted with sodium hydroxide (NaOH, 3 M); (2) Mg:P molar ratio was adjusted with the addition of a stock solution of $MgCl_2$; (3) organic content was simulated with B-grade crystal sugar; (4) temperature and stirring speed were controlled by magnetic heating stirrer.

Phosphorus precipitation experiments were conducted in batch-type reactor with 500 ml of synthetic RMW which contained P, N, and the applied chemicals for organic content and initial pH control. A precipitation experiment started after Mg was added and reactor liquid made to volume with distilled water. Each experiment was performed for 90 min, which included 60 min for the reaction and 30 min for the settlement of struvite.

2.2. Analytical

The difference between the initial and final PO_4-P concentrations in a test reactor was used as the quantitative measurement of the amount of phosphorus removed. In the synthetic wastewater used for this study, complicated reactions among unknown species may not occur and molar amount of phosphorus removed, recovered, and struvite formed (precipitated) are considered equal according to the stoichiometry shown in Eq. (1).

Phosphate (PO_4-P) concentration that remained soluble in wastewater after treatment with magnesium was measured for each precipitation test. For PO_4-P measurement, the reactor suspension, which had been settled for 30 min, was filtered through a 0.45 μm filter paper. The filtered samples were analyzed by phosphorus molybdate/ascorbic acid method of color formation which was detected by a spectrophotometer (Shimadzu UV-1800) at the wavelength of 880 nm.

2.3. Design of response surface method

A five-factor BBD with five center points was constructed under which efficiencies of phosphorus removal (struvite precipitation) were tested. BBD was selected for its efficiency in the design of experiments [14]. The five factors pH, T, Mg:P, G, and S were coded as x_1, x_2, x_3, x_4, and x_5, respectively. The response was the phosphorus removal efficiency, which was defined as $\text{Eff} = \frac{C_{po} - C_{pe}}{C_{po}} \times 100(\%)$, where C_{po} and C_{pe} are initial and final (equilibrium) concentrations of PO_4-P, respectively. Preliminarily, manual screening tests were conducted to select the natural values of all factors; the starting values of the factors were those normally applicable to municipal wastewater treatment. Levels of all factors and their natural values are shown in Table 1. Natural (X) and coded values ($x = -1$, 0, or +1) were related to each other with this equation:

$$x = \frac{X - (X_{\text{high}} + X_{\text{low}})/2}{(X_{\text{high}} - X_{\text{low}})/2} \qquad (2)$$

where X_{low} and X_{high} corresponded to the low-level (−1) and high-level (+1) settings of X, respectively.

Experimental runs with the five factors (k = 5) and five central points (C_o) require a total of 45 test combinations according to the equation of ($2k \times (k-1) + C_o$). Duplicate experiments were performed.

Response surface method allow fitting of a multifactor system to the simplified model of a polynomial function. The second-order (quadratic) model was used to approximate the response

$$y = \beta_0 + \sum_{i=1}^{5} \beta_i x_i + \sum_{i=1}^{5} \beta_{ii} x_i^2 + \sum_{i<j}\sum \beta_{ij} x_i x_j + \in \qquad (3)$$

where y is the dependent variable representing PO_4-P removal efficiency, β_0 is the offset term (constant), β_i is

Table 1
Level of influence factors and their natural values for BBD

		Coded level		
Factors (unit)	Symbol (x_i)	Low (−1)	Center (0)	High (1)
pH	x_1	8	9	10
Temperature (℃)	x_2	20	30	40
Mg:P molar ratio	x_3	1.0	1.5	2.0
G (rpm)	x_4	160	220	280
Organic (mg sugar/l)	x_5	100	350	600

the linear effect, β_{ij} is the interactive effect, β_{ii} the squared term, and x_i x_j are the i^{th} and j^{th} independent variables in coded values.

The optimum (stationary point) was found by setting all the partial derivatives of Eq. (3) to zero with respect to each and every x. From these derivatives, the optimal values of coded factors (x's) can be determined (see Montgomery [15]). Natural values of the variables were determined by converting known x's to X's using the inverse of Eq. (2).

F-test was conducted on the factors and the quadratic model by analysis of variance (ANOVA). F values, with P of 0.05 were calculated to assess the significance of the model and the coefficients of the model. Model fitting and statistical analyses were performed using MINITAB 14 software package (Minitab, In.).

2.4. Kinetics

Experiments were conducted on the kinetics of PO_4-P removal, which is equivalent to struvite formation and precipitation, using batch type reactors separate from those of the RSM tests. The influencing variables that are significant in affecting struvite precipitation were tested for their effects on struvite kinetics. The significant factors were found after RSM optimization results were obtained. Kinetics experiments were conducted during which PO_4-P molar concentrations were measured from initial time (C_{Po}) and series of time points t (C_P) until the concentrations were relatively constant (C_{Pe}), which indicates the state of equilibrium. The kinetics of PO_4-P precipitated as struvite was determined based on:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} \leftrightarrows MgNH_4PO_4 \tag{4}$$

Eq. (4) was a simplification of Eq. (1) by assuming, at alkaline solution, the PO_4^{3-} species was dominant and association of crystallization water was not rate limiting. Mg^{2+}:P was held at 1.0 in this study. Because molar concentration of nitrogen at any time is over nine times higher than that of PO_4-P, nitrogen is considered as a constant and the kinetics of this struvite precipitation system is dependent on molar concentrations of [Mg^{2+}] and [PO_4^{3-}]. The kinetic model of the reversible, two-reactant reaction was applied:

$$-\frac{dC_P}{dt} = k(C_P - C_{Pe})(C_M - C_{me}) \tag{5}$$

where k is the rate constant (mM-P^{-1} min^{-1}), C_M and C_{me} are molar concentrations of magnesium [Mg^{2+}] at time t and at equilibrium, respectively. For any time interval, dissipation of molar masses of PO_4^{3-} and Mg_2^+ are equal (Δ [Mg_2^+] =Δ [PO_4^{3-}]) and therefore, assuming the time to reach equilibrium for both species (in a common reaction) is equal, $(C_M - C_{me}) = (C_p - C_{pe})$. Regardless of any initial Mg:P ratio, the kinetic model (Eq. (5)) becomes:

$$\frac{dC_P}{dt} = -k(C_P - C_{pe})^2 \tag{6}$$

Kinetic rate constant k was determined by regression that fitted the integration of Eq. (6) to experimental data on a PO_4-P course (PO_4-P vs. t). C_{pe} was not a parameter of regression; the initial input values of C_{pe} were chosen from the lowest PO_4-P concentration, which occurred in the latest part of a PO_4-P course where PO_4-P concentrations were relatively constant. Regression was reiterated by changing input C_{pe} when the differences between input and output C_{pe} were larger than 5% of the input.

3. Results and discussion

3.1. Optimum phosphorus removal under multiple influencing factors

Phosphorus removal efficiencies were measured from the tests of a matrix of BBD. A quadratic model was fitted to the responses (percentage of PO_4-P removed). Experimental and predicted values (responses) of phosphorus removal efficiencies are listed in Table 2. Regression of the experimental responses on the quadratic model (Eq. (3)) resulted in a struvite precipitation equation, in terms of coded values of the influencing factors:

$$\begin{aligned} y = {} & 88.7178 + 11.8421x_1 - 0.4581x_2 + 6.2101x_3 \\ & + 1.1120x_4 + 2.3765x_5 - 10.0133x_1^2 + 0.2793x_2^2 \\ & - 6.8110x_3^2 - 2.0712x_4^2 - 0.8696x_5^2 - 0.9035x_1x_2 \\ & + 0.1895x_1x_3 - 5.4969x_1x_4 - 2.8812x_1x_5 + 1.7439x_2x_3 \\ & + 0.2464x_2x_4 + 0.5686x_2x_5 + 0.2211x_3x_4 - 0.5529x_3x_5 \\ & - 2.1988x_4x_5 \end{aligned} \tag{7}$$

According to the quadratic model (Eq. (7)), the optimum phosphorus (PO_4-P) removal efficiency was 90.1%. The optimal operating variables of pH, temperature, Mg to P ratio, mixing, and organic content were 9.86, 26.5°C, 1.64, 80 rpm, and 1,020 mg sugar/l, respectively. The variables that lie outside the coded range of RSM tests were, not surprisingly, mixing (G) and organic content (S). Mixing strength defined by rpm depends on the power of the stirrer, thus the

Table 2
Experimental coded factor levels for Box–Behnken design for optimization of PO4-P removal and experimental and predicted results

						PO4-P removal (%)		
						Experimental		
Run	x_1	x_2	x_3	x_4	x_5	1st	Duplicate[a]	Predicted (y)
1	0	−1	−1	0	0	79.6235		78.1778
2	0	−1	0	0	1	88.5955		90.3932
3	0	0	0	1	−1	84.6781		86.7115
4	0	0	−1	0	−1	68.6296		71.8976
5	−1	−1	0	0	0	63.3222	63.3324	66.6967
6	−1	0	−1	0	0	56.0435	57.0232	54.0311
7	0	0	0	−1	1	89.4042		89.2401
8	0	−1	1	0	0	89.4295		87.1104
9	1	1	0	0	0	90.0360		89.4643
10	0	0	0	−1	−1	77.4247		80.0896
11	0	0	−1	1	0	73.7853	73.7532	74.5167
12	0	0	−1	0	1	74.4677		77.7563
13	0	−1	0	−1	0	89.4042		86.5183
14	1	−1	0	0	0	89.5306	89.5225	92.1873
15	−1	0	0	1	0	72.3730		71.4016
16	0	0	1	0	1	89.8339	88.5955	89.0708
17	1	0	−1	0	0	80.7102		77.3360
18	0	0	1	1	0	87.1043		87.3792
19	0	0	1	−1	0	87.6351		84.7126
20	1	0	0	0	−1	90.0108		90.1816
21	0	1	0	−1	0	85.8660	88.3933	85.1093
22	1	0	0	0	1	89.5306		89.1722
23	0	1	0	0	1	89.9097		90.6143
24	−1	0	0	0	1	75.5797		71.2507
25	0	1	−1	0	0	71.7635	71.0052	73.7739
26	1	0	1	0	0	88.7471		90.1352
27	−1	0	1	0	0	63.3222	63.3127	66.0724
28	−1	1	0	0	0	67.4417		67.5873
29	0	1	0	0	−1	87.3571	87.2012	84.7241
30	0	−1	0	1	0	87.8878		88.2499
31	0	−1	0	0	−1	88.3175	88.4211	86.7776
32	1	0	0	−1	0	89.9097		92.8610
33	0	1	0	1	0	86.5989		87.8265
34	1	0	0	1	0	86.9527		84.0902
35	−1	0	0	0	−1	64.5353		60.7355
36	0	1	1	0	0	88.5955	88.4944	89.6819
37	−1	0	0	−1	0	53.3393		58.1820
38	0	0	−1	−1	0	75.2006		72.7346
39	0	0	0	1	1	87.8625	87.8455	87.0669
40	0	0	1	0	−1	85.5880		85.4236
41–42[b]	0	0	0	0	0	87.9989	88.7119	
43–44	0	0	0	0	0	88.7214	89.1245	
45–46	0	0	0	0	0	88.7320	88.7119	88.7178
47–48	0	0	0	0	0	88.7311	88.7218	
49–50	0	0	0	0	0	88.7222	89.0019	

[a] Results of duplicates are listed when there was a difference at the 2nd decimal place (one hundredth of a percent).

[b] Runs 41–50 were replicates of the central values (total 10 replicates).

prediction of optimum G indicates the appropriate mixing strength whose quantification was not properly represented within the rpm range initially chosen in the RSM tests. The range of organic content used in the original design was inevitably chosen at the neighborhood of COD concentration contained in municipal wastewater.

Fig. 1 shows the plot of experimental responses vs. responses predicted by Eq. (7). The value of co-relationship (r^2) is as high as 0.95, indicating the high level of consistency of the model prediction to the actual (experimental) response. Furthermore, a normal distribution of the residuals (figure not shown) also confirms that the quadratic model is satisfactory in predicting the response of struvite precipitation under the five influencing factors.

Results of ANOVA *F*-tests (not shown) for the response surface quadratic model indicate that the significant terms are the constant term (first term of Eq. (7)), pH, M:P ratio, G, S, pH × pH; Mg:P × Mg:P; G × G; pH × G; pH × S; T × Mg:P, and G × S. The constant term shows that approximately 88.7% of phosphorus can be precipitated as struvite at natural values of the influencing factors. This amount of phosphorus removed is independent of the factors set in the experiment.

Fig. 2 shows the contours of the response surfaces of the combined effects of the four factors whose interactions are significant, namely G × S, Mg:P × T, pH × G, and pH × S. The effects of each factor on struvite precipitation are further discussed below.

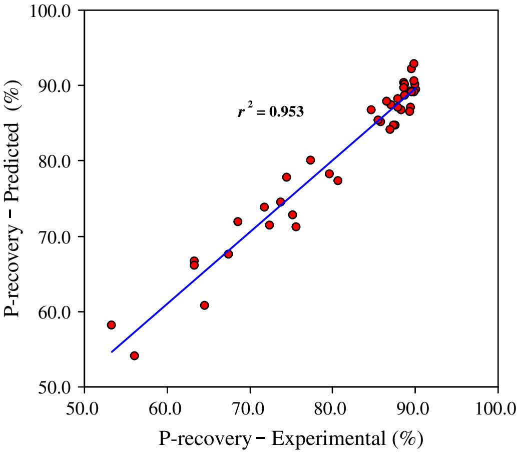

Fig. 1. Scatter diagram of predicted vs. experimental response values for PO_4-P removal efficiency.

3.2. Effects of influencing factors on struvite precipitation—kinetics

Fig. 2(a) shows the effects of G × S on the percentage of PO_4-P removed. PO_4-P removal efficiency decreased with an increase of mixing speed at a fixed amount of sugar in the wastewater. The gradient of increase of PO_4-P removal caused by increase of G is much higher than that affected by amount of sugar.

Fig. 2(b) shows the effects of Mg:P × T on the percentage of PO_4-P removed. The position where Mg:P leads to a maximum phosphorus removal is observed, while temperature has essentially horizontal contours indicating that it causes little effect on struvite precipitation. In fact, ANOVA results show that the variable of temperature (T) alone and all T interactions with other variables are insignificant in influencing PO_4-P removal except Mg:P × T, which is slightly significant at a borderline *P*-value of 0.049.

Fig. 2(c) shows the effects of pH × G on the percentage of PO_4-P removed. Both G and pH cause noticeable effects on PO_4-P removal efficiency, especially with pH. Fig. 2(d) shows the effects of pH × S. Significant effect of pH on struvite precipitation is again shown in this pH × S interaction.

Overall, the effects the factors have on the amount of PO_4-P removal were ranked in the descending order of pH, Mg:P, S, G, and T. According to the coefficients of the respective factors in the quadratic model (Eq. (7)), which coefficients represent changes of PO_4-P removal efficiency upon unit change of the coded value of the factors, the relative ranking scores of 11.8, 6.2, 2.4, 1.1, and 0.5 can be given to pH, Mg:P, S, G, and T, respectively. An optimal temperature was found at 26.5°C. This temperature may not be important because of the mild temperature effect and that any wide and drastic adjustment of wastewater temperature is not practically advantageous.

The effects of the variables on struvite precipitation were further examined with a study of precipitation kinetics. T and Mg:P were excluded from the kinetic tests; Mg:P was considered as an invariant, as Eq. (6) shows, in struvite kinetics, and T variation was considered unnecessary in practical application. Fittings of the PO_4-P removal courses with the second-order kinetic model (Eq. (5)) are shown in Fig. 3. The second-order kinetic model suits the data satisfactorily, with high goodness-of-fit r^2. Comparisons to the first-order kinetics reported, for examples, by Quintana et al. and Nelson et al. [16,17] indicate that (1) this second-order kinetic equation exhibits slight improvement in data fittings over those fitted to the first-order equation; (2) simplicity of use for both equations is about equal. Further comparison of

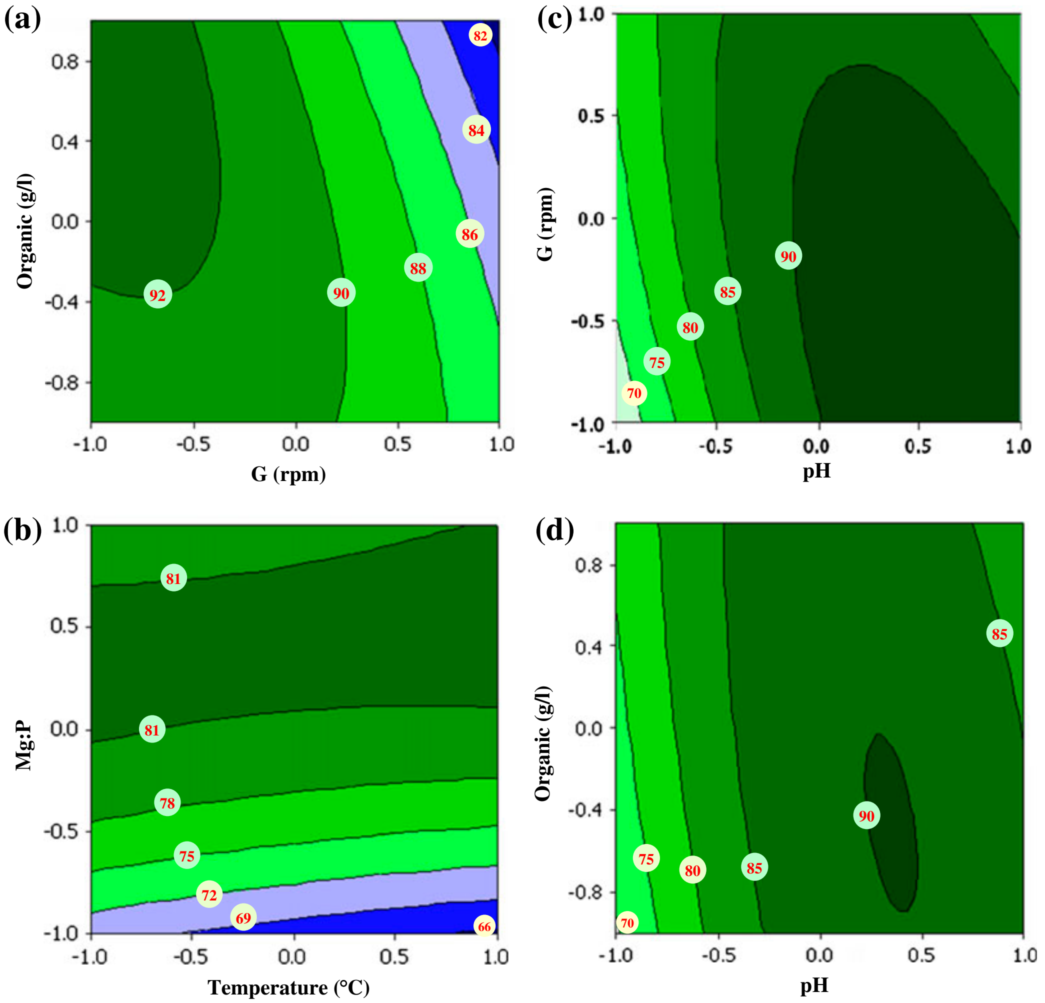

Fig. 2. Combined effect of influencing variables on efficiency of PO_4-P removal, contour plots. (a) S × G, (b) Mg:P × T, (c) pH × G, (d) pH × S.

struvite kinetics formulated by elaborating thermodynamics of the complex and detailed struvite reactions [18] were beyond the simple applicability purpose that was considered an important requirement in this study. The kinetic parameters (k of Eq. (6)), together with the residue (equilibrium) PO_4-P concentrations (C_{pe}), are shown in Table 3. Kinetic rates show that the importance of the variables in affecting struvite precipitation is in the ranking order of pH, G, and S. Residue (equilibrium) PO_4-P concentrations (C_{pe}) are ranked lower in the order of pH, G, and S. Operation conditions affect both the PO_4-P removal rate and final removal efficiency (C_{pe}). Therefore, optimization of struvite precipitation under the relevant operating variables is important to efficient nutrient removal from wastewater.

Fig. 3(a) shows that higher phosphorus removal efficiencies and faster rates can be achieved with pH on the alkaline side. Prominent effect of pH on PO_4-P removal is already seen from Fig. 2(c) and (d), where narrow contours (steep descend) of PO_4-P removal is shown when pH decreases below the optimum. Phosphorus species as PO_4^{3-} is abundant within the pH range of 7–9 [17], and alkaline pH is also favorable for crystallization equilibrium of struvite [19]. Previous results showed that pH higher than 8 is suitable for the formation of struvite [20], and particularly, pH of 8.5–8.7 offers efficient struvite crystallization [8,21]. Most recent findings indicated that the formation of pure struvite occurs at neutral pH [22]. The precipitate formed from the experiments of this study and similarly those precipitates from other studies reported previously may fall short of pure struvite. However, pure struvite precipitation at neutral pH is reported to complete with a very slow rate. This slow rate should make a hidden difficulty that is not easily foreseen

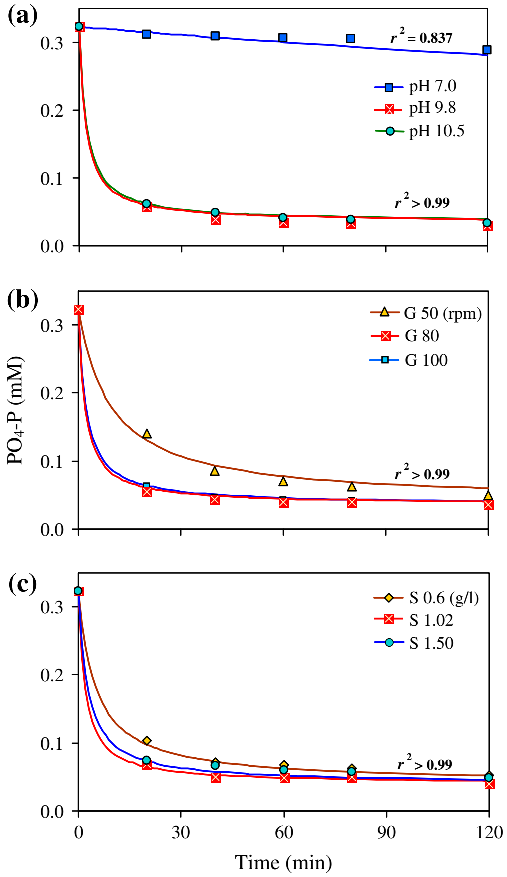

Fig. 3. Data and model fittings (lines) of kinetic tests for PO_4-P removal. (a) Effect of pH, (b) Effect of mixing, and (c) Effect of organic content. Tests of pH = 9.8, G = 80 rpm, and S = 1.02 g/l were under identical conditions.

Table 3
Kinetic coefficients and equilibrium PO_4-P concentration under indicated operating conditions

Operating variable and value		k (mM min)$^{-1}$	C_{pe} (mM)[a]
pH	7.0	0.061	0.060[b]
	9.86[d]	1.858	0.035
	10.5	1.682	0.038
Mixing (rpm)	50	0.370	0.044[c]
	80[d]	1.852	0.036
	100	1.522	0.039
Sugar (g/l)	0.60	0.704	0.045[c]
	1.02[d]	1.832	0.040
	1.50	1.325	0.042
Tempature (℃)	26.5[d]		
Mg:P	1.0[e]		

[a] Equilibrium PO_4-P concentration (C_{pe}) of an operating variable input into Eq. (5) was the last or lowest PO_4-P concentration in PO_4-P course, except where noted (footnote b and c).

[b] Experimental C_{pe} was not found in the time span of the experiment because of slow kinetic rate; input C_{pe} was assumed.

[c] Input C_{pe} adjusted in reiterated fittings of model to data until the differences between input and output C_{pe} were within 5%. (Model output reached equilibrium in less than 720 min (12 h)).

[d] Values at optimum. Tests with variables at their optimal values were identical.

[e] Constant Mg:P for all experiments. Optimum value of Mg:P was 1.64 but k is independent of Mg:P (Eq. (5)).

before this recent publication and the suitability of forming pure struvite for application purposes would not be ranked highly by process engineers.

Fig. 3(b) shows the effects of mixing speed (around the optimum) on the kinetics of struvite precipitation. Kinetic rate constants are essentially similar with mixing at 80 and 100 rpm, while kinetic rate at 50 rpm of mixing is noticeably slower. Struvite precipitation rate supports that mixing speed of 80 rpm is indeed the optimum. Practical consideration with mixing speed would avoid excessive mixing strength due to the possibility of disrupting struvite crystals and thus the settleability and precipitation of struvite particles would decline [23]. The optimal mixing speed found in this study is considered suitable for struvite precipitation, both scientifically and practically.

Fig. 3(c) shows that organic content, represented by sugar, has the highest struvite precipitation rate constant at concentration of 1,020 mg/l. The kinetics tests support this high organic concentration as being the optimum organic concentration of the wastewater undergoing struvite precipitation. The optimal sugar concentration found in this study is beyond the COD concentration of most RMW. The effect of organic matters on struvite had not been sufficiently studied. If indeed a high concentration of COD is universally suitable for struvite precipitation for all wastewaters, only the sludge digester liquid [7] or animal waste [6] may have COD within the range that covers this optimal organic concentration. Whether it is necessary to adjust the organic contents in RMW to meet the optimum may depend on assessment that suits the particular treatment case.

In addition to the examination of the importance of the operational variables in affecting struvite precipitation, the kinetic model, completed with numerical value of its rate constants, also facilitates calculations needed for engineering design of the struvite process.

3.3. Nutrient removal from RMW

This study found that the conditions for efficient struvite precipitation from synthetic wastewater of the concentration of raw municipal sewage are essentially similar to the conditions applicable to CWW. The features, most importantly economical concerns of nutrient removal by struvite precipitation from RMW, may be discussed with comparisons to struvite precipitation from wastewaters of the final stages of wastewater treatment, such as from the liquids of microbial sludge digestion or EBPR sludge digestion units, and swine waste: (1) demands of pH adjustment and Mg addition and high organic concentration are similar for both CWW and RMW wastewaters; (2) flow rate of RMW is higher than the flow rate of CWW, thus RMW may require a larger struvite solid separation system. The location of the struvite process at a municipal wastewater treatment plant must be further evaluated based on sound engineering and economical analyses; (3) molar concentration of N is much higher than P in RMW. Unbalanced N and P removal may result because struvite precipitation uses the fixed 1:1 M ratio of N and P. This study shows that the maximum NH_4-N removal was 10.2% corresponding to the PO_4-P removal of 90.1%, leaving approximately 35 mg/l of NH_4-N untreated. This concentration of nitrogen can be treated by methods, such as biological treatment, that are already required to meet the effluent standards. Finally, the precipitation species that may not be true struvite as indicated from most recent study [22] may or may not be a severe concern in the application point of view. This precipitate purity question is equally suffered for similar phosphorus removal procedures, either from CWW or from RMW wastewaters.

Contrary to the above disadvantages, there must be balancing economical advantages for removing nutrients from RMW by the struvite method. Compared with that from CWW, the struvite method of nutrients removal from RMW can have the following advantages: (1) the cost of struvite precipitation is related to the molar mass of the added chemicals, especially the cost of adding Mg [24]. Since the masses of nutrients are constant for a waste flow, nutrient removal from RMW should not incur exceptionally higher expenditure than from CWW; (2) P and partially N removed from RMW by struvite may reduce or exclude the need of further P removal such as EBPR, from which P must be further recovered from the side stream. Struvite precipitation from RMW in fact can save some major parts of the expensive advanced treatment processes for nutrient removal; (3) liquors that have concentrated nitrogen must have phosphorus supplemented for equivalent nitrogen removal [6,7,21,25]. The proportion of N that is not removed by struvite from RMW can be treated with methods, such as biological denitrification, at minimal or no extra cost of phosphorus supplementation.

4. Conclusion

Struvite precipitation of nutrients from RMW has similar factors of consideration compared to nutrients precipitation from concentrated waste streams. Response surface method suitably found the maximum PO_4-P and NH_4-N removed from synthesized municipal wastewater, under the optimal conditions of struvite precipitation. RSM and ANOVA results showed that pH and Mg:P play an important role in increasing PO_4-P removal efficiency, while mixing speed, amount of organic matter, and temperature, in that order, have comparatively moderate effects. Additional kinetic tests confirm similar effects of the variables on the rate of PO_4-P removal. The optima caused by the influential variables for struvite precipitation from RMW and from high concentration wastewater are essentially similar. Optimal conditions are found that lead to the methods for enhancing the efficiency of struvite precipitation from municipal wastewater.

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