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Phosphorus Recovery and Bioavailability from Chemical Extraction of Municipal Wastewater Treatment's Waste Activated Sludge: A Case of Bangkok Metropolis, Thailand

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ABSTRACT

This study evaluated the extractability and bioavailability of Phosphorus (P) recovered from waste activated sludge (WAS) so as to reduce dependence on the import of non-renewable P resources. P extraction was carried out using sulfuric acid (H_2SO_4). A response surface methodology was used to optimize conditions for the chemical leaching of WAS. The results showed the optimum condition for leaching WAS with 0.1 mol/L H_2SO_4 for 30 min, resulting in 97% P released. The efficiency of P recovery by P precipitation was associated with pH value and Mg:P. At pH 7, 9, and 11, P recovery was 92, 92, and 91% with uncontrolled Mg and 93, 93, and 92% with sea salt (Mg:P, 2:1), respectively. However, the yield of the produced struvite was much lower compared with that of added sea salt. From elemental analysis, the yield of struvite precipitated at pH 9 of Mg:P, 2:1 was about 26%, and the total P content of the precipitate was 12%. Available P was almost 80% after 35 days of operation, which was higher than that of commercial fertilizers. Results of this study are expected to provide fully comprehensive information to decision-makers regarding the suitability of implementing P-composite matter recovered from WAS. This will also help close the loop of the P cycle for food cultivation in the human ecosystem.

1. INTRODUCTION

Phosphorus (P) is an essential element for all living organisms and plays an important role as a fertilizing nutrient in agriculture. Moreover, P is one of the limited and nonrenewable resources and is required for food production (Withers et al., 2015). More than 85% of mined phosphate rock (PR), is used to produce P fertilizer (Geissler, 2015). Notably, the demand for P fertilizer for food production will increase significantly due to the growing world population, predicted to reach nine billion people in 2050 (Chen and Graedel, 2016; Geissler, 2015). PR is rapidly being depleted and is reserves are available in some geographical areas of the world such as Morocco, China and the USA (Van Vuuren et al., 2010). PR reserves are expected to dwindle in the next 50 to 100 years (Cordell and White, 2014). Consequently, P recovery from any P-rich residues has attracted considerable attention.

Among P-composite residues, domestic wastewater contains 5 to 20 g of P (in ortho-phosphates and organic compounds) in one cubic meter (Li et al., 2015). Biological nutrient removal is the most widely used technique to treat domestic wastewater. Phosphates are taken up in excess of normal metabolic requirements and then stored as intracellular bio-polymer polyphosphate (poly-P) within poly-P accumulating organisms (PAOs) (Chen et al., 2012; Wang et al., 2017). In the intervening time, PAOs are enriched by recirculating the waste activated sludge (WAS) (Kodera et al., 2013). Consequently, WAS, as a major byproduct derived from biological WWTP, accumulates a substantial amount of P leading to P

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This paper was selected from the Environment and Natural Resources International Conference (ENRIC 2021) which was held during 16th December 2021 in Thailand removal, in which over 90% of P is transferred to WAS (Balmer, 2004). Considering WAS is continuously produced in large amounts during biological nutrient removal (Wang et al., 2018; Xu et al., 2018; Zhao et al., 2017), P recovery from plentiful, inexpensive WAS has received increasing attention.

According to the work of Thitanuwat et al. (2016), P at the end of pipes in Bangkok Metropolitan Administration (BMA) was reported to come from domestic wastewater, septage sludge, and green garbage. Only 4% was recycled in public parks. In Bangkok, most solid wastes go directly to landfills, which are sinks for P resource and can potentially be used for P recycling. This constitutes 81% of discarded P. Moreover, an annual average of 2,116.7 t P is generated from domestic wastewater in the BMA. WAS is a major byproduct from WWTP in the BMA with 16.3 g P/kg or about 63% (456.1 t P/year) disposed in landfills. In addition, it also contains considerable amounts of P, about 356 mg P/L, together with components valuable for potential fertilizers such as Mg and Ca. WAS, on the other hand, is contaminated with human disease agents such as feces-borne coliform bacteria, viable helminth eggs, and active parasite cysts. Hence, fresh sewage sludge should not be disposed on land unless it has experienced pathogen diminishment (Sreesai et al., 2013). Therefore, direct application of WAS on agricultural fields is prohibited.

Although research on P recovery from sludge by struvite crystallization has been conducted, the method of effective P extraction from sludge requires further study. Finding economical and environmental-friendly methods to fully extract P from WAS is undoubtedly the first step to effectively recover P elements (Tong and Chen, 2009). Thus, many pretreatment processes of excess sludge have been developed. Wang et al. (2013) has reported that 92.8% of the P was recovered in the supernatant from electrochemical pretreatment (EPT) enhanced by anaerobic fermentation (AF) WAS. Leaching is the process of liquifying minerals to remove minerals from a solid. Leaching with acidic or alkaline solutions to recover P from sewage sludge ash and sewage sludge has been reported by (Fang et al., 2018; Shiba and Ntuli, 2017). Many different types of leaching agents include H_2SO_4 (Liang et al., 2019; Ottosen et al., 2013), HCl (Xu et al., 2012), HNO_3 (Gorazda et al., 2016; Sano et al., 2012), and oxalic acid (Liang et al., 2019). Among these extractants, H_2SO_4 is widely used because of its low cost and high efficiency extraction yield. The factors affecting extraction of P by H_2SO_4 include reaction time, H_2SO_4 dosages, reaction temperature, and ratio of sludge/leachate (Fang et al., 2018; Shiba and Ntuli, 2017). Atienza-Martínez et al. (2014) used H_2SO_4 as the extraction agent, and the extraction yield of P from Sludge Incinerated Bottom Ash (SIBA) was 85% after 2 h reaction. Donatello et al. (2010) extracted P from SIBA with H_2SO_4 and obtained a P extraction yield of more than 80%. Based on these facts, H_2SO_4 was selected as the extraction agent in this study. Therefore, determining the effect of sludge chemical leaching methods on P recovery as struvite was necessary.

Recently, P recovery from wastewaters by chemical precipitation has been widely investigated. Struvite is a crystalline substance obtained from the input of chemicals including an alkali source for pH adjustment and an Mg source needed to achieve at least equimolar concentrations (1:1) of Mg^{2+} and PO_4^{3-} in the alkali pH solution. It could be used as P fertilizer or as a raw material for P-composite fertilizers (Rahman et al., 2014; Vaneeckhaute et al., 2017). Regardless of the total amount of P in the compost, the origin of the organic waste influences the type and fractions of P forms, which might alter P-bioavailability (Frossard et al., 2002). Due to the existence of low solubility P, struvite has been considered an excellent P fertilizer and is frequently described as a slow release fertilizer. (Ackerman et al., 2013; Talboys et al., 2016).

The aforementioned wastes comprise recoverable P, in which pre-treatment is needed to concentrate P from wastes prior to recovery process. However, very few studies in Thailand have been carried out to recover P before landfilling or incineration. Therefore, appropriate methods to recover P from such wastes to close the P cycle loop for production in the human ecosystem should be explored. Successful results of this study are expected to pave the way for implementing engineering processes for P recovery nationwide. These will help save the cost of imported fertilizer, and protect the environment from eutrophication, due to excessive P discharge. This study aimed (i) to evaluate the efficiency of chemical P extraction from WAS using sulfuric acid and study the feasibility of engineering and economic P recovery processes; (ii) to investigate speciation of P-composite materials obtained from precipitation of P-containing supernatants produced from chemical P extraction processes; and (iii) to investigate the P-bioavailability from the recovered P product, in comparison with commercial fertilizers.

2. METHODOLOGY

2.1 Waste Activated Sludge (WAS)

The WAS used in this study was collected from the secondary sedimentation tank of Nong Khaem water quality control WWTP, BMA, Thailand. After collecting, the characteristics of WAS were measured, then stored in sealed plastic containers at 4°C, prior to use. The main characteristics of WAS are shown in Table 1, which demonstrates that the samples contained P, Ca, and Mg as major elements. The total solids (TS) content of WAS was diluted with distilled water to 3% of solid content, (w/v) which remains the average TS content found in general WAS (Zhang et al., 2020), to ensure consistency before acid leaching.

Table 1. Characteristics of waste activated sludge (WAS)

Parameter	Value	Unit
Total phosphorus (TP)	356.00±12.47	mg/L
Soluble phosphorus	48.05±0.37	mg/L
Chemical oxygen demand (COD)	16,304.00±10.30	mg/L
Magnesium (Mg)	155.37±0.06	mg/L
Ammonia (NH_3)	168.70±17.03	mg/L
Calcium (Ca)	226.93±2.00	mg/L
Total solids (TS)	35,100.00±24.30	mg/L
Percentage of volatile solids of total solids (VS)	52.28±3.40	%
Total suspended solids (TSS)	31,000.00±23.21	mg/L
Percentage of volatile suspended solids of total suspended solids (VSS)	53.72±2.27	%

2.2 Soil

The soil selected for this study was taken from the upper layer (depth 15 cm) of an agricultural field in Nakhon Pathom, Thailand. The soil was dried for 24 h at room temperature. The dried soil was sieved to obtain a fraction ≥1 cm. and P content was determined by the colorimetric method using vanadomolybdophosphoric acid and UV-spectrophotometer. The soil contained total P content of 0.005 mg/g dry weight.

2.3 Chemical leaching tests

In chemical leaching tests, 500 mL of WAS (3% of solids content) was mixed with H_2SO_4, to prepare four different concentrations of H_2SO_4 (0.01, 0.05, 0.10, and 0.50 mol/L). The mixture was stirred at 200 rpm using a Jar tester at ambient temperature (20 to 25°C). For P extraction, experiments were conducted in triplicate at varying reaction times (15, 30, 45, 60, 90, and 120 min). After leaching treatment, the mixture was separated using 10 µm filter paper (Whatman No. 93). Subsequently, the filtrates determined PO_4^{3-}, Mg, and Ca. The sludge residue was dried at 105°C for 24 h. After drying, it was used to analyze remaining P.

2.4 Optimization and prediction model

The response surface methodology (RSM) of Design Expert 13 Software licensed to the Faculty of Graduate Studies, Mahidol University was used to determine the optimum condition for the leaching process, which could be used to optimize the factors including reaction time and acid concentration (Anderson-Cook et al., 2009; Coetzer et al., 2018). The I-optimally with 16 runs was used. The interactions among the variables and responses to P extraction were determined from the analysis of variance (ANOVA). To quantify the quality of the quadratic prediction models, model terms statistical significance, coefficient of determination (R^2), probability (P-value) with 95% confidence level, and (t-test) at 5% significance level (Prob<0.05) were determined. Moreover, the 3D surface was created to identify the optimum region. Thus, a mathematical model was developed following a second order polynomial as shown in Equation (1).

$$Y = \beta_0 + \beta_i A + \beta_j B + \beta_{ii} A^2 + \beta_{jj} B^2 + \beta_{ij} AB \qquad (1)$$

Where; Y is percentage of P extraction response, β_0, β_i, β_j, β_{ii}, β_{jj}, and β_{ij} are constant, linear effect, quadratic effect, and interaction effect coefficients, respectively; A and B represent the independent variables, viz., reaction time and acid concentration.

2.5 P precipitation

Precipitation tests were conducted for P recovery. The leachate obtained from the optimum condition of leaching process was used as the P-stock solution. In the experiment, two different Mg^{2+}:PO_4^{3-} molar ratios (1.07:1(uncontrolled) and 2:1 (sea salt addition)) were used. For Mg/P=2, sea salt was added as the external source of Mg. The pH of all cases was controlled at 7, 9, and 11 by dropwise addition of 50% sodium hydroxide solution at the beginning of each experiment. These experiments were conducted three times at ambient temperature. The stirring velocity was initially set at 3.33 Hz for 15 min, slow mixing at 1.25 Hz for 30 min, followed by settling for 1 h. After settling, the mixture was separated using a 10 µm filter (Whatman No. 93). Finally, the precipitates formed during this process were separated by filtration and oven dried at 103°C for 24 h. After that, the dried solid precipitates were determined for P-containing solids.

2.6 Phosphorus bioavailability procedures

Pot experiments were carried out to compare P-bioavailability of P-solids precipitates (PSP) obtained from this study with that of commercial fertilizers such as monophosphate (MP) and diammonium phosphate (DAP). The experiments were conducted in plastic pots (size 0.11 m × 0.005 m^2) filled with soil in triplicate for each experiment. Those three fertilizers were measured to 100 mg P per pot (15 g P/m^2). The control (blank) pot contained soil without added P fertilizer. The fertilizer in each pot and blank pot were dissolved with pH 6 tap water 90 mL daily equivalent to the amount of annual rainfall of the country. The experiments were generated until 35-day test duration. Samples were collected daily to analyze P content.

2.7 Analysis and calculations

The total Kjeldahl nitrogen (TKN), TS, VS, TSS, VSS, COD, and total ammonia nitrogen concentrations were measured according to standard methods (APHA, 2012). Mg and Ca were measured with an atomic adsorption spectrophotometer. Data were expressed using mean value and standard deviations (SD). Independent T test and One-way analysis of variance (ANOVA) were used to determine whether statistically significant differences existed among the leaching experiments, 16 runs for acid leaching of P recovery, P-bioavailability and percentage P content in solids and liquids. All tests were performed using SPSS Software, 18.0 for Windows licensed to Mahidol University.

2.7.1 P recovery

The P recovery efficiency defined in Equation (2) was determined by the difference of initial and final PO_4^{3-} concentrations in experiments, as shown in Equation (2).

$$(\%)\ P_{\text{recovery}} = \left[\frac{[PO_4^{3-}-P]_{\text{initial}} - [PO_4^{3-}-P]_{\text{final}}}{[PO_4^{3-}-P]_{\text{initial}}}\right] \times 100 \qquad (2)$$

Where; $[PO_4^{3-} - P]_{initial}$ is the initial phosphate concentrations, mg/L and $[PO_4^{3-} - P]_{final}$ is final phosphate concentrations, mg/L.

2.7.2 Phosphorus crystal content

Phosphorus crystal content was calculated, following Equation (3).

$$\text{P crystal content } (\%) = \left[\frac{C_s \times \text{MW of P crystal}}{M}\right] \times 100 \qquad (3)$$

Where; Cs is the molar concentration of limiting ions (mol/L), the molecular weight of P crystal formed (g/mol) and M is the number of solids formed in the precipitation experiment (g/L).

2.7.3 P bioavailability

P bioavailability was computed, as shown in Equation (4).

$$\%\ \text{P release efficiency} = \frac{P_{\text{mix,t}} - \text{Blank}_t}{P_{\text{initial}}} \times 100 \qquad (4)$$

Where; $P_{mix,t}$ is the mixed concentrations of dissolved P from the pot at time=t, mg, $P_{initial}$ is start phosphorus concentrations (mg) in each fertilizer, $Blank^t$ is dissolved P concentration of soil (Blank pot) at time=t (mg).

3. RESULTS AND DISCUSSION

3.1 Optimization of the extraction parameters by RSM and ANOVA

The results collected from these experiments were fitted in a quadratic polynomial model and regression coefficients obtained. To determine the best model for the response (%P extraction), standard deviations, the predicted sum of squares, and R-squared values were compared (Cornell et al., 2011; Iweka et al., 2021).

The resulting ANOVA data are shown in Table 2. It could be seen that the significant model terms comprised time (A), acid concentration (B), the two-level interactions of time and acid concentration (A×B) and the quadratic effect of acid concentration (B^2) indicating that those terms greatly influenced %P extraction. Based on the mathematical calculations for a good-fit model, the amount of the variation in the response must be close to one (Onsekizoglu et al., 2010). According to the correlation coefficients (R^2) value obtained in this study for P extraction was 0.9889; a good fit between models and experimental data could be concluded. Moreover, the adjusted correlation coefficient, R^2 (adj) was 0.9833. F-tests for "lack of fit" were used to assess the model's suitability. The "lack of fit" in P extraction, was insignificant, with F-value of 0.7080 and p-value of 0.6430, respectively. This confirmed the model's suitability for explaining this process (Falowo et al., 2019). To make predictions about the response for given levels of each factor, an equation in terms of coded factors could be used. In other words, this equation is useful where identifying the relative influence of a factor is important and is accomplished through comparing the factor coefficients against one another. Effective mathematical models as functions of the coded variables for P extraction have been proposed as shown in Equation (5):

$$\%\text{P extraction} = +121.25 + 32.20A + 285B - 1.38AB - 53.25A^2 - 1.6B^2 \quad (5)$$

Where; A is the reaction time (min), B is the acid concentration for chemical leaching (mol/L), for extraction P (min). This equation describes the created model and gives solutions for the dependent variable based on the independent variable combinations, whether they are significant in the response. Optimization of the reaction parameters by response surface methodology (RSM) described by the regression model in Figure 1. Based on the above discussed, both time and acid concentration are important factors for the leaching efficiency of P. The Figure also shows that increasing acid concentration and time affected into increased %P extraction efficiency. However, the leaching efficiency decreases slightly when acid concentration increased above 0.45 (mol/L). As can be seen, this model forecast that optimum values to obtain the highest value of P extraction are: 30 min of reaction time and 0.1 (mol/L) of acid concentration.

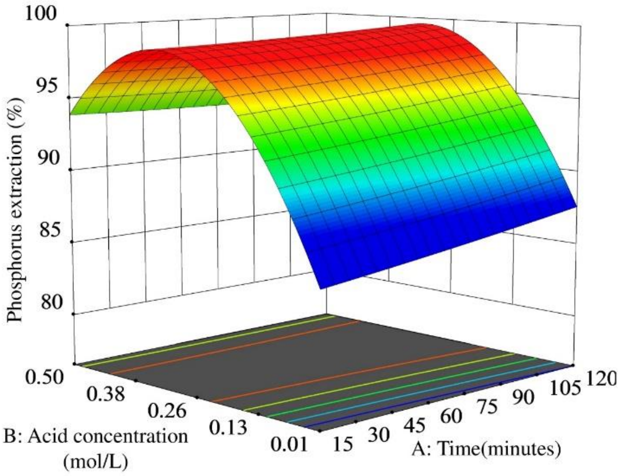

Figure 1. 3D-surface plot for P-extraction in respect to the most influential parameters, i.e., Time and acid concentration (ambient temperature).

Table 2. Analysis of variance table for P extraction

Source	Sum of squares	df	Mean square	F-value	p-value	
Model	6463.56	5	1292.71	177.39	<0.0001	Significant
A-Time	171.37	1	171.37	23.52	0.0007	
B-Acid concentration	5036.23	1	5036.23	691.10	<0.0001	
AB	39.54	1	39.54	5.43	0.0421	
A^2	9.25	1	9.25	1.27	0.2861	
B^2	3854.31	1	3854.31	528.91	<0.0001	
Residual	72.87	10	7.29			
Lack of Fit	30.21	5	6.04	0.7080	0.6430	Not significant
Pure Error	42.67	5	8.53			
Cor. Total	6536.44	15				
			R^2	0.9889		
Std. Dev.	2.70		Adjusted R^2	0.9833		
Mean	83.81		Predicted R^2	0.9783		
C.V. %	3.22		Adeq. Precision	35.1792		

3.2 P recovery via precipitation and P-containing solids speciation

To confirm the feasibility of P recovery from WAS as magnesium ammonium phosphate (MAP) and hydroxyapatite (HAP), P crystallization from the leachate obtained from the optimum condition (0.1 mol/L, 30 min) followed by speciation of precipitates formed were conducted. The reactions of MAP and HAP and their solubility product constants are presented in Equations (6) and (7), respectively.

$$MgNH_4PO_4(s) \rightleftharpoons Mg^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq) \quad (6)$$

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \quad (7)$$

As illustrated in Figure 2, the efficiencies of P recovery from the WAS leachate under uncontrolled magnesium (Mg/P=1.07) were 92, 92, and 91% at pH 7, 9, and 11, respectively. Similarly, for sea salt addition (Mg/P=2), the P recovery efficiencies at pH 7, 9, and 11 were 93, 93, and 92%, respectively. These results indicate that both pH and molar ratio of Mg/P do not affect the %P extraction. However, it is obvious that efficiencies of P recovery for all cases decreased when using pH=11. Previous studies found that a wide range of molar ratios of Mg/P can be used for struvite precipitation (Khaita and Polprasert, 2019; Pinatha et al., 2020). In addition, P recovery efficiency was highly influenced by Mg/P ratios (Maekawa et al., 1995). Perera et al. (2007) reported that increasing the molar ratio of Mg/P increases supersaturation, resulting in more nucleation and crystal growth, but the final pH limits any further precipitation. Similarly, the work of Beal et al. (1999) found that recovery P from swine waste as struvite could be increased with increasing of molar ratio of Mg/P from 0.25 to 1.1 using MgO addition with pH more than 8. Moreover, some studies showed that the Mg source is one factor affecting struvite precipitation. Barbosa et al. (2016) investigated the effect of different Mg sources on P crystallization efficiency from source separated urine, 99% P recovered as struvite was achieved when using MgO as Mg source. However, the different finding may be that the different type of supernatants used in P recovery.

The percentage of various types P-containing solids generated from this experiment also was calculated based on the proportion of P in each compound detected. Based on the results, the %MAP increased when sea salt addition was applied. The higher MAP% was found with sea salt addition (Mg/P=2) while the percentage of MAP were only 2 to 5% for uncontrolled Mg (Mg/P=1.07) at pH 7, 9, and 11. The highest MAP of 26% was found at pH 9 under addition of sea salt (Mg/P=2). This would mean that molar ratio of Mg/P affected to the formation of MAP in this study.

In case of %HAP, the results also show that %HAP under sea salt addition was higher than uncontrolled Mg condition, 8-12% of HAP for Mg/P=2 and 3-5% of HAP for Mg/P=1.07. As discussed above, pH 9 with the addition of sea salt was chosen to be an optimum condition for production of P-containing solids which was used in the P-bioavailability.

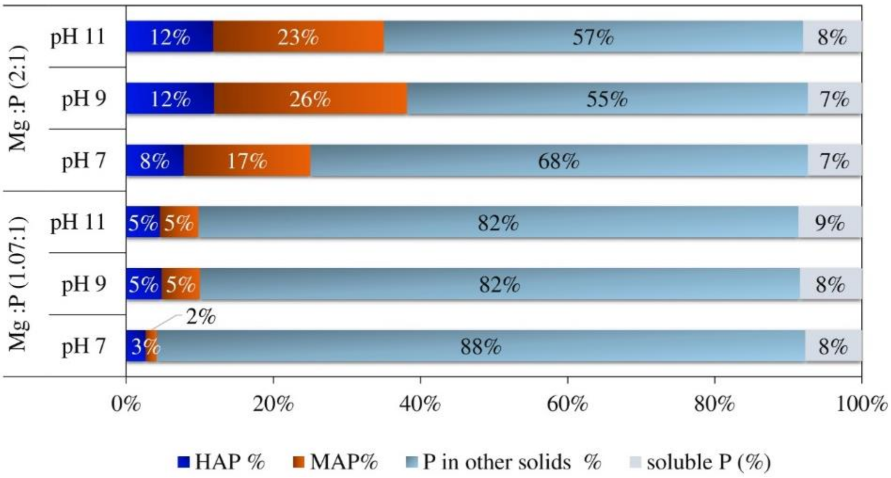

Figure 2. Speciation of P-composite precipitates recovered from WAS under different experimental conditions.

3.3 P recovery as different P fertilizer

The percentage of P content in the precipitates is an important measure for developing an alternative P fertilizer. Table 3 shows a comparison of the percent P content in the solids precipitated from this study and the commercial P fertilizers. The percent P content in the precipitates was in the range of 7-12% for both uncontrolled magnesium (Mg/P=1.07) and sea salt addition (Mg/P=2) with pH from 7 to 11. The highest %P in solids for all cases were found at pH 9, 11% P in solids for Mg/P=1.07 and 12% P in solids for Mg/P=2, which were higher than that of commercial superphosphate (SSP) fertilizer (8.8% P). Therefore, the P-containing solids obtained from both experiments can be used as an alternative P fertilizer. In addition, the precipitates from other experiments with P content less than 8.80% can be used as soil conditioner due to their good nutrient qualities, especially P (Lind et al., 2000). Hence, P-solids precipitates obtained from WAS can be effectively used to produce fertilizer for agricultural crops to achieve the sustainable P management helps to strengthen Thailand's food security.

Table 3. A comparison of P content in solid precipitate of this study and commercial P fertilizers

P recovery from WAS (This study)			Commercial P fertilizer			
Mg/P ratios	pH	%P content in solid precipitate (%dry wt.)	P fertilizer	Formula	%P_2O_5	%P
1.07	pH 7	8	Superphosphate	0-20-0	20	8.80
	pH 9	11	Triple super-phosphate	0-46-0	46	20.24
	pH 11	7	Diammonium phosphate	18-46-0	46	20.24
2	pH 7	11	Monoammonium phosphate	11-52-0	52	22.88
	pH 9	12				
	pH 11	9				

3.4 P bioavailability from WAS recovered product

Comparison of P-bioavailability of P-solids precipitates (PSP) obtained from WAS and commercial fertilizers including DAP and MP was determined by solubility of P compounds in water at pH 6.15 g P/m^2 of these P-fertilizers was dissolved in 90 mL of water for 35-day as shown in Figure 3. The results showed that the highest %P release (more than 5%) was found when DAP was applied. Moreover, %P release from DAP increased with increasing time of dissolution. However, it decreased after dissolution for one week. Compared with DAP, MP has lower %P dissolved efficiency (below 3%). It then slightly decreased after the fifth day. However, for PSP, the results showed that an increase in time provides high %P release efficiency. The highest %P dissolved (nearly 4%) from PSP was found at the middle of the experimental period (Day 17th) and it then dropped lower than 1%. The results indicate that P from both DAP and MP were fast-release fertilizers which is may be inappropriate for growth of plants. At the end of experiment, the amount of P released along with water dissolution (pH 6) was calculated so as to evaluate the amount of P that remained in the pot. The DAP, MAP, and P-precipitating solid were 47%, 31%, and 20% soluble into water after 35 days, respectively. The amount of P remaining in the soil is 7.92 g P/m^2 of DAP, 10.32 g P/m^2 of MP and 11.80 g P/m^2 of PSP which means that about 53%, 69%, and 80% of P in commercial fertilizers (DAP and MP) and PSP remained in the soil, respectively, indicating that PSP has the highest bioavailability for plant uptake.

3.5 Economic assessment

Finally, to complete the results of this study, the analysis of the costs of P recovery process and the possible gains from the sale of the resulting product have been calculated based on the method by Pinatha et al. (2020). Table 4 depicts the potential economic savings for P recovery from the leachate obtained at the optimum condition. The results showed that the highest P-containing precipitates of 0.23 kg P/m^3 was found when using pH 9 with sea salt addition. It noted P-containing solids based on the amount of produced precipitates and %P content in solids. The results also found that the precipitates contained 8% and 7% P content were achieved at pH 7 and pH 11 with molar ratio of Mg:P=1.07:1.00. However, the higher amount of precipitates was obtained from pH 11. This resulted in the amount of P-containing solids at pH 7 was lower than pH 11 with the same Mg:P ratio (1.07:1.00). Chemical additions, especially sulfuric acid, are the major costs of the process due to the extraction of P (pH lower than 1). This also resulted in the large amount of 50% NaOH used to adjust pH in the step of precipitation at pH 7 to 11. Therefore, when average costs in the unit of USD/kg P were compared with the market price of commercial fertilizers, the lowest average costs were found with the addition of sea salt at pH 9. This indicates that sea salt addition can reduce the total costs that mostly came from acid addition by increasing both the production of precipitates and %P in solids. Thus, additional economic savings could also be possible when the market fertilizer price in the future is higher than the average costs obtained.

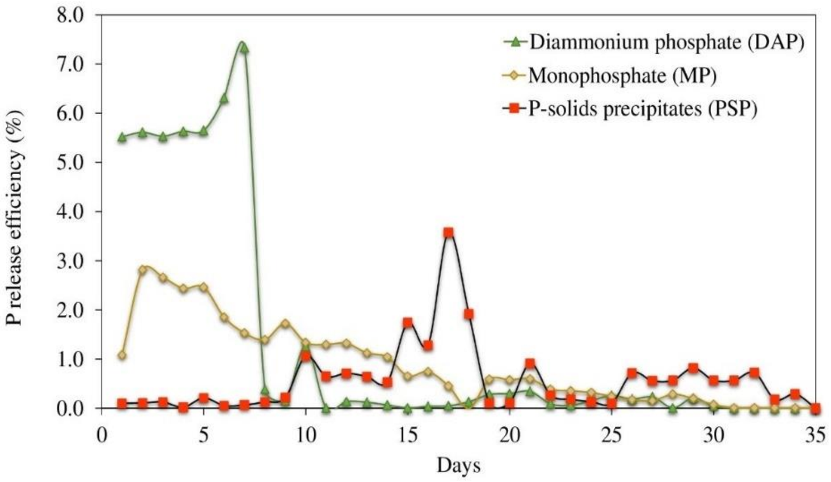

Figure 3. Percentage of P release efficiency for P-bioavailability test (%)

Table 4. Cost analysis of P recovery process using different pH and molar ratio of Mg/P.

Parameters	pH 7		pH 9		pH 11	
	(1.07:1)	(2:1)	(1.07:1)	(2:1)	(1.07:1)	(2:1)
Chemical additions (kg/m^3)						
Acid H_2SO_4	10.30	10.30	10.30	10.30	10.30	10.30
NaOH 50%	1.44	1.44	1.52	1.52	2.28	2.28
Sea salt	0.00	0.33	0.00	0.33	0.00	0.33
Material costs (USD/kg)						
Mg source (sea salt)[a]	0.06	0.06	0.06	0.06	0.06	0.06
50% NaOH[b]	0.20	0.20	0.20	0.20	0.20	0.20
Acid H_2SO_4[c]	0.18	0.18	0.18	0.18	0.18	0.18
Waste activated sludge	0.00	0.00	0.00	0.00	0.00	0.00
Energy consumption (kWh/m^3)						
Rapid mixing (15 min)	0.0626	0.0626	0.0626	0.0626	0.0626	0.0626
Slow mixing (30 min)	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013
Electricity cost per unit (USD kW/h)[d]	0.12	0.12	0.12	0.12	0.12	0.12
Products produced (kg/m^3)						
Obtained solids from precipitation	1.03	1.30	1.11	1.88	1.20	1.60
%P content in solids precipitate	8.00	11.00	11.00	12.00	7.00	9.00
P-containing solids (kg P/m^3)	0.082	0.150	0.120	0.230	0.084	0.140
Total costs (USD/kg P)						
(1) Average costs	25.78	14.17	17.40	9.56	26.53	16.03
(2) Market fertilizer prize[e]	3.52±5.00	3.52±5.00	3.52±5.00	3.52±5.00	3.52±5.00	3.52±5.00
(2)-(1) Profit margin	-22±-21	-11±-9	-14±-12	-6±5	-23±-22	-13±-11

±Standard division
[a]Snowy Sky, Xuetian Salt Group Co., Ltd, China (https://www.alibaba.com)
[b]50% AMPS SODIUM SALT Solution, Shandong Kejian Chemical Co., China (https://www.alibaba.com)
[c]RCI LABSCAN LIMITED, Thailand (https://www.rcilabscan.com/product/sulfuric-acid-98-electropure/)
[d]Thailand's electricity cost from Metropolitan Electricity Authority (www.mea.or.th)
[e]OAE.go.th (Lowest price for N-P-K formula 18-46-0 and highest price for formula 16-16-8; P as P_2O_5 and K as K_2O).

4. CONCLUSION

P recovery from WAS, using chemical leaching and precipitation with sea salt addition, appears to be a promising method for recovering the limiting nutrient P. The optimum condition for P leaching (0.1 mol/L H_2SO_4, 30 min) found from RSM could achieved nearly 100% P extraction efficiency. The highest P recovery efficiency (%) was found at pH 9 with sea salt addition, resulting in 26% MAP formed. The precipitating solids contained about 12% P. Moreover, the percentage bioavailability of P uptake from WAS-recovered solid P was about 80%, which is much better than those of commercial fertilizers. This indicates that recovered P-solids from WAS is technically feasible to be utilized as fertilizing compound for plant cultivation and the sustainable P management helps to strengthen Thailand's food security. Therefore, the results found in this study will help understand P leaching and precipitating from WAS and guide decision-makers for its implementation. Consequently, this will lead to closing the loop of P-for-food management in the human ecosystem.

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REFERENCES

Ackerman JN, Zvomuya F, Cicek N, Flaten D. Evaluation of manure-derived struvite as a phosphorus source for canola. Canadian Journal of Plant Science 2013;93(3):419-24.

American Public Health Association (APHA). Standard Methods for the Examination of Water and Waste Water. 22nd ed. Washington, DC, USA: APHA; 2012.

Anderson-Cook CM, Borror CM, Montgomery DC. Response surface design evaluation and comparison. Journal of Statistical Planning and Inference 2009;139(2):629-41.

Atienza-Martínez M, Gea G, Arauzo J, Kersten SR, Kootstra AMJJb. Phosphorus recovery from sewage sludge char ash. Bioenergy 2014;65:42-50.

Balmer P. Phosphorus recovery: An overview of potentials and possibilities. Water Science and Technology 2004;49(10): 185-90.

Barbosa SG, Peixoto L, Meulman B, Alves MM, Pereira MA. A design of experiments to assess phosphorous removal and crystal properties in struvite precipitation of source separated urine using different Mg sources. Chemical Engineering Journal 2016;298:146-53.

Beal LJ, Burns RT, Stalder KJ. Effect of anaerobic digestion on struvite production for nutrient removal from swine waste prior to land application. Proceedings of the ASAE Annual International Meeting; 1999 July 18-21; Sheraton Centre: Canada; 1999.

Chen M, Graedel T. A half-century of global phosphorus flows, stocks, production, consumption, recycling, and environmental impacts. Global Environmental Change 2016;36:139-52.

Chen Y, Wang D, Zhu X, Zheng X, Feng L. Long-term effects of copper nanoparticles on wastewater biological nutrient removal and N_2O generation in the activated sludge process. Environmental Science and Technology 2012;46(22):12452-8.

Coetzer R, Joubert T, Viljoen C, Nel R, Strydom C. Response surface models for synthetic jet fuel properties. Applied Petrochemical Research 2018;8(1):39-53.

Cordell D, White S. Life's bottleneck: Sustaining the world's phosphorus for a food secure future. Annual Review of Environment and Resources 2014;39:161-88.

Cornell JA. Experiments with Mixtures: Designs, Models, and the Analysis of Mixture Data. Volume 403. John Wiley and Sons; 2011.

Donatello S, Freeman-Pask A, Tyrer M, Cheeseman CJC. Effect of milling and acid washing on the pozzolanic activity of incinerator sewage sludge ash. Composites Part C 2010;32(1):54-61.

Falowo OA, Oloko-Oba MI, Betiku E. Biodiesel production intensification via microwave irradiation-assisted trans-esterification of oil blend using nanoparticles from elephant-ear tree pod husk as a base heterogeneous catalyst. Chemical Engineering and Processing-Process Intensification 2019; 140:157-70.

Fang L, Li, Guo MZ, Cheeseman CR, Tsang DCW, Donatello S, et al. Phosphorus recovery and leaching of trace elements from incinerated sewage sludge ash (ISSA). Chemosphere. 2018;193:278-87.

Frossard E, Skrabal P, Sinaj S, Bangerter F, Traore O. Forms and exchangeability of inorganic phosphate in composted solid organic wastes. Nutrient Cycling in Agroecosystems 2002;62(2):103-13.

Geissler B, Mew MC, Weber O, Steiner G. Efficiency performance of the world's leading corporations in phosphate rock mining. Resources, Conservation and Recycling 2015;105:246-58.

Gorazda K, Tarko B, Wzorek Z, Nowak AK, Kulczycka J, Henclik AJOC. Characteristic of wet method of phosphorus recovery from polish sewage sludge ash with nitric acid. Open Chemistry 2016;14(1):37-45.

Iweka SC, Owuama K, Chukwuneke JL, Falowo OA. Optimization of biogas yield from anaerobic co-digestion of corn-chaff and cow dung digestate: RSM and python approach. Heliyon 2021;7(11):e08255.

Khaita C, Polprasert C. Effect of organic matter on struvite precipitation of phosphorus contained in tapioca-starch wastewater. Thai Environmental Engineering Journal 2019; 33(1):31-9.

Kodera H, Hatamoto M, Abe K, Kindaichi T, Ozaki N, Ohashi A. Phosphate recovery as concentrated solution from treated wastewater by a PAO-enriched biofilm reactor. Water Research 2013;47(6):2025-32.

Li WW, Yu HQ, Rittmann BE. Chemistry: Reuse water pollutants. Nature 2015;528:29-31.

Liang S, Chen H, Zeng X, Li Z, Yu W, Xiao K, et al. A comparison between sulfuric acid and oxalic acid leaching with subsequent purification and precipitation for phosphorus recovery from sewage sludge incineration ash. Water Research 2019; 159:242-51.

Lind B-B, Ban Z, Bydén S. Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite. Bioresource Technology 2000;73(2):169-74.

Maekawa T, Liao CM, Feng XD. Nitrogen and phosphorus removal for swine wastewater using intermittent aeration batch reactor followed by ammonium crystallization process. Water Research 1995;29(12):2643-50.

Onsekizoglu P, Bahceci KS, Acar J. The use of factorial design for modeling membrane distillation. Journal of Membrane Science 2010;349(1-2):225-30.

Ottosen LM, Kirkelund GM, Jensen PE. Extracting phosphorous from incinerated sewage sludge ash rich in iron or aluminum. Chemosphere 2013;91(7):963-9.

Perera P, Han ZY, Chen YX, Wu WX. Recovery of nitrogen and phosphorous as struvite from swine waste biogas digester effluent. Biomedical and Environmental Sciences 2007; 20(5):343-50.

Pinatha Y, Polprasert C, Englande Jr AJ. Product and cost perspectives of phosphorus recovery from human urine using solid waste ash and sea salt addition: A case of Thailand. Science of the Total Environment 2020;713:Article No. 136514.

Rahman MM, Salleh MAM, Rashid U, Ahsan A, Hossain MM, Ra CS. Production of slow release crystal fertilizer from wastewaters through struvite crystallization: A review. Arabian Journal of Chemistry 2014;7(1):139-55.

Sano A, Kanomata M, Inoue H, Sugiura N, Xu KQ, Inamori YJC. Extraction of raw sewage sludge containing iron phosphate for phosphorus recovery. Chemosphere 2012;89(10):1243-7.

Shiba NC, Ntuli F. Extraction and precipitation of phosphorus from sewage sludge. Waste Management 2017;60:191-200.

Sreesai S, Peapueng P, Tippayamongkonkun T, Sthiannopkao S. Assessment of a potential agricultural application of Bangkok-digested sewage sludge and finished compost products. Waste Management and Research 2013;31(9):925-36.

Talboys PJ, Heppell J, Roose T, Healey JR, Jones DL, Withers PJ. Struvite: A slow-release fertiliser for sustainable phosphorus management? Plant and Soil 2016;401(1-2):109-23.

Thitanuwat B, Polprasert C, Englande Jr AJ. Quantification of phosphorus flows throughout the consumption system of Bangkok Metropolis, Thailand. Science of the Total Environment 2016;542:1106-16.

Tong J, Chen Y. Recovery of nitrogen and phosphorus from alkaline fermentation liquid of waste activated sludge and application of the fermentation liquid to promote biological municipal wastewater treatment. Water Research 2009; 43(12):2969-76.

Van Vuuren DP, Bouwman AF, Beusen AH. Phosphorus demand for the 1970-2100 period: A scenario analysis of resource depletion. Global Environmental Change 2010;20(3):428-39.

Vaneeckhaute C, Lebuf V, Michels E, Belia E, Vanrolleghem PA, Tack FM, et al. Nutrient recovery from digestate: Systematic technology review and product classification. Waste and Biomass Valorization 2017;8(1):21-40.

Wang Q, Li Js, Tang P, Fang L, Poon CS. Sustainable reclamation of phosphorus from incinerated sewage sludge ash as value-added struvite by chemical extraction, purification and crystallization. Journal of Cleaner Production 2018;181: 717-25.

Wang D, Fu Q, Xu Q, Liu Y, Ngo HH, Yang Q, et al. Free nitrous acid-based nitrifying sludge treatment in a two-sludge system enhances nutrient removal from low-carbon wastewater. Bioresource Technology 2017;244:920-8.

Wang X, Wang Y, Zhang X, Feng H, Li C, Xu T. Phosphate recovery from excess sludge by conventional electrodialysis (CED) and electrodialysis with bipolar membranes (EDBM). Industrial and Engineering Chemistry Research 2013;52(45):15896-904.

Withers PJ, Elser JJ, Hilton J, Ohtake H, Schipper WJ, Van Dijk KC. Greening the global phosphorus cycle: How green chemistry can help achieve planetary P sustainability. Green Chemistry 2015;17(4):2087-99.

Xu D-C, Zhong C-Q, Yin K-H, Peng S-H, Zhu T-T, Cheng G. Alkaline solubilization of excess mixed sludge and the recovery of released phosphorus as magnesium ammonium phosphate. Bioresource Technology 2018;249:783-90.

Xu H, He P, Gu W, Wang G, Shao L. Recovery of phosphorus as struvite from sewage sludge ash. Journal of Environmental Sciences 2012;24(8):1533-8.

Zhang L, Chen Y, Ma C, Liu L, Pan J, Li B, et al. Improving heavy metals removal, dewaterability and pathogen removal of waste activated sludge using enhanced chemical leaching. Journal of Cleaner Production 2020;271:Article No. 122512.

Zhao J, Gui L, Wang Q, Liu Y, Wang D, Ni BJ, et al. Aged refuse enhances anaerobic digestion of waste activated sludge. Water Research 2017;123:724-33.

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