Optimization and Kinetic Study of Phosphorus Dissolution from Primary Settled-Nightsoil Sludge

Wanida Pimpeach[1,3], Withida Patthanaissaranukool[2,3], Chongchin Polprasert[1,3], Supawadee Polprasert[2,3], Suwisa Mahasandana[1,3], and Bunyarit Panyapinyopol[1,3*]

[1]*Department of Sanitary Engineering, Faculty of Public Health, Mahidol University, Bangkok 10400, Thailand*
[2]*Department of Environmental Health Sciences, Faculty of Public Health, Mahidol University, Bangkok 10400, Thailand*
[3]*Center of Excellence on Environmental Health and Toxicology (EHT), OPS, MHESI, Bangkok 10400, Thailand*

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*** Corresponding author:**
E-mail: bunyarit.pan@mahidol.ac.th

ABSTRACT

In this study, chemical extraction using different acid concentrations, solids concentrations, and reaction time with subsequent interactions mechanism were carried out to evaluate the potential of phosphorus (P) recovery from primary settled-nightsoil sludge (PSNS). The response surface methodology (RSM) with Box-Behnken experimental design and one-way ANOVA analysis were also employed to establish optimal P leaching conditions. The extraction efficiency relied mainly on acid and solids concentration. The second-order polynomial model was successfully developed for extracting process designs. Approximately 93% of P could effectively be extracted from PSNS of 20,000 mg/L with 0.5 M of H_2SO_4 at reaction time of 45 min (optimum condition). Kinetic studies showed that the pseudo-second order was fit to describe leaching of P and metals. Moreover, the rate of kinetic constants (k_2) of the P, Fe, Mg, and Ca under optimum condition were found to be 0.1607, 0.1099, 0.0317, and 0.0053 g/mg·min, respectively. The 99% leaching of maximum extracted P concentration at the equilibrium (9.6673 mg/g) took place in less than one hour. The findings of a suitable simple and low-cost method P dissolution from PSNS not only provides understanding of leaching kinetics, but also helps to pave a way of recovering P from a renewable resource in the field of waste utilization.

1. INTRODUCTION

The importance of global phosphate rock (PR) reserves shortage in the next 50 to 100 years has been reported (Van Vuuren et al., 2010; Cordell et al., 2009). Global food security has been threatened with phosphorus (P) scarcity problems in countries with limited PR deposits, especially Thailand (Cordell et al., 2011; Thitanuwat et al., 2016). It becomes necessary to develop a sustainable method to recover P from the other sources. Several waste materials have been identified as potentially useful sources of P (Shiba and Ntuli, 2017; Li et al., 2022a; Ramaswamy et al., 2022), but research on P recovery from human excreta remains fairly limited. The studies of Liu et al. (2008) and Cordell et al. (2009) estimated the annual global quantity of reused P totals 0.3 to 1.5 million metric tons of P generated from human excreta and greywater. In view of the characteristics of Human Fecal Sludge (HFS) such as their high levels of key plant nutrients, mainly nitrogen (N), phosphorus (P), and potassium (K), it provides a potential source for recovery (Jonsson et al., 2005; Vinnerås et al., 2006; Wignarajah et al., 2006; Calloway and Margen, 1971).

Separate collection of septage sludge is implemented only in a few countries, especially in Thailand. The Bangkok Metropolitan Administration (BMA)'s central nightsoil treatment plants can generate 5,324.8 tons of primary settled nightsoil sludge (PSNS) annually that contains considerable amounts of phosphorus (9.6 g P/kg, total solids) (Thitanuwat et al., 2016). The generated PSNS is commonly composted with green garbage to produce organic fertilizer used in public parks and roadsides. However, such use can often cause environmental

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problems, especially the potential presence of pathogens particularly helminth eggs in fecal sludge, which is a major public health concern (WHO, 2006; Heinss et al., 1998). For this reason, the direct application of PSNS in the agricultural field is consequently limited. Therefore, it remains essential to intercept pathogens spread from PSNS before land application.

Numerous studies of P recovery using crystallization have been extensively reported with the objectives to recover P from leachate in the form of both magnesium ammonium phosphate (struvite) (Xu et al., 2012) and calcium phosphate (Ding et al., 2022). Struvite is best known as a slow-release fertilizer proven technically feasible and economically beneficial (Li et al., 2022b). However, pre-treatment is needed to release P from PSNS into solution thereby enhancing P availability for P recovery. The common method widely used to extract phosphorus from wastes is acid or acid-based leaching (Fang et al., 2020; Khaing et al., 2022). Moreover, influencing factors including pH, extraction time, liquid to solid ratio (L:S ratio), molar concentration of acid solution, and sludge concentration have also been investigated (Ali and Kim, 2016; Shiba and Ntuli, 2017). Acid concentration is a significant factor for enhancing P leaching process. The work of Shiba and Ntuli (2007) reported that the highest leaching efficiency of P from sewage sludge could be achieved at an extraction time for 2 h with 1 M of sulfuric acid and solid loading of 5%. In addition, nearly 100% of total P was released form incinerated sewage sludge ash when using 0.19 M H_2SO_4, extraction time of 2 h, and L:S ratio of 20 (Ottosen et al., 2013). Various types of acid and alkali have been extensively studied. P extraction efficiency using inorganic acids is higher than that of other extractants. Among these different inorganic acids, sulfuric acid has found high extraction efficiency (Shiba and Ntuli, 2017; Fang et al., 2018). However, after acid leaching, the inorganic constituents are not only P but also other metals such as Ca and Mg left in the leachates. Therefore, from the viewpoint of effective P recovery, chemical precipitation can be employed in line with extraction (Ali and Kim, 2016). Nevertheless, there are little information is available concerning P extraction from PSNS. Therefore, it is interesting to investigate effects of independent variables on leaching of PSNS.

A large number of studies have investigated individual and interaction effects of variables on extraction and adsorption/desorption efficiencies using response surface methodology (RSM) (Reuna and Väisänen, 2018; Rasoulzadeh et al., 2021a; Mohammadi et al., 2017). The obtained results from RSM can be used for optimizing process capability (Asgari et al., 2020; Rasoulzadeh et al., 2021b). In addition, RSM also provides reasonable regression equations which are used for process design (Luyckx et al., 2020). Some studies employed adsorption adsorption-desorption mechanism to determine reaction pathway and equilibrium (Rathi and Kumar, 2021; Rasoulzadeh et al., 2021c). Various studies have been performed using nonlinear adsorption kinetic models, especially, pseudo-second order (Rasoulzadeh et al., 2021c; Barca et al., 2019).

This work was to establish chemical P extraction technology for P recovery process together with utilization of primary settled-nightsoil sludge as a sustainable P-rich resource rather than to dispose it as a waste, in order to solve the shortage of natural P resources in the near future. Optimum conditions and factors affecting P extraction were evaluated using response surface methodology (RSM) and ANOVA. In addition, the second-order polynomial model was successfully developed for extracting process designs which could maximize P leaching efficiency with low energy consumption. The kinetics of P leaching were presented so as to determine the rate constants and maximum equilibrium capacities of extraction. Also, because leaching generates a metal laden solution, this works aimed to study the leaching of major elements such as Fe, Ca, and Mg. Successful results obtained from this study are expected to minimize waste by 3R (reduce, reuse, and recycling). Using PSNS as a renewable resource to produce phosphate containing fertilizers offers solutions to many problems and helps ensure future supplies of phosphates, while addressing waste management issues.

2. METHODOLOGY

2.1 Descriptions of PSNS

PSNS was collected from a dewatering process of the Nong Khaem nightsoil treatment plant under the Bangkok Metropolitan Administration (BMA). Samples were dried at 105ºC for three days and then homogenized in a bucket. The composite samples were placed in sealed bags at a laboratory. Subsequently, the dried PSNS was crushed by a pestle and mortar to obtain a fine powder. The powdered samples were sieved by passing through a 2 mm screen and the resulting sludge with particle sizes smaller than 2 mm were separated and stored in a polyethylene bottle at room temperature in the laboratory.

2.2 Experimental design for acid leaching and optimization

The extraction experiments were conducted at room temperature. PSNS was measured in 10,000, 20,000, 30,000, and 50,000 mg and then mixed with 1 L of acid solution ranging from 0.01 to 0.50 M H_2SO_4). Extraction time ranged from 0.25 to 2.00 h at ambient temperature. The leachates were then filtered through a 10 µm filter (Whatman no.93) and the pH recorded afterwards. The schematic of this research is presented in Figure 1. To determine interaction effects of three variables on P leaching efficiency, the response surface methodology (RSM) of design expert® 13 Software with Box-Behnken design (BBD-RSM) was selected to design P extraction experiments which were performed randomly under 15 conditions with three central points. The coded variables and their values are shown in Table 1. The following three influential parameters were investigated: extraction time (A), acid concentration (B), and solids concentration (C). To verify the relationship of independent parameters and their interactions on response (P extraction), the statistical analysis was established with 0.05 confidence level. Thus, the optimum condition for P extraction, the quadratic equation model was employed as represented by Equation (1).

$$y = \beta_0 + \beta_A A + \beta_B B + \beta_C C + \beta_{AA} A^2 + \beta_{BB} B^2 + \beta_{CC} C^2 + \beta_{AB} AB + \beta_{AC} AC + \beta_{BC} BC \quad (1)$$

Where; y is the predicted response (P extraction efficiency (%)); β_0 is constant coefficient; β_A, β_B and β_C are coefficients of linear expressions; β_{AA}, β_{BB}, and β_{CC} are quadratic coefficients; β_{AB}, β_{AC}, and β_{BC} are interaction coefficients; A, B, and C represent three independent variables viz. extraction time (A), acid concentration (B), and solids concentration (C).

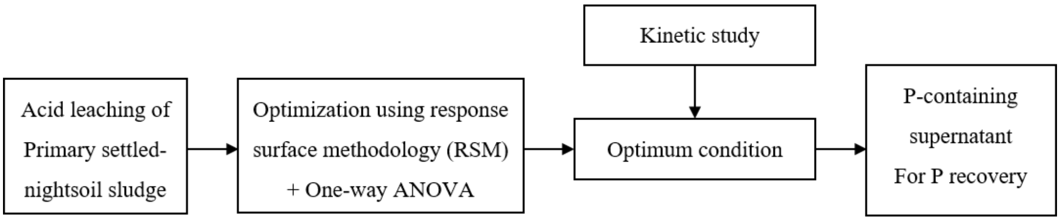

Figure 1. Schematic diagram for optimization and kinetic study of P extraction from primary settled-nightsoil sludge

Table 1. The 3-levels Box-Behnken design with coded and actual variables for optimization of P leaching from primary settled-nightsoil sludge

Variables	Units	Coded levels		
		-1	0	1
Extraction time	h	0.25	1.00	2.00
Acid concentration	M	0.01	0.10	0.50
Solids concentration	mg/L	10,000	30,000	50,000

2.3 Analytical methods

A spectrophotometer (Evolution 201 UV-Visible) using the vanadomolybdophosphoric acid colorimetric method was employed to determine P concentration in both solid and aqueous phases. The total solids (TS), total volatile solids (VS), and total kjeldahl nitrogen (TKN) were analyzed using the procedure described in the Standard Methods (APHA, 2012). Metal analyses were performed by means of atomic absorption spectrometry (AAS) according to standard methods (APHA, 2012). The pH was measured using a pH meter (YSI 1200).

2.4 Statistical analysis

All experimental conditions were described as observed mean and standard error (±SE), and statistical analysis was established as significant at $p<0.05$. Statistical analyses were performed using SPSS Statistics, Version 18.0. Standard deviation, mean averages and standard error were used in this study. One-way ANOVA (analysis of variance) was used to test the data for significant differences in the effect of variance of acid concentration, solids concentration, and extraction times on P extraction.

All batch experiments were repeated in triplicate and the mean value was accepted as the final value.

2.5 Calculations

Extraction efficiency of P was defined as the percentage of P released from PSNS (solid phrase) in relation to the initial P in solution, calculated as Equation (2):

$$\text{P extraction (\%)} = \frac{([PO_4^{3-}-P]_{released} * (L{:}S)\ ratio)}{M_{input}} \times 100 \qquad (2)$$

Where; $[PO_4^{3-}-P]_{released}$ is the concentration of P in solution obtained at each reaction time (mg/L), L:S ratio is the liquid (sulfuric acid solution (L)) to solid amount of PSNS (g) ratios, and M_{input} is mass of P in the primary settled-nightsoil sludge at the beginning.

3. RESULTS AND DISCUSSION

3.1 Characteristic of PSNS

The characteristics of PSNS are presented in Table 2, demonstrating that the main components of PSNS were P, N, Ca, Mg, and Fe. The total P was found to be 1.0 wt.% which appeared to be an alternative resource for P recovery. The Ca concentration was much higher than Mg and Fe. The Ca concentration related to the ranges of generation rates in feces 0.1-3.6 (g Ca/cap/day) (wet basis) (Wignarajah et al., 2006). Similarly, Mg concentration was very low, having a range in feces of 0.15-0.35 (g Mg/cap/day) (wet basis) (Eastwood et al., 1984; Calloway and Margen, 1971). PSNS contains relatively lower concentrations of Fe than incinerated sewage sludge ash (ISSA) (Kleemann et al., 2017).

Table 2. Characteristics of primary settled-nightsoil sludge

Parameters	Unit	Primary settled-nightsoil sludge
C/N ratio	-	10-17
pH	-	6.13
Moisture	%	74.50±2.36
Volatile solid	%	69.10±2.80
Total phosphorus	mg/kg	10,260±420
Total kjeldahl nitrogen	mg/kg	36,750±90
Calcium: Ca	mg/kg	33,357±1,727
Magnesium: Mg	mg/kg	2,018±60
Iron: Fe	mg/kg	8,408±333
Parasites eggs	eggs/g	<1 (12.5% detected probability) (Trichuris trichiura) <1 (12.5% detected probability) (Hook worm Egg) >30 (12.5% detected probability) (Nematode larva) >30 (12.5% detected probability) (Teania spp.eggs) >20 (12.5% detected probability) (Ascaris spp.eggs)

3.2 Second-order model and ANOVA analysis

Based on the results obtained from comparison of different models, the experimental data were fitted to a second-order polynomial model and regression coefficients obtained (Table 3). The goodness-of-fit of the model can be checked from the coefficient of determination (R^2) which was high, 99.94%, implying good correlation between the predicted values and the observed data. The adjusted R^2-value of 99.83% indicated that all factors included in the model were significant and affecting the response variable. The high predicted R^2-value of 99.32% proved that this model could predict proper responses for new observations. High values of both adjusted and predicted R^2 also meant that the model fit to the data.

Table 3. Comparing models on summary statistics

Source	Sequential p-value	Lack of fit p-value	R^2	Adjusted R^2	Predicted R^2
Linear	0.1558	0.0016	0.3663	0.1935	-0.1384
2FI	0.9995	0.0011	0.3674	-0.1070	-1.4282
Quadratic	<0.0001	0.5057	0.9994	0.9983	0.9932

The ANOVA analysis results for the quadratic models of primary settled- nightsoil sludge (PSNS) leaching were provided in Table 4; the F-value of 921.09 implied that the model was accurate. The corresponding p-value was less than 0.0001 which could identify the significance of terms. Thus, the model was proven significant and could be used to optimize leaching. Figure 2 displays the external student residuals and normal% probability plot. The plots illustrated that no abnormality occurred in this experimentation and model. Moreover, it could be observed that the actual values obtained from the experiment were close to the predicted values calculated by the quadratic models, indicating that the equation was reliable (Table 5).

The quadratic equations for the leaching of PSNS in terms of coded factors and actual factors were obtained as shown in Equation (3) and Equation (4).

$$y = 135.48 + 1.48A + 32.18B - 4.00C - 2.64A^2 - 78.71B^2 + 3.50C^2 + 0.5819(A \times B) + 0.7107(A \times C) + 0.7107(A \times C) + 1.46(B \times C) \quad (3)$$

$$Y = 28.75432 + 7.54273A + 788.09344B \; 0.000847C - 3.44762A^2 - 1311.30244B^2 + 8.75324 \times 10^{-9}C^2 + 2.71458(A \times B) + 0.000041(A \times C) + 0.000299(B \times C) \quad (4)$$

Where; y is the predicted response (P extraction efficiency (%)); A, B, and C represent three independent variables: extraction time (A), acid concentration (B) and solids concentration (C).

Table 4. ANOVA table for quadratic model of primary settled nightsoil sludge leaching at ambient temperature (response: % P extraction)

Source	Sum of squares	df	Mean square	F-value	p-value	
Model	11,235.46	9	1,248.38	921.09	<0.0001	Significant
A-extraction time	15.12	1	15.12	11.16	0.0206	
B-acid concentration	8,214.68	1	8,214.68	6,060.99	<0.0001	
C-solids concentration	108.36	1	108.36	79.95	0.0003	
AB	1.64	1	1.64	1.21	0.3215	
AC	2.04	1	2.04	1.50	0.2748	
BC	10.26	1	10.26	7.57	0.0402	
A^2	24.46	1	24.46	18.04	0.0081	
B^2	6,945.27	1	6,945.27	5,124.38	<0.0001	
C^2	45.19	1	45.19	33.35	0.0022	
Residual	6.78	5	1.36			
Lack of fit	4.24	3	1.41	1.11	0.5057	Not significant
Pure error	2.54	2	1.27			
Cor total	11,242.24	14				

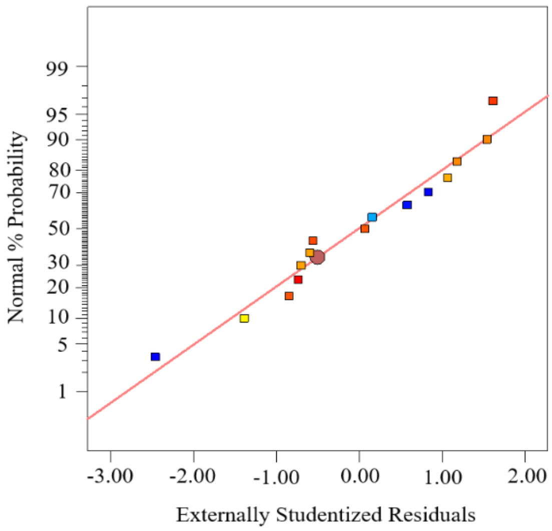

Figure 2. Studentized residuals and normal% probability plot

Table 5. Experimental design matrix of BBD-RSM in actual factors with experimental and predicted values

Run order	Standard order	Actual levels of variables			Experiment value	Predicted value
		Extraction time (h)	Acid concentration (M)	Solids concentration (mg/L)		
1	14	1.00	0.10	30,000	84.7	83.4
2	10	1.00	0.50	10,000	94.4	94.7
3	13	1.00	0.10	30,000	82.7	83.4
4	11	1.00	0.01	50,000	22.8	22.3
5	15	1.00	0.10	30,000	82.8	83.4
6	8	2.00	0.10	50,000	81.9	81.4
7	2	2.00	0.01	30,000	21.6	22.9
8	6	2.00	0.10	10,000	90.5	89.8
9	4	2.00	0.50	30,000	88.4	88.4
10	9	1.00	0.01	10,000	33.6	33.5
11	5	0.25	0.10	10,000	88.5	89.0
12	12	1.00	0.50	50,000	89.2	89.5
13	7	0.25	0.10	50,000	77.0	77.7
14	3	0.25	0.50	30,000	84.8	84.2
15	1	0.25	0.01	30,000	21.7	21.0

3.3 Effect of three variables on P extraction efficiency

Figure 3 (a-c) illustrates interactive effect of acid concentration, solids concentration, and reaction times on P extraction efficiency. The results showed that most P was still extracted when acid concentrations were above 0.15 M. An increase in solid loading caused a small decrease in the percentage of P extracted. In addition, the extended contact time did not result in more P leaching. The plot also showed at higher solids concentrations (above 30,000 mg/L) and lower acid concentrations, P leaching decreased as shown in green (50% P extraction line). Thus, solids concentration must be in the range 10,000 to 30,000 mg/L to maximize leaching efficiency. Shiba and Ntuli (2017) studied P extraction of sewage sludge and claimed that the amount of P extracted increased with rise of solids loading up to 50 g/L which totaled about 82% of P extracted. However, solids concentrations between 50 to 100 g/L exhibited low P extraction efficiency (Nosrati et al., 2013). In this work, decreasing P extraction efficiency started to reduce after solids concentrations were above 30,000 mg/L. This may be due to the presence of high total volatile suspended solids (about 69.1%) in the PSNS which easily releases P. Therefore, it could be claimed with confidence that solids concentration is one factor affecting P extraction efficiency.

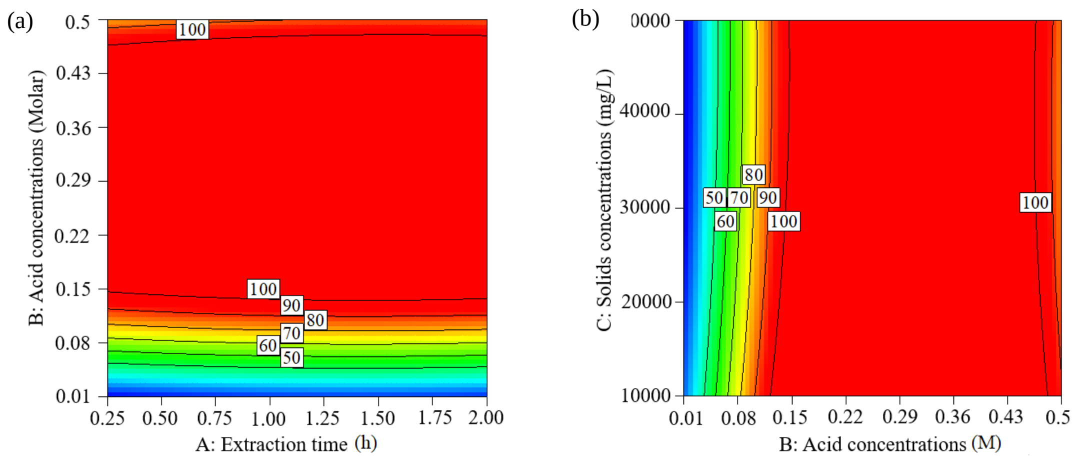

Figure 3. P extraction (%) at ambient temperature with respect to: (a) contour plots of extraction time (h) and acid concentration (M) with solids concentration at 50,000 mg/L, (b) contour plots of acid concentration (M) and solids concentration (mg/L) with extraction time at 0.25 h, and (c) contour plots of extraction time (h) and solids concentration (mg/L) with acid concentration of 0.1 M

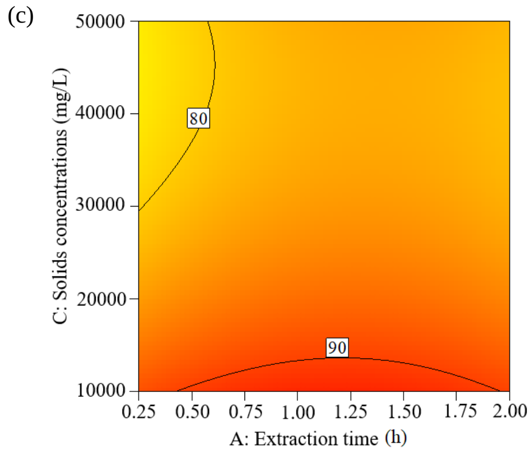

Figure 3. P extraction (%) at ambient temperature with respect to: (a) contour plots of extraction time (h) and acid concentration (M) with solids concentration at 50,000 mg/L, (b) contour plots of acid concentration (M) and solids concentration (mg/L) with extraction time at 0.25 h, and (c) contour plots of extraction time (h) and solids concentration (mg/L) with acid concentration of 0.1 M (cont.)

3.4 Optimization of P extraction

Based on the above results, high P extraction efficiency (>85%) was obtained at acid concentrations range from 0.1 and 0.5 M, and with solids concentrations of 10,000 to 30,000 M. In addition, higher extraction times did not achieve greater P extraction, this was discussed in section 3.5. However, from an economic point of view, using high solids concentration with low acid concentration is more interesting due to the lower extraction liquid costs for optimal P extraction. Figure 4 shows comparative results of P extraction under various acid:solids loading ratios (g:g), revealing only the results of leaching that have high P extraction efficiency (>80%). A single factor analysis of variance test indicated that the difference in mean of % P extraction between an acid:solids loading ratio of 5.2:1 and 2.6:1 was not statistically significant (p-value=1.000). Conversely, comparing the mean %P extraction at 2.6:1 and 1.7:1 of leaching, comparing between using solids concentrations of 20,000 mg/L and 30,000 mg/L at an acid concentration of 0.5 M, respectively, showed a significant difference in mean values (p-value <0.0001). Therefore, the acid:solids loading ratio of 2.6:1 with 0.5 M H_2SO_4 and solids concentration of 20,000 mg/L (L:S ratio=50) was chosen for optimum leaching condition.

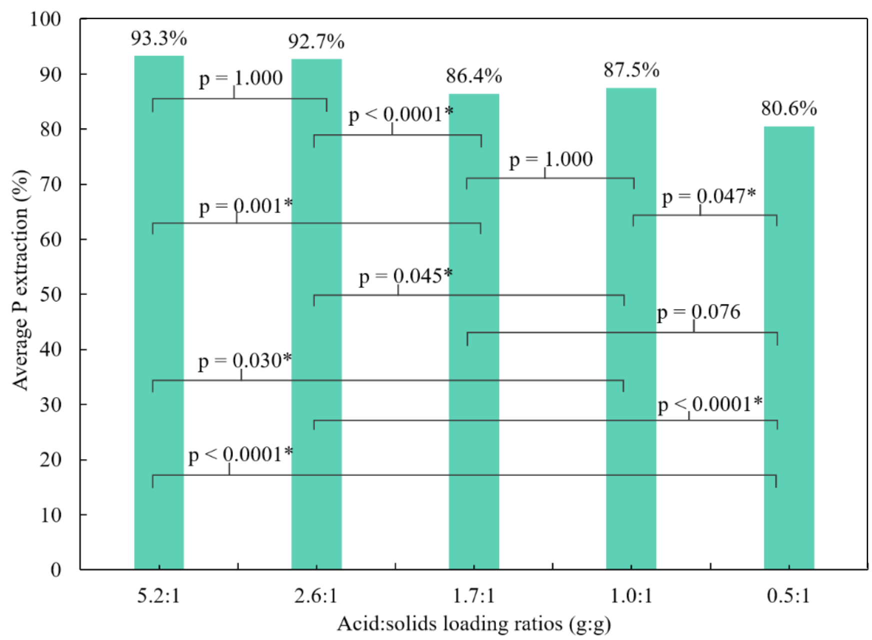

Figure 4. Comparative results of P extraction under various acid:solids loading ratios (*The mean difference was significant at the 0.05 level).

This optimum condition is also comparable to what other studies obtained from different leaching methods of P from wastes. Compared with organic acid, inorganic acid approaches, especially H_2SO_4, have been more widely investigated to extract P from wastes because of high leaching efficiency, up to 82-100% (Table 6) (Khaing et al., 2022; Shiba and Ntuli, 2017; Wang et al., 2018; Fang et al., 2018). Similarly, due to the double concentration of H^+ ions, sulfuric acid can release more P than nitric acid at the same concentration (Fang et al., 2018). Other researchers also reported that more than 95% P extraction efficiency was achieved after 120 min, while the leaching efficiency rapidly increased up to 15 min, and then slowly increased afterwards. Thus, many studies suggested that within 2 h was the optimum duration for leaching P from ISSA (Wang et al., 2018; Fang et al., 2018). Related research has also investigated the influencing factors for P extraction from sludge. As discussed above, an L:S ratio of 50 was considered the optimum condition for this study. However, an L:S ratio of 20 with 0.1 to 1 M of H_2SO_4 was sufficient for leaching P from sewage sludge and ISSA (Shiba and Ntuli, 2017; Wang et al., 2018; Fang et al., 2018).

Table 6. Comparison of P extraction efficiency from different conditions of leaching and sludge types

Type of wastes	Type of acid	Molar of acid (mol/L)	L:S ratio ($mL_{(acid)}$ /$g_{(sludge)}$)	Quantity of acid ($g_{(acid)}$/$g_{(dried\ sludge)}$)	Extraction time (h)	Temperature (°C)	% P extraction	Reference
Primary settled nightsoil sludge	H_2SO_4	0.50	50	2.50	0.75	Room temperature	93.6	This study
Waste activated sludge	H_2SO_4	0.10	35	0.30	0.50	Room temperature	97.0	Khaing et al. (2022)
Incinerated sewage sludge ash	H_2SO_4	0.05	150	0.70	2.00	Room temperature	>95.0	Liang et al. (2019)
Sewage sludge	H_2SO_4	1.00	20	2.00	2.00	100	82.0	Shiba and Ntuli (2017)
WAO residual	Citric acid	1.00	10	1.90	24.00	Room temperature	61.0	Barca et al. (2019)
WAO residual	HCl	1.00	10	0.40	24.00	Room temperature	65.0	
Incinerated sewage sludge ash	H_2SO_4	0.10	20	0.20	2.00	Room temperature	88.3	Wang et al. (2018)
Incinerated sewage sludge ash	H_2SO_4	0.20	20	0.40	2.00	Room temperature	94.0	Fang et al. (2018)

Remark :WAO residual=Solid residues obtained from wet air oxidation of sewage sludge

3.5 Extraction kinetics

The study of leaching kinetics involves understanding the mechanism of interactions between solid matrix and solvent in leaching. Various models exist to describe the kinetics of adsorption or desorption. The ones that have been used most commonly in previous studies are nonlinear adsorption kinetic models such as pseudo-first order, pseudo-second order, and intraparticle diffusion (Barca et al., 2019; Rasoulzadeh et al., 2021b; Rathi and Kumar, 2021). In this study, the rate of adsorption/desorption of the optimum condition follows the pseudo-second order kinetics equation:

$$(\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \times t)$$

Where: q_t denotes extraction capacity at time t (mg/g); q_e denotes extraction capacity at equilibrium (mg/g); and k_2=the constant rate of the pseudo second order (g/(mg·min)).

Figure 5, shows the high determination coefficient for P, Fe, Mg, and Ca extraction of 0.9999, 0.9999, 0.9897, and 0.9944, respectively, indicating that the extraction of these four elements was probably controlled by chemical desorption rather than diffusion (Ho and McKay, 1998; Rasoulzadeh et al., 2021b). This also proved that at the beginning of extraction, the leaching rate is fast and much lower until equilibrium is reached (Dutta et al., 2016). The experimental results also showed that after 45 min extracted P was around 99% of maximum extracted P concentration at the equilibrium (9.6673 mg/g) obtained from the model which could be chosen as the optimum time to extract P from primary settled-nightsoil sludge (Table 7). Referring to Figure 5, the kinetic constants (k_2) of the leaching under optimum condition had the order of P (k_2=0.1607 g/mg·min) > Fe (k_2=0.1099 g/mg·min) > Mg (k_2=0.0317 g/mg·min) > Ca (k_2= 0.0053 g/mg·min), meaning that P was extracted faster than other elements in the same contact time.

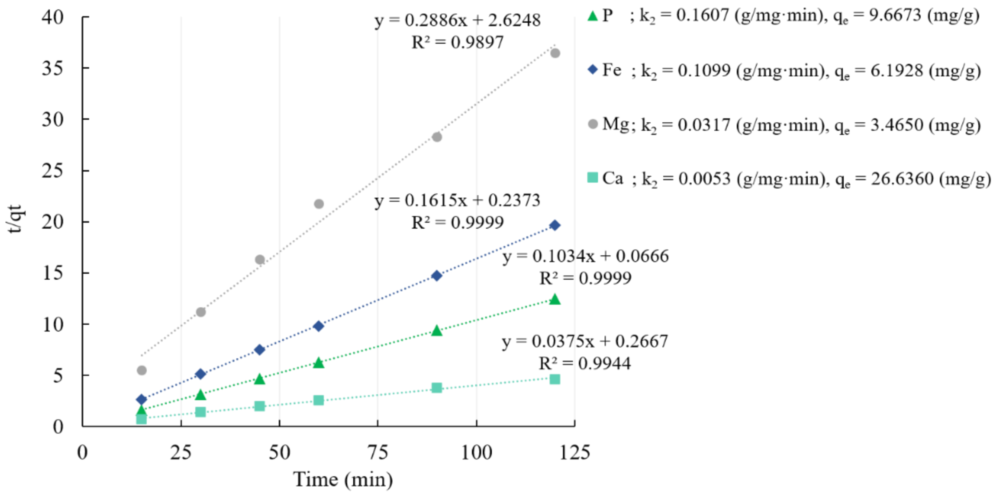

Figure 5. Pseudo-second-order kinetic modeling results of the P, Fe, Mg, and Ca extraction from primary settled-nightsoil sludge using solids concentration of 20,000 mg/L and 0.5 M H_2SO_4. (k_2=the constant rate of the pseudo second order, q_e=extracted concentration at the equilibrium)

Table 7. The acid leaching results using for pseudo-second order kinetic

Time (min)	% P extraction	% Fe extraction	% Mg extraction	% Ca extraction	P		Fe		Mg		Ca	
					q_t (mg/g)	t/q_t	q_t (mg/g)	t/q_t	q_t (mg/g)	t/q_t	q_t (mg/g)	t/q_t
15	90.67	86.90	81.60	64.00	9.3026	1.612	5.657	2.652	2.719	5.516	20.421	0.735
30	91.95	89.50	80.10	67.60	9.4340	3.180	5.825	5.150	2.670	11.236	21.567	1.391
45	93.23	92.00	82.70	70.40	9.5653	4.704	5.988	7.515	2.755	16.334	22.458	2.004
60	93.23	93.70	82.70	73.90	9.5653	6.273	6.102	9.833	2.755	21.777	23.567	2.546
90	93.23	93.70	95.50	74.00	9.5653	9.409	6.102	14.750	3.181	28.292	23.608	3.812
120	93.87	93.80	98.70	81.30	9.6310	12.460	6.105	19.656	3.289	36.489	25.929	4.628

4. CONCLUSION

In order to establish a simple, low-cost method for extracting P from PSNS, acid leaching with three independent variables (extraction time, acid concentration, and solids concentration) was investigated. A 3-levels Box-Behnken experimental design based on response surface methodology (RSM) and one-way ANOVA was applied to determine influence of experiments variables subsequent with optimal P extraction condition. The results were fitted into a second-order polynomial equation. The analysis of variance results obtained from RSM showed that three factors (extraction time, concentration of acid, and solids concentration) are statistically significant ($p<0.05$). Thus, it was observed that efficiency of P extraction increased with rise of acid concentration (over 0.15) and extraction time and dropped on increasing solids concentration. The optimal condition for the acid concentration, solids concentration, and reaction time of 0.5 M H_2SO_4, 20,000 mg/L, and 45 min, respectively, could be determined. Under this condition, the low-energy consumption with maximum P extraction efficiency of 92.7% was achieved. Kinetic study of optimum condition was performed. The mechanism of extraction is best described by pseudo-second order, which confirms the leaching of P, Ca, Fe, and Mg controlled by a chemical desorption. The results of kinetic constants (k_2) indicated that extraction of P was rapidly completed compared to extraction of other elements. Therefore, it is concluded that PSNS could be potentially used as an alternative recourse of P recovery.

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