Adsorption onto Ash Particles and Common Ion Effect for Phosphorus Recovery from Urinal Wastewater

Yada Pinatha, Chongchin Polprasert, and Andrew J. Englande Jr.

Abstract— *The aim of the study was to evaluate the effect of ash addition on phosphorus (P) recovery from urine through chemical processes. P recovery efficiency was improved in association with an increase of pH value. At pH 7, 9, and 11, P was recovered into solid precipitates maximally at 75%, 99%, and 99%, respectively with a P content as P crystals of about 70%, 60%, and 50%, respectively. The addition of incinerator ash led to the enhancement of P recovery via adsorption and precipitation. The behavior of P adsorption onto lignite and solid waste ashes of experiments with synthetic urine was fitted based on the Langmuir and Freundlich isotherms. Results of human urine adsorption studies found Freundlich isotherm provided a better fit for data. However adsorption capacities were much lower as compared to synthetic urine. The addition of 2.5 g·L^{-1} lignite fly ash and solid waste fly ash into human urine having 0.09%P led to a P-containing ash that contained P about equal to the P content in commercial superphosphate fertilizer at 8.89% and 8.93%, respectively. Results therefore indicate that recoverable P from urinal wastewater can be effectively used to produce fertilizer for agricultural cultivation by common ion precipitation and adsorption processes.*

Keywords— **About four key words or phrases in alphabetical order, separated by commas.**

1. INTRODUCTION

Phosphorus (P) plays a key metabolic role for living organisms including structural support, genetic component, and energy transfer and as a vital nutrient required for food production. Population growth and economic development are expected to further increase the need for enhanced agricultural production. Consequently, the agricultural sector will require an even larger amount of P. Numerous studies have been reported concerning sustainable use of P due to it being a non-renewable resource and potential depletion of its global supply predicted in a few centuries [1], [2], [3], [4]. Concerns over accessibility to P, price incentives and the need for more advanced technologies for better production efficiency result in an economic scarcity of P which may cause a future global food security challenge [5].

During past decades, researchers focused on reducing P losses discharged to the environment through municipal and industrial effluent streams by developing ways to improve P recovery with biological and chemical processes [6], [7]. P reduction and its subsequent recovery can be used to protect water eutrophication and provide for enhanced food security. The increase of P recirculation within production or treatment systems plays an important role in reducing adverse effects upon the water environment and strengthening food cultivation [8]. However, P recovery as a P-containing product either as calcium phosphates that are similar to P rocks or as magnesium ammonium phosphate that is a slow released fertilizer which can be reused in agricultural cultivation is difficult [9], [10], [11].

As P is mainly circulated in food production and consumption systems, previous studies have been conducted to quantify P flow throughout these systems using Mass Flow Analysis. It has been reported that P output is available in urban wastes such as food waste, domestic wastewater, human waste, and etc. [12], [13], [14].

Among these wastes, human waste (e.g. human faeces and urine) has drawn attention to its use as a P source for P recovery due to human waste being enriched with several essentially important elements including nitrogen, phosphorus, potassium, micronutrients e.g. calcium and magnesium and others [15], [16]. Human wastes have been frequently used as an alternative fertilizer either as night soil or liquid fertilizer to improve agricultural productivity for more than 5,000 years [2], [17]. However, urine offers a biological waste that is a more valuable resource for fertilization than faces due to its high nutrients and hygienic quality [18]. Human urine has found large-scale application in supplementing agricultural productivity as fertilizer in recent years [19]. Therefore, human urine utilized as a P source for P recovery will also help to ensure a close-looped for P in food production and consumption systems.

In recent years, P recovery from wastewaters by chemical and biological treatment has been widely investigated. Among the number of recovery techniques, crystallization and adsorption are widely used and known as useful and economical processes [20], [21], [22]. Crystallization, also called metal salts precipitation, is

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the process used to form insoluble solid crystals. The formation of P crystals e.g. struvite and calcium phosphate is dependent on several factors including the presence of excess supersaturation of relative ions (P, Mg, N, and/or Ca), pH value of solution, turbulence and temperature [2], [23]. The advantage of this process is that it obtains high purity P crystals and nutrients in the crystal which release at a slower rate compared to other fertilizers.

Surface adsorption is one type of coprecipitation that is likely to cause significant contaminant removal by precipitates with large specific surface areas [24]. Various researchers have focused on sorption properties of coal fly ash and municipal solid waste incineration fly ash [25], [26], [27]. Generally organic wastes that could be converted into adsorbents and applied to the pollutant adsorption process have been investigated [28]. These fly ashes have also been given great attention as potential P adsorption materials since they are enriched with oxides of calcium, magnesium, aluminum and iron that can strongly adsorb or form precipitates with phosphate. A large quantity of ash produced in Thailand is generated from public utilities activities, including those from coal-fired power plants and solid waste incineration. Around 14.6 M ton y^{-1} of ash have been generated through both processes in Thailand. These are currently transported for final disposal in landfills [29], [30].

From the aforementioned studies, this research was conducted so as to evaluate the benefit of ash addition for P recovery from human wastes since ash contains several elements (calcium, magnesium, phosphorus, and nitrogen) that may react to form phosphate precipitates. The objectives of this study, therefore, are: (1) to evaluate the effect of selected ash addition for P recovery from urinal wastewater; and, (2) to identify and determine the magnitude of P-solids forming mechanisms occurring in the reaction complexes. It is anticipated that results obtained from this study may help improve P recovery from human urine so as to produce P fertilizer for agricultural cultivation. Moreover, this would not only reduce P import to the country but also recycle inert material destined to landfills for useful reuse.

2. MATERIAL AND METHODS

Human Urine

Human urine was collected from the public toilet of the Faculty of Public health, Mahidol University. The urine samples were kept in air-tight containers and stored at 4°C in the refrigerator. Urine used in all experiments was undiluted and received no pretreatment before testing. Characteristics of the collected urine are presented in Table 1.

Table 1. Characteristics of raw materials

Materials	Unit of parameter	N	P	K	Ca	Mg	TDS
Human urine 0.09%P	mg/L	5,301	917	-	75.5	21.8	28,903
Synthetic urine 0.04% P	mg/L	180.8	400	-	789	313.9	6,186
Synthetic urine 0.12% P	mg/L	542.4	1,200	-	2,368	941.6	18,557
Lignite fly ash (LFA)	%	0.06	n.d.	0.01[b]	22.3[c]	0.28[d]	-
Lignite bottom ash (LBA)	%	0.06	n.d.	0.79[b]	1.35[c]	1.02[d]	-
Solid waste fly ash (SFA)	%	0.10	1.22[a]	4.63[b]	41.8[c]	1.42[d]	-
Solid waste bottom ash (SBA)	%	0.09	2.47[a]	2.54[b]	20.9[c]	1.09[d]	-

Remark: a = percentage of P_2O_5 b = percentage of K_2O c = percentage of CaO d = percentage of MgO n.d. = not detectable
(-) = no data

Synthetic Urine

Struvite ($MgNH_4PO_4{\cdot}6H_2O$) and calcium phosphate ($Ca_3(PO_4)_2$) are popular forms of phosphate crystal [9], [10], [11]. However, several ions such as carbonate ion (CO_3^{2-}), aluminum ion (Al^{3+}), and heavy metals such as copper ion (Cu^{2+}) and zinc ion (Zn^{2+}) may interfere in struvite and calcium phosphate crystallization [31], [32], [33]. Hence, the components of these ions were removed from the synthetic urine recipe. In this study, synthetic urine was prepared by dissolving $MgCl_2{\cdot}6H_2O$, NH_4Cl, $CaCl_2$, and KH_2PO_4 into deionized water (DI water) to minimize interference from other ions. The compositions of 0.04% P and 0.12% P synthetic urine are presented in Table 1.

As shown in Table 1, three concentrations of urine solution were used as a P source in this study. Both concentrations of synthetic urine (0.04% P and 0.12% P) were prepared by chemical reagents with the same molar ratio of Mg:Ca:N:P at 1:1.5:1:1 which enhance P crystal formation. Human urine has a molar ratio of Mg:Ca:N:P about equal to 1:2.1:422:33 and therefore contains very low concentrations of Ca and Mg when compared with synthetic urine.

Adsorbents

Adsorbents in the experiment were collected from two sources: the Mae Moh power plant and Phuket Municipality solid waste incinerator. Ashes from both sources were segregated into fly and bottom ashes. Therefore, four types of ash were used in this study. These were lignite fly ash (LFA), lignite bottom ash (LBA), solid waste fly ash (SFA), and solid waste bottom ash (SBA). The collected adsorbents were oven heated at 103°C for 6 h in order to reach a constant weight and then bottom ashes were crushed to a fine powder. The characteristics of the adsorbents used in this study are presented in Table 1.

P Recovery via Precipitation

Batch experiments were conducted for phosphate crystal precipitation. These experiments were carried out with 100 mL of synthetic urine or human urine in 250 mL beakers. The effect of pH (7, 9, and 11) and initial P concentration (0.04% P, 0.09% P, and 0.12% P) on adsorption efficiency was investigated. Samples were stirred at 400 rpm for 7 min, followed by 60 rpm for 15 min by magnetic stirrer. Samples were next left for 40 min to allow crystal settling before filtering through filter paper. The solid particles were dried in the oven at 103°C for 6 h and then their characteristics were analyzed.

P Recovery via Coprecipitation

Each type of ash from four cultures was weighed at 0.25, 0.50, or 1.00 g. Then, 100 mL of synthetic urine or human urine was mixed with ash in 250 mL beakers. All experiments were conducted in triplicate at neutral pH. In this part of the experiment, the effects of ash type, ash weight, and initial P concentration were investigated. Solution were stirred at 400 and 60 rpm for 7 and 15 min, respectively, using a magnetic stirrer. Then, they were left 40 min to encourage crystal formation and filtered using filter paper. Characterization of constituents in both solid and aqueous phases was conducted after acidic digestion.

Common Ion Effect on P Recovery

To examine the common ion effect on phosphorus recovery, the laboratory chemicals CaCl2 and $MgCl_2 \cdot 6H_2O$ were added into the urine solution at 0.5, 0.30, 0.60, and 1.20 $g \cdot L^{-1}$ to provide equal concentrations of Ca and Mg content in the ash. The procedures for these experiments were the same as for those used for the precipitation experiments.

Analysis and Calculations

Compositions and concentrations of the four major ions in both solid and aqueous phases were determined. Nitrogen was measured by the Total Kjeldahl Nitrogen (TKN) method. Phosphorus was determined by the colorimetric method using vanadomolybdophosphoric acid and UV-spectrophotometer. Concentrations of calcium and magnesium were measured using an atomic absorption spectrophotometer (AAS). In addition, the pH of solutions was determined using a benchtop pH meter. The data are generally expressed using mean values and standard deviations (S.D.). Independent-Samples T Test and One-Way ANOVA were used for statistical analysis to determine the significant difference of percentage P recovery and percentage P content in solids and liquids. Isotherm results of the experiments were analyzed by linear regression. All statistical tests were performed by using SPSS Statistics 18.0 for Windows. Data were indicated as a statistically significant difference at the 95% confidential level. The equilibrium of P between solid and aqueous phases, P recovery efficiency, phosphate crystal content, and adsorption isotherms were determined by calculation. The equations used for calculations are given below:

P mass balance

$$\text{P lost from liquid} = \text{P gained by solids}$$

$$(C_0 - C_1)V = (q_1 - q_0)B \quad (1)$$

where C_0 and C_1 are the initial and final phosphorus concentration in the aqueous solution ($mg \cdot L^{-1}$), respectively; V is volume of solution (L); q_0 and q_1 are the initial and final phosphorus concentrations of solids ($mg \cdot g^{-1}$), respectively; and B is mass of adsorbent (g).

P recovery efficiency

$$\%\text{P recovery} = [(C_0 - C_1) / C_0] * 100\% \quad (2)$$

where C_0 and C_1 are the initial and final phosphorus concentrations in the aqueous solution ($mg \cdot L^{-1}$), respectively.

P crystal content

$$\%\text{P crystal content} = [(C * \text{MW of P crystal}) / \text{mass of precipitate}] * 100\% \quad (3)$$

Where C is the decreased concentration of limiting value of reference element ($mol \cdot L^{-1}$); MW of P crystal is the molecular weight of P crystal formed ($g \cdot mol^{-1}$).

Identification of P-solids forming mechanism

Two mechanisms including precipitation and adsorption were examined from the percentage of phosphorus recovery via the coprecipitation process. The relativity of these mechanisms is shown in Eq. (4),

$$100\% = \%\text{ Precipitation} + \%\text{ Adsorption} \quad (4)$$

As the experiments of coprecipitation were conducted at neutral pH (pH 7), the percentages of phosphorus recovery determined from the amount of P precipitate in the precipitation process at pH 7 were used as reference data to evaluate the contribution of mechanisms in the coprecipitation process. Therefore, the amount of newly formed solids (weight of P solids excluding weight of ash added) was used to calculate the contribution of precipitation mechanisms in the coprecipitation process. The percentage of precipitation occurring in the coprecipitation process was calculated, using Eq. (5),

$$\%\text{ Precipitation} = (\%PR_{prec.} / \%PR_{copre}) * 100\% \quad (5)$$

where $\%PR_{prec.}$ and $\%PR_{copre.}$ are the percentages of phosphorus recovery via precipitation and coprecipitation processes, respectively.

The results from Eq. (5) were substituted into Eq. (4) to determine %P recovery by adsorption occurring in the coprecipitation process.

Adsorption isotherm

Two adsorption isotherms were evaluated to determined which best described sorption phenomena under the conditions of this study.

Langmuir adsorption isotherm

$$Q_e = (Q_m k C_e) / (1 + k C_e) \quad (6)$$

where Q_e is the adsorption capacity at equilibrium; C_e is the equilibrium concentration of phosphate ions ($mg \cdot L^{-1}$); Q_m is the maximum adsorption capacity (maximum value of Q_e) with unit of $mg \cdot g^{-1}$; k is a Langmuir constant related to the energy or net enthalpy of adsorption.

Freundlich adsorption isotherm

$$Q_e = K_F C_e^{1/n} \quad (7)$$

where Q_e is the adsorption capacity at equilibrium; K_F and n are Freundlich constants; and C_e is the equilibrium concentration of phosphate ions (mg·L^{-1}).

3. RESULTS AND DISCUSSION

P Recovery via Precipitation

Based on the composition of urine solutions, two species of phosphate crystal may have formed in this study. These are struvite ($MgNH_4PO_4$; MAP) and calcium phosphate ($Ca_3(PO_4)_2$; CaP). The reactions of MAP and CaP and their solubility product constants are presented in Eq. (8) and (9), respectively.

$$MgNH_4PO_4(s) \rightleftharpoons Mg^{2+}(aq) + NH_4^{+}(aq) + PO_4^{3-}(aq) \quad K_{sp} = 10^{-13.26} \ [2] \quad (8)$$

$$Ca_3(PO_4)_2\,(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \quad K_{sp} = 10^{-28.92} \ [34] \quad (9)$$

pH and initial P concentration were varied to form phosphate crystals via the precipitation process. White crystals were the product of this process. The formation of white crystals resulted in the reduction of ion concentrations (Mg, Ca, N, and P) in the urine solutions. The effect of pH and initial P concentration on P crystal formation from the urine solutions tested is summarized in Table 2.

Table 2. Effect of initial pH and initial P concentration on P crystallization

P source	Initial pH	Final pH	Newly formed solid (g/L)	Decreased concentration (mol/L)				%P recovery
				P	Ca	Mg	N	
Synthetic urine 0.04% P	7.00	7.02	1.62	1.09	0.94	0.22	0.20	75.03
	9.00	8.90	3.37	1.28	1.36	0.40	0.42	98.61
	11.00	10.46	4.27	1.29	1.60	0.71	0.84	99.66
Human urine 0.09% P	7.00	7.67	0.44	0.30	0.19	0.09	0.10	10.06
	9.00	8.96	0.46	0.28	0.19	0.09	0.27	9.54
	11.00	10.89	0.67	0.68	0.19	0.09	0.88	23.04
Synthetic urine 0.12% P	7.00	6.94	4.65	3.25	2.97	0.62	0.58	74.03
	9.00	8.74	9.24	3.86	3.91	1.30	1.58	99.54
	11.00	10.57	11.23	3.87	4.74	2.09	2.19	99.81

As illustrated in Table 2, the recoverable amount of P contained in solid particles improved significantly at higher pH values. The percentages of P recovery from human urine due to precipitation were found as 10.06%, 9.54% and 23.04% at pH 7, 9, and 11, respectively. At pH 7, 9, and 11, approximately 75%, 99%, and 99%, of P was recovered in solid particles, respectively, for synthetic urine. Additionally, the change in relative ion concentrations was found to follow the change in pH of the solutions. This is due to hydrogen ion (H^+) release during crystal formation [35]. Nonetheless, the percentages of P recovery from synthetic urine at 0.04% P had a higher P recovery efficiency than that for human urine since synthetic urine is characterized by higher relative ionic ratios which favor formation of P as solid particles. Results, therefore, indicate that the P content contained in solid particles formed for both human and synthetic urine precipitation depends on the concentrations of relative ions such as magnesium, ammonia and calcium.

The ion with the lowest molar concentration as illustrated in Table 2 was selected as the reference element to evaluate P crystals content in the precipitates for each P source [35], [36]. Importantly, it is not only one species of P crystal that could possibly form as mentioned above. A comparison of solubility (S) of MAP and CaP was made using K_{sp} calculation by Eqs. (8) and (9). Solubilities of MAP and CaP were determined as $3.8\text{x}10^{-5}$ and $1.29\text{x}10^{-6}$ M, respectively. This indicates that MAP has a higher solubility than CaP. It is therefore expected that P would be recovered in the form of CaP first followed by MAP for the remaining P present in solution. The percentages of P in solid particles and liquid in the precipitation process under the variations of pH and initial P concentrations used in this study are illustrated in Fig. 1.

Results shown in Fig. 1 indicate it is difficult to observe recoverable P in the form of P crystals from the human urine experiments since P was recovered in P crystals less than 2% of the total P. This may be due to the lower concentrations of Mg and Ca in human urine compared to synthetic urine, thereby leading to lesser P crystals formed [37]. P was effectively recovered, however, in solid particles, especially P crystals, using synthetic urine as the P source. As indicated, the formation of P crystals and its impurities improved at higher pH levels. At neutral pH (pH 7), approximately 75% of total P was recovered into solid particles. Of these, P crystals were formed using 70% of P in solution. The majority of precipitate was likely in the form of CaP followed by MAP at 45–48% and 22–26%, respectively. Although the P recovery rate reached more than 98% at pH values of 9 and 11 for the synthetic urine experiments, only 46–65% of the recoverable P formed as CaP. The absence of MAP in solid particles indicates that Ca^{2+} may inhibit the reaction of MAP formation at higher pH values or that other insoluble P-solids were formed [38].

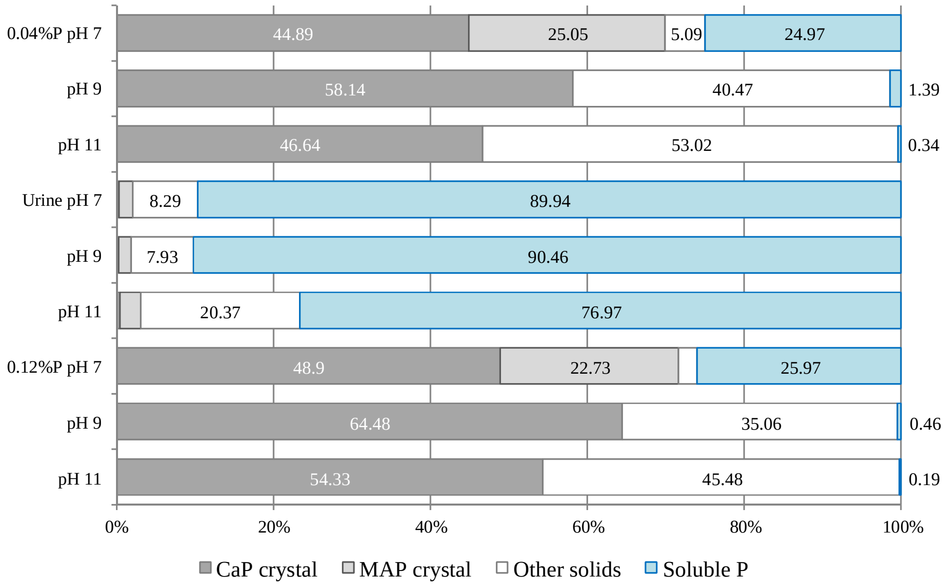

Fig. 1 Percentages of P in solids and liquid

P Recovery via Coprecipitation

Effect of Ash Type, Ash Dosage, and Initial P Concentration

From the results of the precipitation process, the percentage of P recovery observed was as high as 75% at neutral pH; while, the remaining P (25%) was present in soluble form. Ash from a lignite power plant and a solid waste incinerator was used as P adsorbent to evaluate potential enhanced P recovery since these were enriched with oxides of Mg and Ca [25], [26], [27]. Coprecipitation was evaluated at pH 7 by varying three conditions: ash type; ash dosage; and, initial P concentration. A comparison of observed P recovery via the coprecipitation process is presented in Fig. 2.

As shown in Fig. 2, the percentages of P recovery from the experiment with ash addition increased with an increase of ash dosage, especially when using human urine as P source. This was due to an increase in adsorbent surface area and accessible adsorption functional sites [26], [39]. The percentages of P recovery with lignite fly ash (LFA), lignite bottom ash (LBA), solid waste fly ash (SFA), and solid waste bottom ash (SBA) addition were higher than those due to precipitation. For example, the percentages of P recovery by 2.5, 5.0 and 10.0 $g{\cdot}L^{-1}$ LFA addition at 0.04% P synthetic urine increased from 75.03% (precipitation) to 88.59%, 90.65% and 99.72%, respectively. At 0.09% P human urine, the precipitation process recovered P by solid precipitation at 10.06%. When LFA was added into the human urine solution, the percentages of P recovery were 28.05%, 32.20% and 38.85% for 2.5, 5.0 and 10.0 $g{\cdot}L^{-1}$ ash dosage, respectively. The percentages of P recovery of the 0.12% P synthetic urine experiment improved compared to precipitation process from 74.03% to 80.11%, 83.74% and 87.35% for 2.5, 5.0 and 10.0 $g{\cdot}L^{-1}$ ash dosages, respectively. Similar to LFA, the percentages of P recovery for the experiment with LBA, SFA and SBA addition continuously increased in association with increased ash dosage.

However, the percentages of P content in solid precipitates were found to decrease with an increase in ash dosage. The highest P content in solid precipitate was found with no ash addition (precipitation process) at around 18.40±2.02% P. When adding ash into the urine solution, the final P content of solid precipitates sharply decreased. For example, the percentages of P content for the experiment at 0.09% P human urine found no ash addition to have the highest P content in precipitate at 19.89%, followed by 2.5 $g{\cdot}L^{-1}$ ash addition at 8.93%, 5.0 $g{\cdot}L^{-1}$ at 6.97%, and 10 $g{\cdot}L^{-1}$ at 3.68%.

Coprecipitation Mechanisms

Based on the above results, improvement of P recovery efficiency by ash addition resulted from two mechanisms – adsorption and precipitation. These two mechanisms and their effect on precipitation and adsorption, therefore, were examined based on ash type. Results on the amount of precipitate and percentage of P recovery at neutral pH from the precipitation process are presented in Table 2. These were used as reference data to evaluate the contribution of each mechanism occurring during the coprecipitation process. Results are illustrated in Fig 3.

When ash was added into the urine solution the contribution of each P recovery mechanism was examined as a function of type ash and initial P concentration. An increase in ash dosage led to a slight increase in % adsorption. However, no significant % adsorption increase at higher ash dosages was observed due to the achievement of saturation level beyond a given adsorbent dosage [26], [40].

Adsorption was the main mechanisms contributing to P recovery for LFA, SFA, and SBA at 82.23±5.67, 89.21±4.58 and 82.30±6.23%, respectively, for 0.04% P synthetic urine. When using human urine having 0.09%

P as a P source, results also determined adsorption as the main mechanism contributing to P recovery via coprecipitation for LFA, SFA, and SBA at 88.92±1.85, 79.65±3.32 and 72.14±2.73%, respectively. For the higher P concentration (0.12% P), it was found that the precipitation contribution increased and was slightly higher than the adsorption observed in some experiments. Precipitation achieved the higher contribution of P removal for all LBA testing via coprecipitation. The precipitation contribution for P removal was determined to be 67.04±2.52, 87.81±1.59 and 72.54±2.51% at 0.04% P, 0.09% P and 0.12% P, respectively. These results may be due to the fact that LBA contains very small amounts of magnesium and calcium in its ash and thus percentages of P adsorption onto ash particles via coprecipitation were dependent on the ash content of magnesium and calcium.

Adsorption capacity was found to depend on the contribution of % adsorption occurring in the coprecipitation process as mentioned above. A statistical analysis found that adsorption capacity results of LFA, SFA, and SBA using synthetic urine yielded no significant difference (p-value $\geq$ 0.05). These ashes have a higher P adsorption capacity than LBA at by about 50% at 0.04% P and 20% at 0.12% P when using synthetic urine (p-value $<$ 0.05). Results indicate the greatest adsorption capacity for human urine (0.09% P) was observed for LFA, followed by SFA, SBA, and LBA at 88.92%, 79.65%, 72.14% and 12.19%, respectively.

Adsorption Isotherm

Based on adsorption isotherm modeling, the Langmuir and Freundlich isotherms in Eqs. (6) and (7) were applied to evaluate P adsorption capacity at neutral pH onto ash particles under the conditions of this study. Linear correlations of Langmuir and Freundlich isotherms are plotted in Fig. 4 and 5, respectively. Resultant isotherm constants are presented in Table 3.

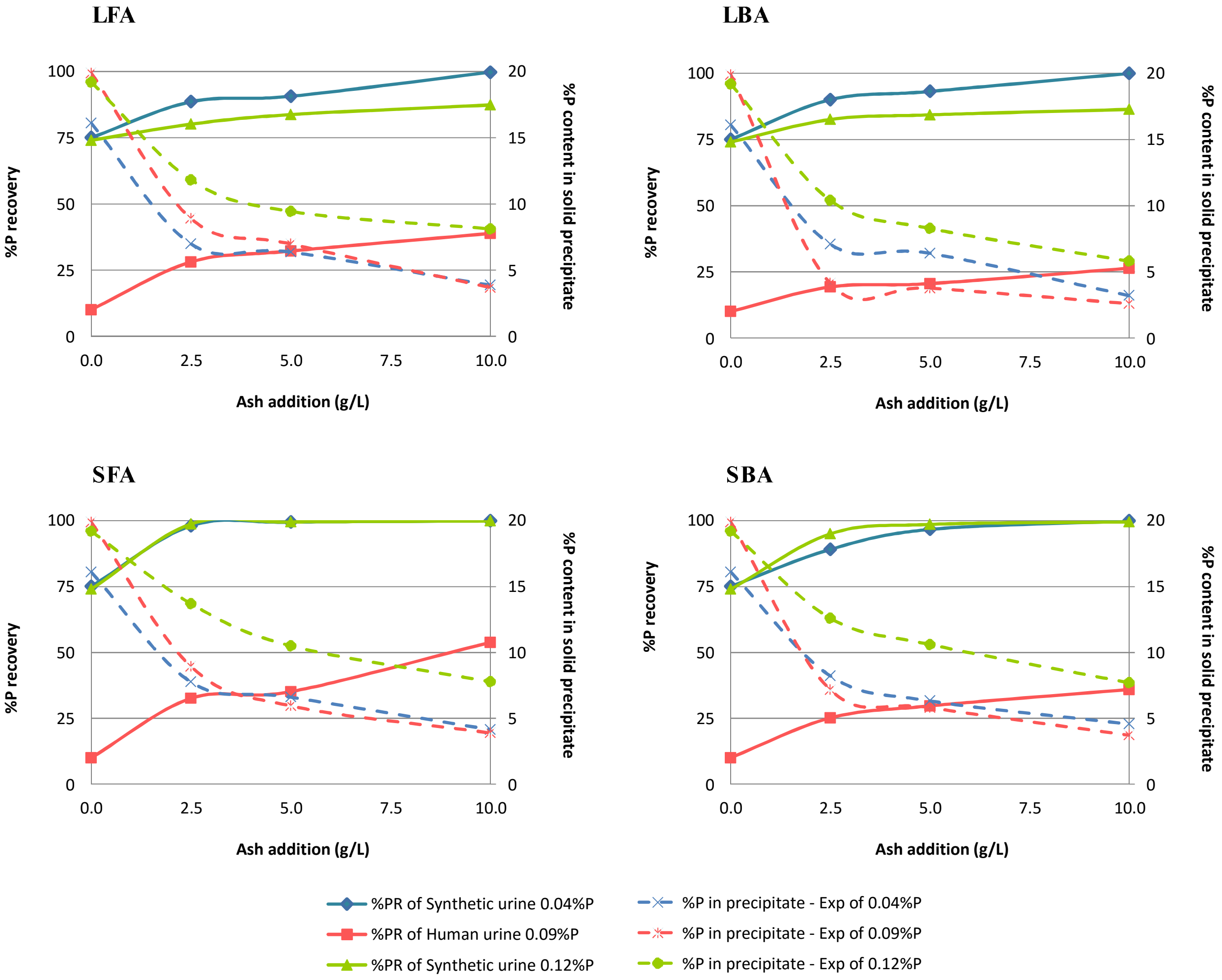

Fig. 2. Percentages of P recovery and percentages of P content in solid precipitates

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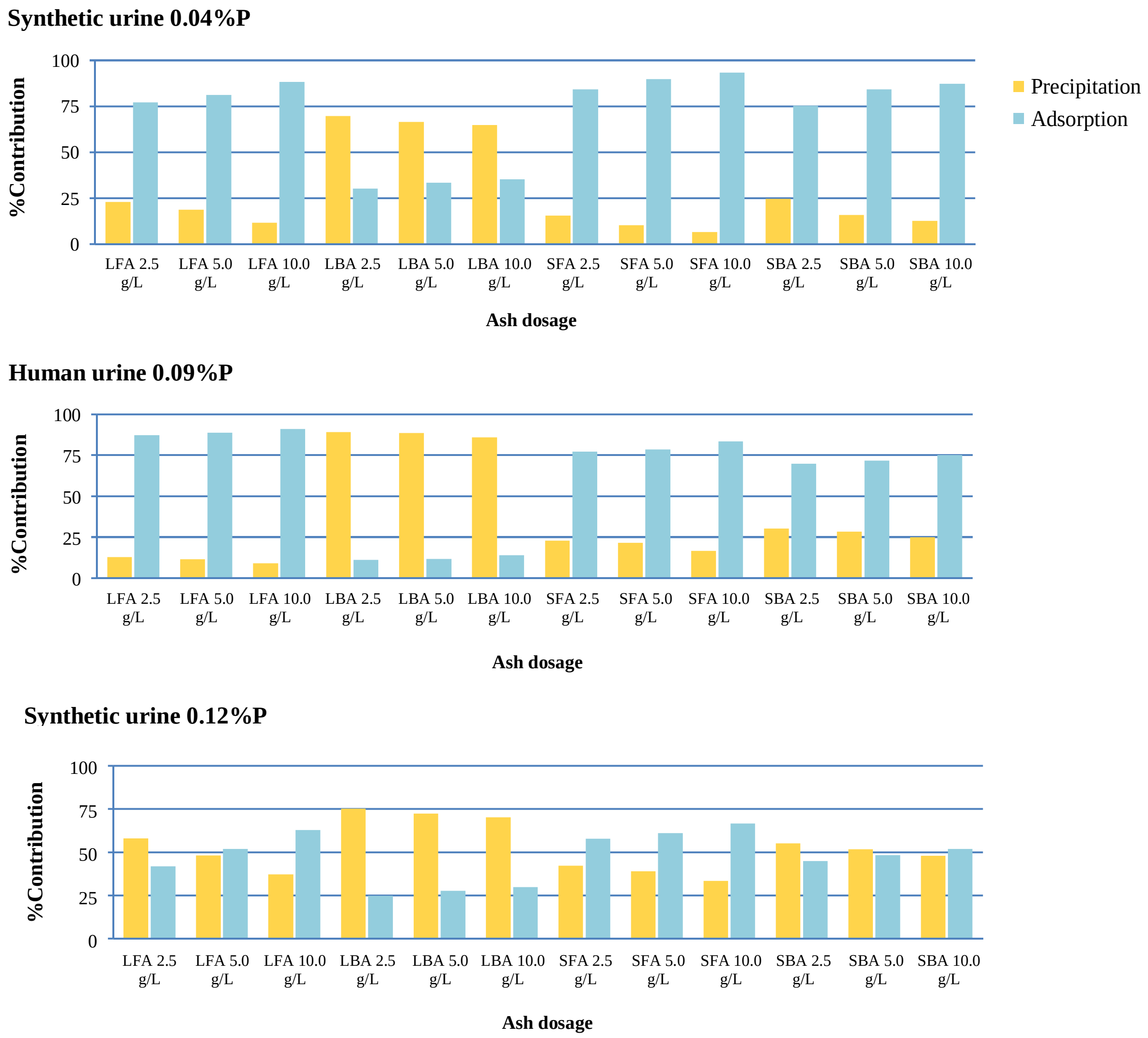


Fig. 3. Percentage of P recovery mechanism contribution in the coprecipitation process.

As shown in Fig. 4and 5, the correlations between P concentration and P adsorption capacity are plotted independently as adsorption isotherms for P recovery from synthetic urine and human urine experiments due to differences in urine solution characteristics. Results of the synthetic urine runs indicate both isotherm models represent a good equation fit (R^2 between 0.6346 and 0.9359), especially for the Langmuir model. Results indicate that there are significant relationships between the variables in the linear regression model for the data set (p-value < 0.05). The maximum adsorption capacity for synthetic urine of P adsorption onto ash was found in the range of 85.47–114.94 mg·g^{-1} using the Langmuir isotherm. Enhanced P recovery into solid precipitates via P adsorption and P crystal precipitation as mentioned in Section 3.2.2 may be the reason. A high P content in solid precipitates and also a high P recovery capacity even with 0.04% P synthetic urine was also observed. LBA demonstrated the highest k at 11.01 L·mg^{-1}, followed by SBA, LFA, and SFA, respectively. This indicates that LBA exhibited the greatest bond strength for adsorbent and adsorbate interaction [41]. The Freundlich isotherm constants for P adsorption onto lignite and solid waste ashes at pH 7 for synthetic urine were found as nearly identical values. K_F and n values were determined in the range of 40.93–60.56 mg·g^{-1} and 4.04–7.69, respectively. High K_F and high n values indicate that lignite and solid waste ashes have high adsorption capacities to recover P from synthetic urine at 0.04% P and 0.12% P [42].

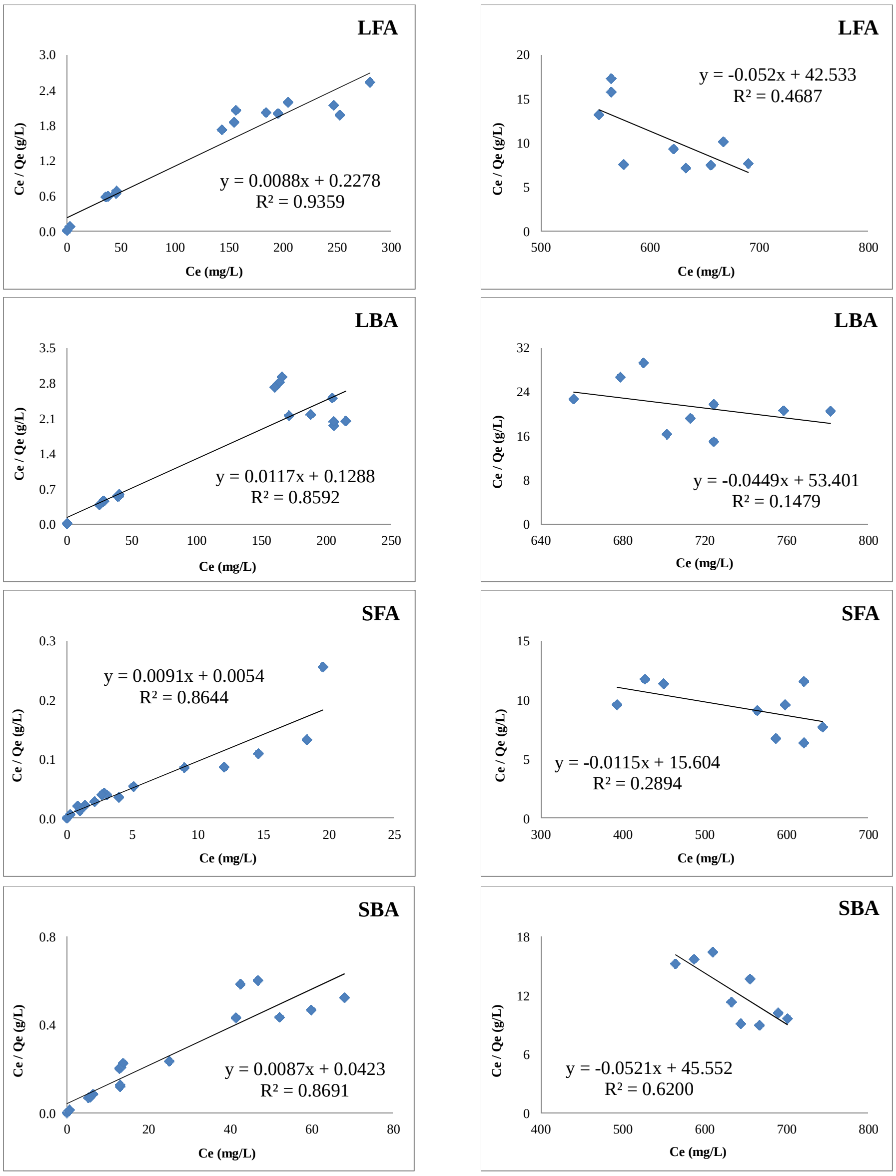
A poor correlation of data with the Langmuir isotherm was observed for experiments of ash addition into human urine (R^2 between 0.1479 and 0.6200). A negative correlation was observed between P concentration and P adsorption capacity. The Langmuir adsorption parameters (Q_m and k) were found having negative signs indicating the behavior of P adsorption from human urine onto lignite and solid waste ashes was poorly described by the Langmuir isotherm model [43], [44]. A better fit of isotherm data was observed for the Freundlich isotherm for human urine. SFA demonstrated the highest K_F at 1.79×10^{-3} mg·g^{-1} and the highest n at 0.60. It was followed by LBA, SBA, and LFA, respectively. The K_F values for P adsorption from human urine were determined to be very low, while values for n were found high. This indicates poor adsorption of P throughout the concentration range studied. Results of Freundlich constants therefore indicate that lignite and solid waste ashes have low adsorption capacities for human urine having 0.09% P [45].

Common Ion Effect on P Recovery from Urinal Wastewater

According to common ion effect theory, the addition of even small amounts of relative ions into solution interfered with the equilibrium of the ion concentrations thereby resulting in a new solubility product for the solution. The ions in aqueous solution may also form an insoluble precipitate at equilibrium. The effect of common ions on P recovery efficiency is shown in Fig. 6. As indicated, the efficiency of P recovery increased with an increase of common ion dosage. Enhancement of percent P recovery was observed greatest with an increase of common ion dosage for human urine. Unlike human urine, P recovery efficiency only slightly increased when using both concentrations of synthetic urine as the P solution. The main reason for the difference of common ion effect on P recovery between synthetic urine and human urine is due to the difference of initial Ca and Mg concentrations. Synthetic urine had a much higher Ca and Mg content than that in human urine. Results indicate therefore that the common ions Ca and Mg had only a slight effect on P recovery at high Ca and Mg concentrations [46].

P Recovery as Alternative P Fertilizer

Human kidneys excrete a substantial excess of P at around 1 g·d^{-1} in the form of urine [47], [48]. In this study, human urine having around 900 mg P·L^{-1} was used as a P source. Importantly, the percentage of P content in its solid precipitate is an important measure to achieve an alternative P fertilizer. A comparison of percentage of P content in solid precipitates of this study and commercial P fertilizers is illustrated in Table 4.



4a

4b

Fig. 4. Langmuir isotherms of (4a) synthetic urine and (4b) human urine.

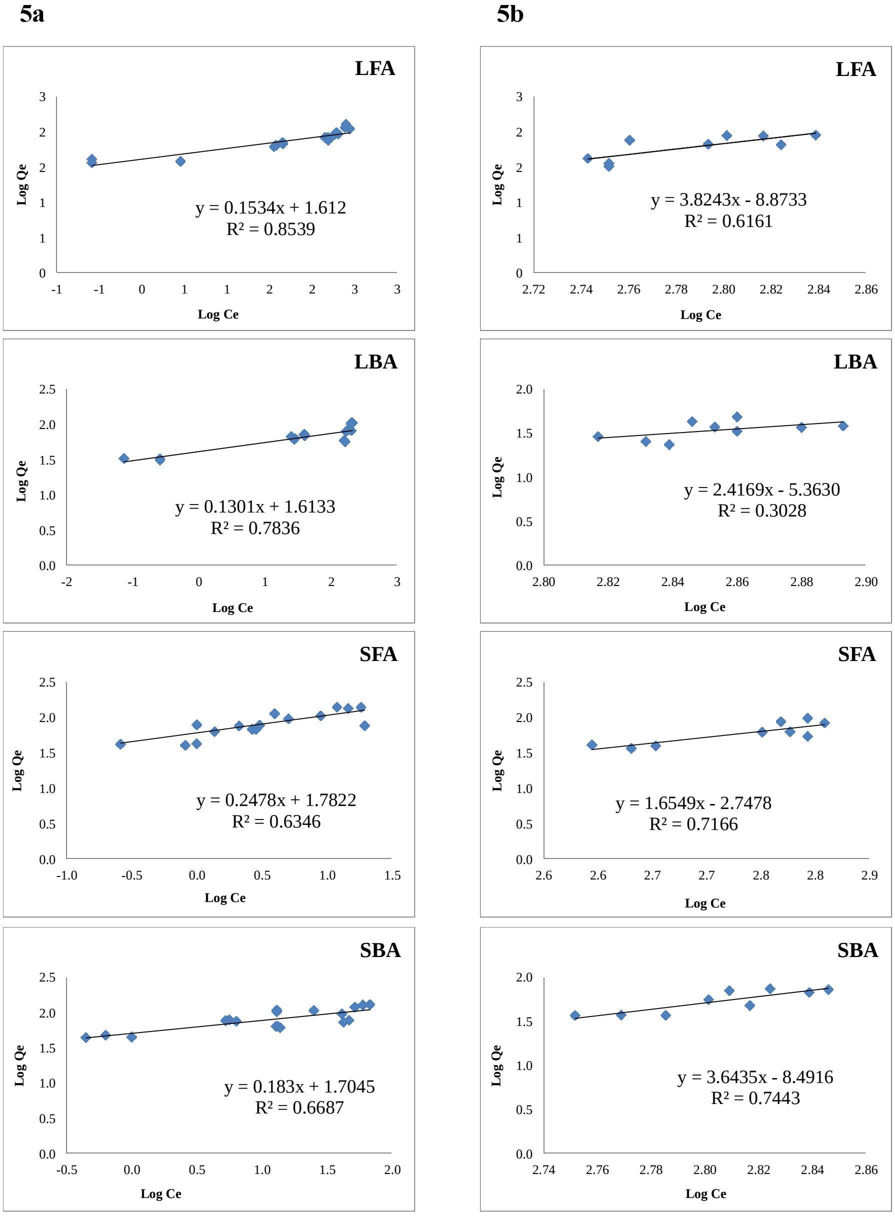


Fig. 5. Freundlich isotherms of (5a) synthetic urine and (5b) human urine.

Table 3. P adsorption constants obtained from linear forms

P source	Adsorbent	Adsorption constants					
		Langmuir			Freundlich		
		Q_m (mg·g^{-1})	k (L·mg^{-1})	R^2	K_F (mg·g^{-1})	n	R^2
Synthetic urine	LFA	113.64	3.11	0.9359	40.93	6.52	0.8539
	LBA	85.47	11.01	0.8592	41.05	7.69	0.7836
	SFA	109.89	0.59	0.8644	60.56	4.04	0.6346
	SBA	114.94	4.86	0.8691	50.64	5.46	0.6687
Human urine	LFA	-19.23	-817.91	0.4687	1.34×10^{-9}	0.26	0.6161
	LBA	-22.27	-1189.24	0.1479	4.33×10^{-6}	0.41	0.3028
	SFA	-86.96	-1,356.92	0.2894	1.79×10^{-3}	0.60	0.7166
	SBA	-19.19	-874.14	0.6200	3.22×10^{-9}	0.27	0.7443

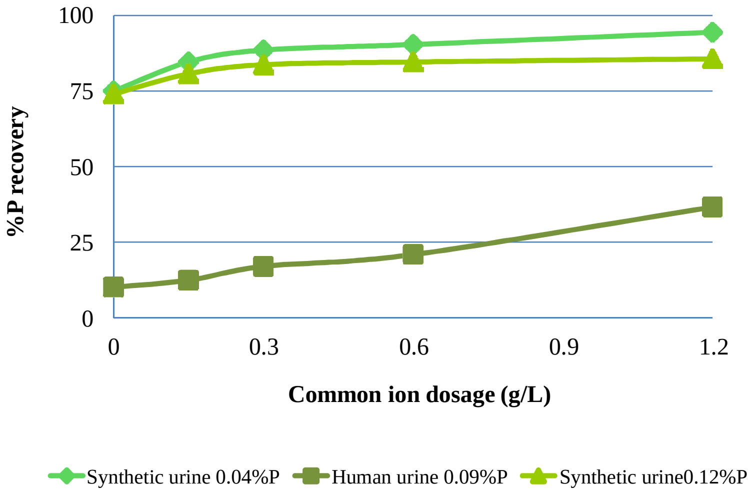


Fig. 6. Percentage of P recovery for common ion effect experiments.

Table 4. A comparison of P content in solid precipitate of this study and commercial P fertilizers

P recovery from human urine (This study)				
Ash dosage ($g \cdot L^{-1}$)	%P content in solid precipitate (%dry wt)			
	LFA	LBA	SFA	SBA
2.5	8.89	4.13	8.93	7.16
5.0	6.97	3.77	5.94	5.81
10.0	3.68	2.60	3.89	3.72

Commercial P fertilizer			
P fertilizer	Formula	$\%P_2O_5$	%P
Superphosphate (SSP)	0–20–0	20.00	8.80
Triple super- phosphate (TSP)	0–46–0	46.00	20.24
Diammonium phosphate (DAP)	18–46–0	46.00	20.24
Monoammonium phosphate (MAP)	11–52–0	52.00	22.88

As shown in Table 4, the percentages of P content in solid precipitate for all ash types evaluated increased in the range of 2.60–8.89% as compare to initial P content in ash particles as shown in Table 1. Of these, the percentages of P content in solid precipitates at an ash dose of 2.5 $g \cdot L^{-1}$ for LFA and SFA addition into human urine having 0.09% P were about equal to P content in commercial superphosphate fertilizer at 8.89% and 8.93%, respectively. Therefore, P-containing ash obtained from both test runs may be used as alternative P fertilizer. Additionally, the precipitates from other experiments with a P content lower than 8.80% may be used as soil conditioner due to good nutrient qualities, especially P [49]. The recoverable P-containing product from urine mixed with other soil conditioners may potentially be fertilizer that contains many essential nutrients and contributes less heavy metals to farmland [50].

Results indicate that both LFA and SFA can achieve the same P content as commercial P fertilizer (P 8.80%). As shown in Fig. 2 the percentages of P recovery were observed at 28.05% and 32.62%, respectively for 2.5 $g \cdot L^{-1}$ ash dosage. Therefore, approximately 70% of P remained in urine solution meaning that this may be available for P recovery using follow up treatment. Alternative reclamation treatment processes are currently being investigated. Ash is recommended as an alternative P capture material (especially LFA and SFA) which has the potential to achieve as high a P content as commercial fertilizer. Importantly, applying ash as a P adsorbent will also reduce disposal cost as well as expand landfill lifetime. Results indicated P precipitation with waste contains high Mg or Ca content (e.g. food waste [51], [52]) should be a research focus to achieve maximum P content in solid precipitate. Sustainable P management helps strengthen Thailand's food security. Recoverable P can be effectively used to produce fertilizer for agricultural cultivation to help attain this goal.

4. CONCLUSION

Efficiency of P recovery from the precipitation process improved at higher pH levels. However, the percent formation of P crystal declined from 70% at pH 7 to 60 and 50% at pH 9 and 11, respectively. LFA was found to have the highest adsorption capacity for human urine, followed by SFA, SBA, and LBA. Adsorption capacity was determined based on Langmuir and Freundlich isotherms. Common ion addition (especially Ca and Mg) into human urine solution led to an increase in surface nucleation and greater P precipitation. Precipitates of 2.5 $g \cdot L^{-1}$ LFA and SFA addition had a P content about equal to superphosphate fertilizer at 8.89% and 8.93%, respectively.

ACKNOWLEDGMENT

Financial support from the Thailand Research Fund given to Yada Pinatha through the Royal Golden Jubilee Ph.D. Scholarship Program (Grant No. PHD/0030/2557) is greatly appreciated. This work is also part of a 2015 research project, “The study of phosphorus recovery – chemical and biological processes”, under the research plan “Potential recovery and recycling of phosphorus from urban wastes to agricultural plantations in Thailand” supported by Mahidol University (Grant # 59/2558). The authors also would like to thank EGAT and Phuket Municipality for ashes given for this study.

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