

# PHOSPHORUS RECOVERY FROM URINE BY ADDING DIFFERENCE SOURCES OF MAGNESIUM ION, APPLYING FOR RURAL, COASTAL AND ISLAND AREAS IN VIETNAM

Do Hong Anh<sup>a,\*</sup>, Nguyen Viet Anh<sup>a</sup>

<sup>a</sup>*Faculty of Environmental Engineering, National University of Civil Engineering,  
55 Giai Phong road, Hai Ba Trung district, Hanoi, Vietnam*

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## **Abstract**

In coastal areas and islands, farmlands often lack of nutrients. This research assessed the precipitation of phosphorus presenting in urine in the form of struvite of magnesium ammonium phosphate (MAP) by adding of supplement of  $Mg^{2+}$  ion from  $MgCl_2$  solution contained in seawater (Cat Ba island area). The urine and seawater have been mixed at different ratios. The results have shown  $[Mg]:[PO_4]$  ratios ranging from 0.75 to 5.26 allowed the precipitation of more than 90% of the phosphorus in the urine. Seawater – to – urine ratios of 0.67/1, 1.3/1, 3.2/1, 5/1, 7/1 and 9/1 in volume would give phosphorus recovery efficiency of 99%, 92%, 96%, 96%, 95% and 99%, respectively. Seawater in the studied area could be an appropriate  $Mg^{2+}$  ion source to produce MAP from urine diverting dry toilets. Recovered phosphorus can be used as slow releasing fertilizer for farming.

**Keywords:** MAP: phosphorus recovery; seawater; urine; struvite.

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## **1. Introduction**

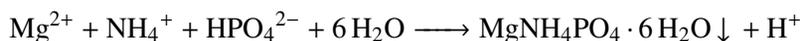
According to General statistic office of Vietnam, there are 65% of population living in rural areas including coastal and island areas [1]. Almost of them have main source of income from agriculture activities. Modern agriculture is highly dependent on artificial fertilizers. Many reports warn for the depletion of phosphorus, one of the key elements in artificial fertilizers. The reserves may already have been depleted for about 50 to 100 years [2]. For this reason, the recovery and recycling of phosphorus become essential to cope with the rapidly increasing demand. In rural areas especially coastal and island areas, crop soil need more nutrients because their geological conditions are mainly sand and gravel.

Wolgast and Jonsson [3, 4] estimated that the average annual per capita urine production was 500 L. In additionally, 90% of the tot-N, 60-65% of tot-P and 50-80% of K are partitioned by the human body and excreted in the urine. More recently, in a survey of three case study locations across South Thailand, Schouw [5] observed the per capita daily production rates for urine and faeces to be 0.6-1.2 L and 120-400 g, respectively. A Vietnamese case study conducted by Polprasert et al. [6] estimated the production of urine as 0.82-1.2 kg person<sup>-1</sup> d<sup>-1</sup> and faeces as 130-140 g person<sup>-1</sup> d<sup>-1</sup>.

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\*Corresponding author. *E-mail address:* [anhdh@nuce.edu.vn](mailto:anhdh@nuce.edu.vn) (Anh, D. H.)

Antonini et al. [7] reported that they used magnesium oxide as the precipitant and dosed it at a molar ratio of 1.5 mol Mg mol P<sup>-1</sup>. The mechanism for phosphorus precipitation was shown in the equation below



The precipitate was later collected in a filter bag attached to the outflow of the reactor. The phosphate removal was as high as 98% [7]. Abegglen [8] dosed magnesium at a molar ratio of 1.8 mol Mg mol P<sup>-1</sup> and observed phosphate removal efficiencies higher than 95%. The reactor type used in the above studies has proven to be very suitable for pilot studies with a reliable power supply, but the investment costs are still rather high. In our study, we wanted to build struvite reactors, which conform to the requirements of low-cost sanitation systems in rural areas in Vietnam, i.e. where the struvite process uses only locally available inputs, without in-depth technical knowledge, and without continuous electricity supply.

Besides the results with MgO and MgCl<sub>2</sub> as external magnesium sources for struvite precipitation from urine are promising (e.g. [9, 10]). Seawater is an infinite alternative source of water and ions [11–13]. The salinity of seawater is usually 35 parts per thousand in most marine areas. The interesting thing about this dissolved salt is that it is always made up of the same types of salts and they are always in the same proportion to each other (even if the salinity is different from or higher than the average). According to field survey data collected by Institute of Environmental Science and Engineering (IESE) from 2016 to 2018, in Cat Ba island's costal area, seawater salinity was low ranging from 20% to 25%. It was much lower than previous result [11, 14].

Furthermore, seawater can also facilitate phosphorus recovery from urine through chemical precipitation due to the presence of key ions like magnesium and calcium [11–13]. Tran Duc Ha [14] reported that, the magnesium content in most marine areas is in concentration of 1.295 ‰ equal to 1295 mg/l approximately, accounting for 3.68% of total salt, Kumashiro [13] also reported that, magnesium in seawater was contained around 1250 mg/l. Tran Duc Ha [14] reported that, in coastal areas in Nam Dinh and Hai Phong, ions concentration in seawater were 1080 mg/l and 1160 mg/l of Mg<sup>2+</sup>, respectively and 330 mg/l and 334 mg/l of Ca<sup>2+</sup>, respectively. Tran Duc Ha also reported that, some marine areas in the Central of Vietnam have high salinity of 30 – 35 ‰, for example, Deo Ngang, Da Nang, Sa Huynh, Dzung Quat, Quy Nhon, Nha Trang areas. The other areas which have lower salinity, often appear near river estuary with salinity range of 12 and 25 ‰ [15].

The study conducted by Liu et al. [16] reported that, struvite recovery condition in SUPR (Seawater – catalysed Urine P Recovery) with completely ureolysed urine plus seawater at the volume ratios of 1:2 and 1:5. Rubio-Rincón et al., 2014 reported that up to 99% phosphorus removal was observed at seawater-to-urine volume ratios below 3.3:1.0 (as the ones reached by water-less and water-saving urinals). Above this ratio the hydrolysis process in non-hydrolyzed urine is inhibited. Phosphorus removal occurred through the formation and precipitation of struvite; less struvite crystals were observed at Ca/PO<sub>4</sub>-P ratios higher than 0.8. The process was pH dependent and requires a pH of around 8.5 (whereas the initial pH of urine is around 6.0) [9, 17]. Thus, it relies on the (partial) hydrolysis of urea which contributed to the increase of the pH and the concentration of ammonium [18]. The latter was favoring the precipitation of phosphate crystals [19]. However, the high salt content of seawater could hinder the ability of the enzyme urease to attach to the urea, inhibiting the (biological) hydrolysis process [20, 21]. Hence, suitable seawater-to urine mixing ratios need to be defined.

It has already shown to be a promising solution to contribute to alleviate expenses of magnesium chemical for people living in low income areas, especially in the island areas where seawater are

available sources. For the purpose of investigating either the appropriate mixing ratio of magnesium ion to phosphate or impact of present ions in seawater for highly efficient recovery of phosphorus, applying to coastal areas where salinity in seawater vary from 20% - 25% [11], the research team conducted experiments with two types of magnesium sources,  $MgCl_2$  solution and synthetic offshore water. Therefore, this study aims to assess the feasibility of phosphorus recovery from urine.

This study is aimed at investigating: 1) the effectiveness of ion  $Mg^{2+}$  from difference sources (artificial water with chemical mixture, synthetic offshore water) as precipitants for phosphate precipitation from urine and its precipitation rate; 2) the optimal conditions for the phosphate precipitation including pH and the offshore water to urine ratio; 3) the quality of the precipitates; and 4) evaluation of nitrogen remaining after reaction, 5) application of phosphorus recovery by seawater from Cat Ba island.

## 2. Material and methods

### 2.1. Location of pilot testing

The military barracks of Cat Ba island was chosen as a location for pilot testing because 02 urine diverting public toilets (UDT) were constructed there, for recovery of excreta and urine as nutrient for garden. There is also available seawater sources for setting up experiment on phosphate precipitation from urine by adding  $Mg^{2+}$  ion source from seawater.

### 2.2. Material

**Urine (UU):** Urine was collected from UDT at Catba military barracks. The urinal was connected with a urine container and storage time in one month to produce ureolysed urine (UU). The ureolysed urine applied in entire study was collected from container and transfer to Hanoi within a day and stored at room temperature to achieve a stable ammonia concentration. It was ascertained by [17], when seawater was added after 10 hours of hydrolysis, the salt contained in seawater did not represent the main inhibitor of urine hydrolysis. Thus, possibly the early additions of seawater and/or rapid release of ammonium in the beginning of hydrolysis process might hinder the hydrolysis of urea, to ensure full P-removal, seawater should be added hydrolysis of urea was achieved [17]. The UU had a final concentration of  $2060 PO_4^{3-} mg L^{-1}$ ,  $4141 TN^{-} mg L^{-1}$ .

**$MgCl_2$  solution:** a 20-mM magnesium ( $Mg^{2+}$ ) solution were prepared by using 1litre of deionized water included: 18.8 mg  $MgCl_2$ , after mixing the solution had a concentration of  $18.8 mg MgCl_2 L^{-1}$  was used for experiment.

**Offshore water (OW):** The synthetic offshore water use in experiments was prepared base on the composition reported by Anderson, 2008, [11] and produced by adding sea salt collected from coastal salt field to simulate seawater. The synthetic offshore water had  $Mg^{2+}$  concentration of  $1,385 mg L^{-1}$ ,  $Ca^{2+}$  concentration of  $427 mg L^{-1}$ , an electrical conductivity of 68.8 mS/cm, pH of 8.09.

**Seawater (SW):** 40 liters of real seawater was collected from the beach at Cat Ba island and transfer to Hanoi within a day and stored at  $4^{\circ}C$  prior to use. Prior to use, seawater was filtered through sieve with pore size of  $100 \mu m$  to remove any debris present. The initial pH and electrical conductivity of seawater were 8.01 and 425 mS/cm, respectively. The seawater had concentration of  $927 mg Mg L^{-1}$ ,  $272 mg Ca L^{-1}$ . It is similar to [14]. The  $Mg^{2+}$  and  $Ca^{2+}$  contains in seawater around Cat Ba island were lower than results reported in [13] and [11]. It can be due to the fact that the seawater near beach was diluted with rainfall, river water or wastewater.

### 2.3. Reasearch approach

The experiments were excuted to assess the feasibility to use difference sources of magnesium ion for phosphorus recovery from urine as struvite in rural areas. The experiments conducted to compare the urine P recovery efficiency with different precipitant sources, including magnesium solution and offshore water. Magnesium solution or offshore water was mixed with UU respectively at difference volumetric mixing ratios so the Mg/P molar ratios were set at 0.08, 0.15, 0.37, 0.75, 1.88, 3.01, 4.14, 5.26 and 100 respectively; ultrapure water (UPW) was used as the control solution. The precipitates formed in the last of each ratios of Mg/P with difference magnesium sources were characterized accordingly. Some good results of Mg to P molar ratio for highly phosphorus recovery will be test with real seawater from Cat Ba island to verify the findings.

### 2.4. Experimental setup and chemical analyses

All experiment were performed in beakers of 600 ml with maximum working volume of 500 ml. They were continuously mixed with a magnetic stirrer for 3 hours, covered with tin sheet which only opened after the test completion. Experiments were performed at room temperature (at round 33°C). Samples were taken at the start of the test, five minutes after magnesium ion source solutions was added and at the end of the test (after 3 hours). Samples were collected by twice. For the determination of soluble compound, 0.45 μm pore size filters were used, and total soluble phosphorus (TSP) analysis undertaken. All samples were analyzed at laboratory immediately.

All the precipitates formed at each beaker was filtered out through 0.45 μm syringe filter and dried at 46°C for 48 hours – 72 hours to minimize struvite decomposition [22, 23]. Then, the weights of syringe filter were carried out before and after filtrations to determine the amount of struvite precipitation. Working solutions with adding of magnesium ion sources from MgCl<sub>2</sub> solution (Seri A), offshore water (Seri C) and seawater (Seri D) are shown in Tables 1, 3 and 4, respectively. Seri B experiment uses mixture solution of ultra pure water and UU for control, is shown in Table 2.

Table 1. Parameter applied in P precipitate with MgCl<sub>2</sub> solution

Seri A	A4	A5	A6	A7	A8	A9	A10	A11	A12
V <sub>UU</sub> , ml	200	200	200	200	200	200	200	200	5
V <sub>MgCl<sub>2</sub></sub> , ml	5	10	25	50	125	200	275	350	500
[Mg]:[PO <sub>4</sub> ]	0.08	0.15	0.37	0.75	1.88	3.01	4.14	5.26	100
V <sub>MgCl<sub>2</sub></sub> : V <sub>UU</sub>	1:40	1:20	1:8	1:4	1:1.6	1:1	1.375:1	1.75:1	37:1

Table 2. Parameter applied in P precipitate with deionized water as the control solution

Seri B	B0	B6	B7	B8	B9
V <sub>urine</sub> , ml	200	200	200	200	200
V <sub>ultrapure water</sub> , ml	0	25	50	125	200
V <sub>ultrapure water</sub> : V <sub>UU</sub>	0:200	1:8	1:4	1:1.6	1:1

The analytical determination of ammonia and orthophosphate was performed in accordance to standard methods. TSP was measured by reaction of orthophosphate ions with an acid solution containing molybdate and antimony ions to form an antimony phosphomolybdate complex. Reduction

Table 3. Parameter applied in P precipitate with sythentic offshore water

Seri C	C4	C5	C6	C7	C8	C9	C10	C11	C12
V <sub>UU</sub> , ml	400	400	300	200	100	75	50	50	3
V <sub>OW</sub> , ml	26	52	97.5	130	162.5	195	178.8	227.5	259.3
[Mg]:[PO <sub>4</sub> ]	0.08	0.15	0.37	0.75	1.88	3.01	4.14	5.26	100
[Ca]:[PO <sub>4</sub> ]	0.01	0.03	0.07	0.14	0.35	0.56	0.77	0.98	18.20
V <sub>OW</sub> : V <sub>UU</sub>	1:16	1:8	1:3	1:1.5	1.63:1	2.6:1	3.6:1	5.6:1	86:1

Table 4. Parameter applied in P precipitate with real seawater

Seri D	D6	D7	D8	D9	D10	D11
V <sub>UU</sub> , ml	300	200	100	75	50	50
V <sub>SW</sub> , ml	194.2	258.9	323.6	388.3	356.0	453.1
[Mg]:[PO <sub>4</sub> ]	0.37	0.75	1.88	3.01	4.14	5.26
[Ca]:[PO <sub>4</sub> ]	0.07	0.13	0.33	0.53	0.73	0.93
V <sub>SW</sub> : V <sub>UU</sub>	1:1.5	1.3:1	3.2:1	5:1	7:1	9:1

of the complex with ascorbic acid to form a strongly coloured molybdenum blue complex. Measurement of the absorbance of this complex to determine the concentration of orthophosphate present by spectrometer with wavelength of 880 nm (UV-VIS DR/890). NH<sub>3</sub> was measured by reaction of ammonia compounds combine with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5 aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue colored compound. The blue color is masked by the yellow color from the excess reagent present to give a green colored solution. The measurement wavelength is 650 nm for spectrophotometers (UV-VIS DR/890). pH and electrical conductivity were measured with a multifunctional portable meter (HQ40D, Hach, USA).

### 2.5. Calculations

TSP was calculated as the difference between the initial and the final ortho-phosphate concentrations from the tests (TSP<sub>initial</sub>, TSP<sub>final</sub>, respectively). The initial ortho-phosphate concentration was corrected according to the dilution used in the experiment. The maximum P recovery efficiency was determined from Eq. (1).

$$\%P = \left( 1 - \frac{TSP_{\text{final}} * V_s}{TSP_{\text{initial}} * V_u} \right) \quad (1)$$

where % P is the percentage of ortho-phosphate precipitated; TSP<sub>initial</sub> and TSP<sub>final</sub> are the initial and final concentrations of soluble ortho-phosphate, respectively; and, V<sub>u</sub> and V<sub>s</sub> are the initial volume of urine and the final volume of the soluble, respectively.

The concentration of ortho-phosphate precipitated in the experiment (PO<sub>4</sub><sup>3-</sup>-P) was used to estimate the potential formation of struvite assuming that for struvite formation, 1 mol PO<sub>4</sub><sup>3-</sup>-P to 1 mol NH<sub>4</sub>-N is needed per mol of struvite formed. In order to estimate the concentrations of struvite or magnesium ammonia-phosphate (MAP) precipitated during the execution of the experiments, a similar approach to that applied by Hao et al. [24] was applied. Then, it was assumed that struvite was the only crystal of ammonia formed. Thus, the 45 mg of crystals formed in the experiments were

redissolved fully by adding volume of 3 ml 2M HCl to lower the pH to around 2.0. The solution was transferred to beaker of 250 ml, added more deionized water for increasing of pH. Then, the concentrations of ammonia (NH<sub>3</sub>-N) and ortho-phosphate (PO<sub>4</sub>-P) were measured and the molar ratios of NH<sub>3</sub>-N/PO<sub>4</sub>-P were calculated from Eq. (2). Thereafter, the concentration of struvite or MAP formed was estimated based on the struvite composition (MgNH<sub>4</sub>PO<sub>4</sub> · 6 H<sub>2</sub>O).

$$\frac{[\text{PO}_4 - \text{P}]}{[\text{NH}_3 - \text{N}]} = \frac{\text{PO}_4}{\text{M}_{\text{PO}_4}} * \frac{\text{M}_{\text{NH}_3}}{\text{NH}_3} \quad (2)$$

where PO<sub>4</sub> and NH<sub>3</sub> are the ortho-phosphate and ammonia concentration of struvite re-dissolving solution, respectively; and, M<sub>NH<sub>3</sub></sub> and M<sub>PO<sub>4</sub></sub> are molar mass of ortho-phosphate and ammonia, respectively.

### 3. Results and discussion

#### 3.1. Phosphorus and ammonium recovery efficiency

Fig. 1(a) shows the final pH, the measured the removed percentage of TSP after experimenting time with different molecular ratios of Mg<sup>2+</sup> to PO<sub>4</sub><sup>3-</sup>, and different magnesium ion sources. It also shows that, the pH in mixed solutions are stable in all beakers, range between 8 and 9, it was suitable for forming of struvite MAP [25], the P recovery increased from less than 20% to more than 90%. The pH shifted to lower values for an increase of the Mg<sup>2+</sup> to PO<sub>4</sub><sup>3-</sup> molar ratio from 0.08 to 5.26, the level of pH depended on the Mg<sup>2+</sup> to PO<sub>4</sub><sup>3-</sup> molar ratio due to struvite precipitation and similar to Korchef et al., 2011 [26].

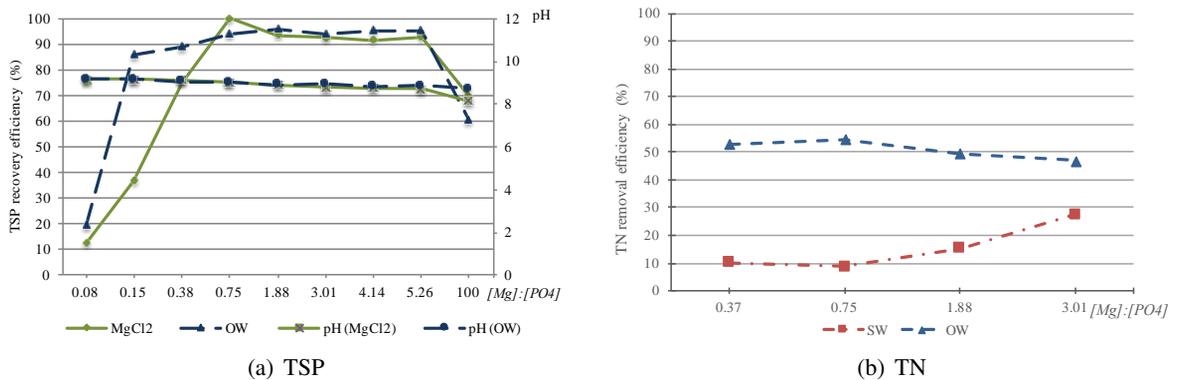


Figure 1. Recovery efficiencies of “MgCl<sub>2</sub> solution” to be comparable with “OW”

Fig. 1(a) also shows that, a decreasing trend was observed in TSP removal as Mg to P molar ratio increased, although, TSP removal was approximately constant between 0.75 – 5.26. Mg-to-PO<sub>4</sub> molar ratio of 0.38 and 5.26 to 1.0 removed up to 90% TSP, similar to previous studies on P recovery reported by [27], at Mg to PO<sub>4</sub> molar ratios of 1.15 and 5.48 phosphorus removal increased from 70% to more than 95%, and P removal did not increase significantly at higher Mg-to-PO<sub>4</sub>. I was consistent with the result by [27] in which the P removal efficiencies even decrease impressly at Mg-to-PO<sub>4</sub> molar ratio of 100. With the same molar ratios of Mg-to-PO<sub>4</sub>, the removal efficiency in experiment which added MgCl<sub>2</sub> solution is little higher than experiment with OW, it can be impacted by present of calcium ion to form of precipitation MAP, similar to previous study reported by Hao et al. [24].

At Mg-to-PO<sub>4</sub> molar ratio of 100, P removal efficiencies in series A, C achieved the same results of 60.6% and 60%, respectively. At Mg-to-PO<sub>4</sub> molar ratio of 0.38 and 3.01 TN removal efficiencies are much lower than TSP one, for the experiment seri D, Fig. 1(b) showed only slight ammonium removals of 10.1%, 8.6%, 15.4% and 27.5%, respectively. It can be caused by Mg<sup>2+</sup> that could favor the formation of hydroxyapatite (HAP- Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) and K-struvite (MgKPO<sub>4</sub> · 6 H<sub>2</sub>O).

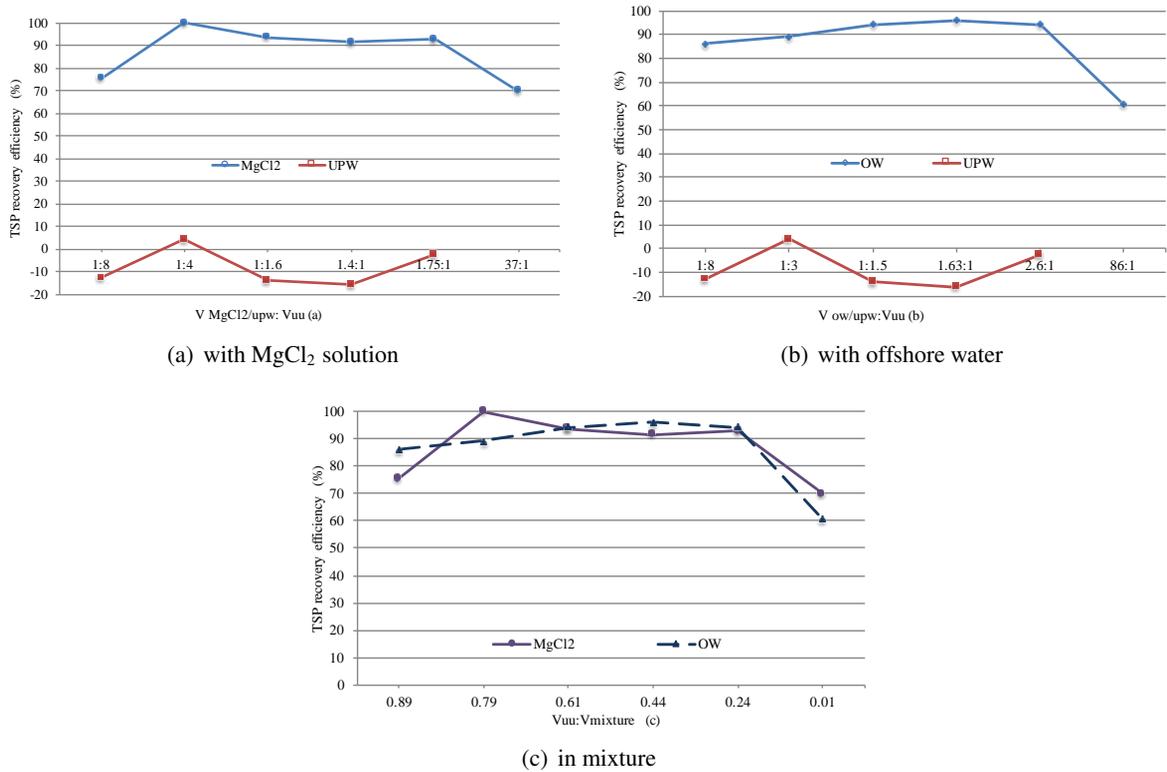


Figure 2. Relationship between TSP recovery efficiencies and volume ratios of UU and diference magnesium ion sources

Fig. 2 shows that, the precipitation did not happen when added ultrapure water into UU, even it makes present solid in UU to dissolve into solution. In experiment B, TSP concentration in the final solution was higher than initial one so almost TSP removal efficiencies of Seri B below zero, was observed indicating that no P precipitates would form in the absence of Mg or Ca (Table 2). The results in (c) in mixture Fig. 2 confirm that offshore water can be an effective precipitant for urine P precipitation. As long as volume ratio UU fraction is between 24% and 61%. However, at 99% UU fraction, the efficiency dropped to only 60%, due to insufficient Mg<sup>2+</sup> and Ca<sup>2+</sup>. According to the stoichiometric ratio of P to Mg in MAP, the maximum ratio of UU to OW should be 4.7 for complete P recovery, corresponding to an 83% UU fraction. On the other hand, excessive dilution of UU by OW also leads to reduction of the P recovery, in mixture of UU and MgCl<sub>2</sub> solution, OW, UU fraction to 1% reduced the P recovery to 60% and 70%, respectively. Moreover, when the P concentration is relatively low, calcium and carbonate may complete against magnesium and phosphate for site in MAP crystal structures, thus hindering the effective crystal growth [28]. In summary, with Vietnamese specific condition of nutrition and OW characteristic, in high urine P recovery efficiency can be

achieved when 24 – 79% UU fraction is applied in mixture of UU and OW.

All the previous experiment were performed with magnesium ion sources taken from synthetic substance. To validate the obtained results with urine and seawater with lower salinity which populate in most areas Vietnamese island, the experiment was carried out using urine and real seawater taken from the beach of Cat Ba island (Seri D). Thus, the Mg to P molar ratios result for highly phosphorus recover of 0.38, 0.75; 1.88; 3.01; 4.14; 5.26 were selected (Table 4). Fig. 3 shows the same result with previous experiment with synthetic subsance, phosphorus recovery efficiencies were still high, ranging between 90% and 100%. The final concentrations of soluble phosphate were below 100 mg/l (Table 5). However, it is still higher than Vietnamese standard level of QCVN 14/2008 on wastewater quality, accepting Mg to P molar ratio of 5.26. This result was much lower than experiment results with chlorine magnesium solution and synthetic offshore water. It certified that a big amount of phosphorus ion was precipitated with present calcium ion in seawater, similar to the study [29].

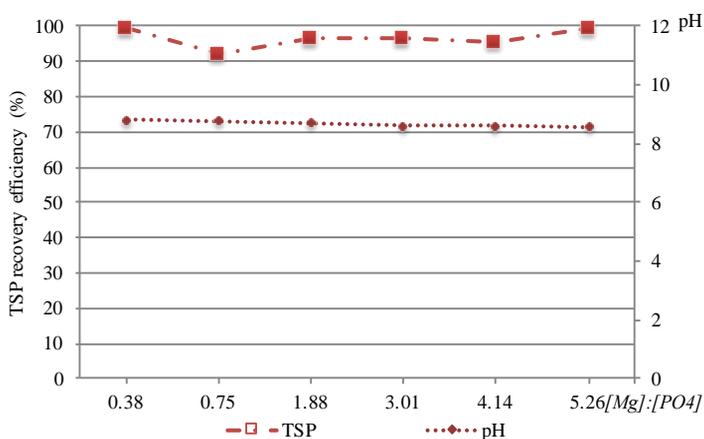


Figure 3. TSP recovery efficiencies in the mixture of urine and real seawater

After experimenting time, the final solution contains high concentration of total nitrogen (Table 5), it shown that, struvite forming process gave low nitrogen recovery, similar results with previous study [30] and [31]. Moreover, Maurer et al. [32] investigated compositon of urine in difference urine collection systems, there is much more ammonium than phosphate present in urine on a molar basis. As a consequence, about 3% of the nitrogen can be eliminated by magnesium addition only so that the effect on the pH value is small [32]. Etter et al. [12] had shown the similar results, the recovery of ammonium through struvite precipitation may be only 5% and other macronutrients may not be recovered; the authors, using the case of study of Nepal also emphasized that the struvite allows harnessing only 13% monetary value of urine as a fertilizer.

### 3.2. Struvite Precipitation characteristic

The result has been shown in Fig. 4 an observation, comparatively, the recover efficiency of precipitant achieved the highest result with precipitation of mixture of UU and SW, it happened in almost range of Mg to P molar ratios. Maximum amount of precipitant was observed with the mixture solution of UU and SW at Mg to P molar ratio of 5.26 (40 mg/ml UU), while UU-Mg solution and UU-OW achieved maximum precipitate recoveries of 8 and 26 mg/ml UU at Mg-P molar ratios of 3.01 and 100, respectively.

Table 5. Nutrien concentration in final solution

[Mg]:[PO <sub>4</sub> ]	0.08	0.15	0.37	0.75	1.88	3.01	4.14	5.26	100
Seri A	A4	A5	A6	A7	A8	A9	A10	A11	A12
TSP final (mg/l)	1939	1364	493	0	88	84	80	59	18
T-N final (mg/l)			6250	5300	4000				
Seri C	C4	C5	C6	C7	C8	C9	C10	C11	C12
TSP final (mg/l)	1181	194	129	55	24	25	16	13	7
T-N final (mg/l)	3000		5000	3867	2700	2067			
Seri D			D6	D7	D8	D9	D10	D11	
TSP final (mg/l)			9	72	17	11	12	2	
T-N final (mg/l)			3216	2350	1183	692			

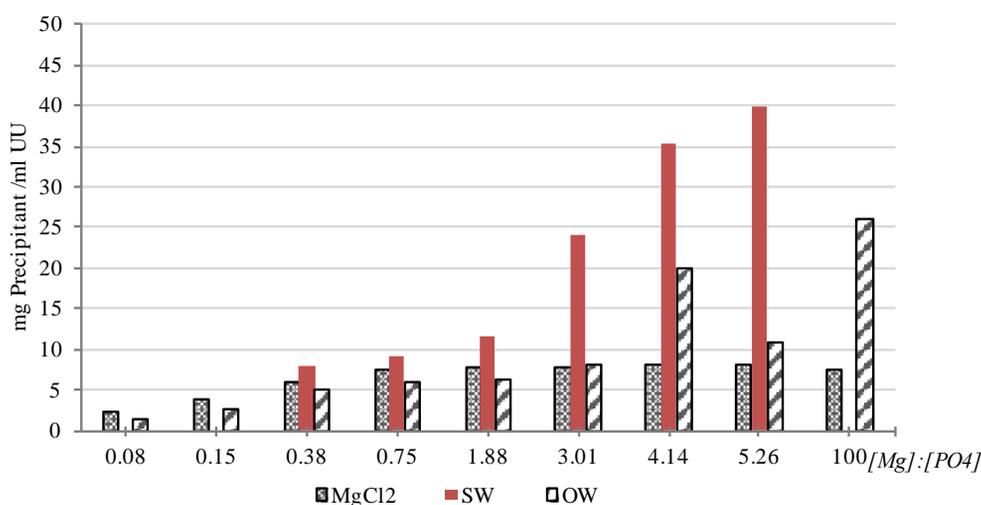


Figure 4. Struvite recovery efficiencies

Urine and seawater mixtures contain various ions such as Mg<sup>2+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>) sulphate) (SO<sub>4</sub><sup>2-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>) potentially resulting in the formation of diverse precipitates and possible impurities. Characterization of these precipitates is thus deemed necessary in order to confirm the potential use of MAP products produced from a system as a P fertilizer. Hence, the precipitates from UU and OW/SM mixtures with different volumetric ratios were characterized.

Comparatively, the composition of the precipitates formed in the mixtures of OW and SW with difference urine fraction (Seri A, Seri C, Seri D) at Mg to P molar ratios of 0.38, 0.75, 1.88 and 5.26 are shown in Table 6. The precipitate forming in mixture of UU and 20 mM magnesium solution (A7, A8) has PO<sub>4</sub> to NH<sub>3</sub> molar ratios were 1:1 approximately, similar to the stoichiometric. While, the amount of PO<sub>4</sub> content of precipitant was higher than NH<sub>3</sub> content, indicating some of P in the mixture of OW and SW precipitated out as calcium and magnesium ion to form MKP (magnesium kali phosphate) and HAP (hydroxyapatite – Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) [18, 33].

With the same of Mg to PO<sub>4</sub> molar ratio of 1.88 in mixtures of A8, C8, D8 beakers, mixture in A8 had N content higher than C8 and D8 respectively, indicating that, the present of other ion in

Table 6. Struvite precipitate characteristic

	[Mg]:[P]	[PO <sub>4</sub> ]	[NH <sub>3</sub> ]	Molar ratio in precipitate
C6	0.38	0.00014	0.00011	1.24
D6	0.38	0.00022	0.00021	1.05
A7	0.75	0.00027	0.00025	1.07
C7	0.75	0.00010	7.353E-05	1.46
D7	0.75	0.00011	0.00009	1.26
A8	1.88	0.00024	0.00021	1.10
C8	1.88	0.00013	8.82353E-05	1.50
D8	1.88	0.00017	0.00011	1.58
C11	5.26	0.00099	0	
D11	5.26	0.00009	0	

OW/SW impacted to form struvite. A lower UU fraction reduce contents in the struvite in the urine and OW/SW mixtures (Table 6), at Mg to P ratio of 5.26 there is not any N contents in the precipitate, indicating of the precipitate exists forming of calcium or/and magnesium compound.

#### 4. Conclusions and recommendations

Urine from eco-san toilet which is the urine diverting dry toilet can be used for recover nutrient high nutrient content of slow release fertilizer under crystal forming (MAP, MKP, HAP...). By this way, it can help for easier storage and transportation.

Ureolysed urine with high pH (8-9) creates optimal condition in mixture of urine and seawater for the phosphorus precipitation.

Adding of magnesium ion into ureolysed urine to achieve Mg to PO<sub>4</sub><sup>3-</sup> molar ratio between 0.75 and 5.26 can recover more than 90% of phosphorus.

The ion source from offshore water can give phosphate recover efficiencies of 89.04; 94.1; 95.86; 94.06; 95.25; 95.31% at offshore water to ureolysis urine 0.33; 0.65; 1.63; 2.6; 3.58; 5.56 :1, respectively. According to above result, the phosphorus recover rate was highest result when volumetric ratios of offshore water to UU were 0.65: 1 or 5.56:1.

The increasing of Mg to P molar ratio decreases MAP content in precipitate. Mg to P molar ratios of 0.38, 0.75, 1.88 will precipitate struvite with high MAP content, while there is not any MAP content in precipitate when this ratio is 5.26. The crystallized precipitate should be filtered then dried in atmosphere condition before storage and enduse.

Seawater also can be used as a source of ions (magnesium and calcium) for struvite precipitation for recover phosphorus from urine which collected from dry eco-san toilet. Phosphate removal efficiencies of 99.31; 92.01; 96.49; 96.5; 95.25; 99.26%, achieved at seawater to ureolysis urine volumetric ratios of 0.67; 1.3; 3.2; 5; 7; 9:1, respectively.

The highest recover efficiency of phosphorus had been achieved when volume ratios of seawater to UU were 0.67:1 or 9:1. Resulting that, the coastal areas can use seawater to add to urine tank with volumetric ratio above to recover/precipitation of phosphorus for reuse as fertilizer.

Nitrogen recover efficiency stopped at low level. The highest remove rate of nitrogen was 30% and 50% in mixture of UU and SW/OW, respectively, indicating that, the further step need to be executed to

recover nitrogen in the solution which phosphate been recovered, before discharging to water recourse. Removing of nitrogen by adsorption can be potential way.

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