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Effect of Organic Matter on Struvite Precipitation of Phosphorus Contained in Tapioca-starch Wastewater

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ABSTRACT

Phosphorus (P) recovery receives more attention as a means to curb water pollution caused by discharge of nutrient-laden effluent. This study was conducted so as to investigate the effect of organic matter on P recovery from raw tapioca-starch wastewater and anaerobically-digested effluent. With total COD of 17,907 mg/L, 40 mg P/L, molar ratios of Mg:Ca = 0.4:1 and Mg:N:P = 0.4:17:1, P precipitation in raw starch wastewater was found to be impeded, resulting in low P recovery efficiency of 18.2, 23.4 and 40.4% at pH = 7, 9 and 11, respectively. This may be due to low concentrations of Mg and P available for the precipitation reaction as they were bound in the organic solids. In the anaerobically-digested effluent with total COD of 4,181 mg/L, 68.mg P/L, the molar ratio of Mg:N:P was found to be 1.5:11.8:1, leading to increased P recovery efficiency of 56.5, 83.5 and 91.2% at pH = 7, 9 and 11, respectively. Overall, findings of this study reveal that the anaerobically-digested effluent is preferable to raw starch wastewater for P recovery since most P and other relevant precipitating ions (Mg^{2+} and NH_4^+) are liberated from organic solids and are readily available for chemical precipitation. Consequently, struvite precipitates formed could be used to produce a good-quality product as slow release fertilizer.

Keywords : chemical precipitation; struvite; magnesium ammonium phosphate;
tapioca starch wastewater; organic matter

INTRODUCTION

Phosphorus (P) is essential to life on Earth and frequently limits the productivity of ecosystems, including agricultural productivities. Thailand is an agriculture-based country of which a large proportion of population predominantly derives their livelihood from agricultural sectors. Chemical fertilizers including nitrogen (N), phosphorus (P), and potassium (K) are, hence, one of important factors to achieve high crop yield and their import from abroad is continuously increasing. The world's phosphate rock, which is used as raw materials for the production of P fertilizer, is decreasing and thus becoming urgent environmental, economic and societal issues for the countries without its reserve, like Thailand. Currently, scientists focus on the problem of decreasing and deteriorating phosphorus resources, leading to lost phosphorus reserves in the future. It has been predicted that phosphate rock reserves could become depleting within 100 years [1-3]. Thus, alternative and renewable sources of P need to be sought, especially by recovery and recycling from wastewater. As such, significant actions must be focused on phosphorus recovery rather than its removal.

Cassava is one of the most important economic crops in Thailand. The agro-processing industry transforms agricultural harvest, such as tapioca root, into starch power. In the tapioca starch production process, large amounts of water are used to remove sand, impurity and other solids, resulting in wastewater discharged with high organic matter. The anaerobic process is normally used to treat tapioca starch wastewater as to convert organics into biogas, which is further recycled as fuel to be used in starch manufacturing process [4]. However, anaerobic digester's effluent still has nutrients beneficial to plants, including nitrogen and phosphorus, which can be recovered through chemical precipitation and adsorption, to produce P-containing precipitates such as struvite and hydroxyapatite. Among these, struvite ($MgNH_4PO_4 \cdot 6H_2O$) is a crystalline substance consisting of magnesium, ammonium, and phosphorus in equal molar concentrations. It is a slow-releasing fertilizer that provides plants the nutrition elements without burning the root [5]. In Thailand, however, very few studies concerning P recovery from tapioca starch wastewater have been carried out. In this study, hence, precipitation experiments were conducted so to gain more knowledge on P recovery in the form of struvite and other P containing solid precipitates. With the addition of magnesium compounds, effect of organic matter on struvite formation in tapioca starch wastewater would be evaluated.

METHODOLOGY

Struvite Precipitation

Tapioca starch wastewater used in this study came from the General Starch Limited (GSL) factory located in Nakhon Ratchasima Province, Thailand. The experiments were conducted with influent and effluent of the Anaerobic Digester (AD). Prior to experimentation, the samples were preserved by acidifying to pH of 1.5-2.0 with concentrated H_2SO_4 and stored at 4°C in the refrigerator. Two types of sample used in the precipitation experiments were filtered and unfiltered as to investigate the effect of organic solids on P precipitation efficiency. Sample filtration was carried out, using filter paper with 10 μm pore size (Whatman Grade No. 93). Precipitation-influencing parameters studied include organic solids, pH, and molar ratios of Mg:P. In precipitation test, 400 mL was added to a 1,000-ml beaker and pH was controlled at predetermined values of 7, 9 and 11, using droplets of 1 M NaOH solution. The Mg:P ratio was determined from stoichiometric calculation considering the initial concentration of AD's influent and effluent. As magnesium was the limiting element in the influent, a concentrated solution of Mg was added to achieve the desired Mg:P molars ratio of 1.1:1 and 2:1, using $MgCl_2 \cdot 6H_2O$. After blended, samples were stirred continuously with jar testers, using two different mixing speeds: flash mixing (coagulation) at 200 rpm for 15 min and slow mixing (flocculation) at 75 rpm for 30 min. Flowchart of the experimental scheme is summarily shown in Figure 1.

Prior to liquid withdrawal for parameter analyses, samples were allowed to settle for 60 min so as to separate the crystallized precipitates. The supernatant was then filtered through 10 μm paper filter. Afterwards, filtrates were analyzed to determine the concentrations

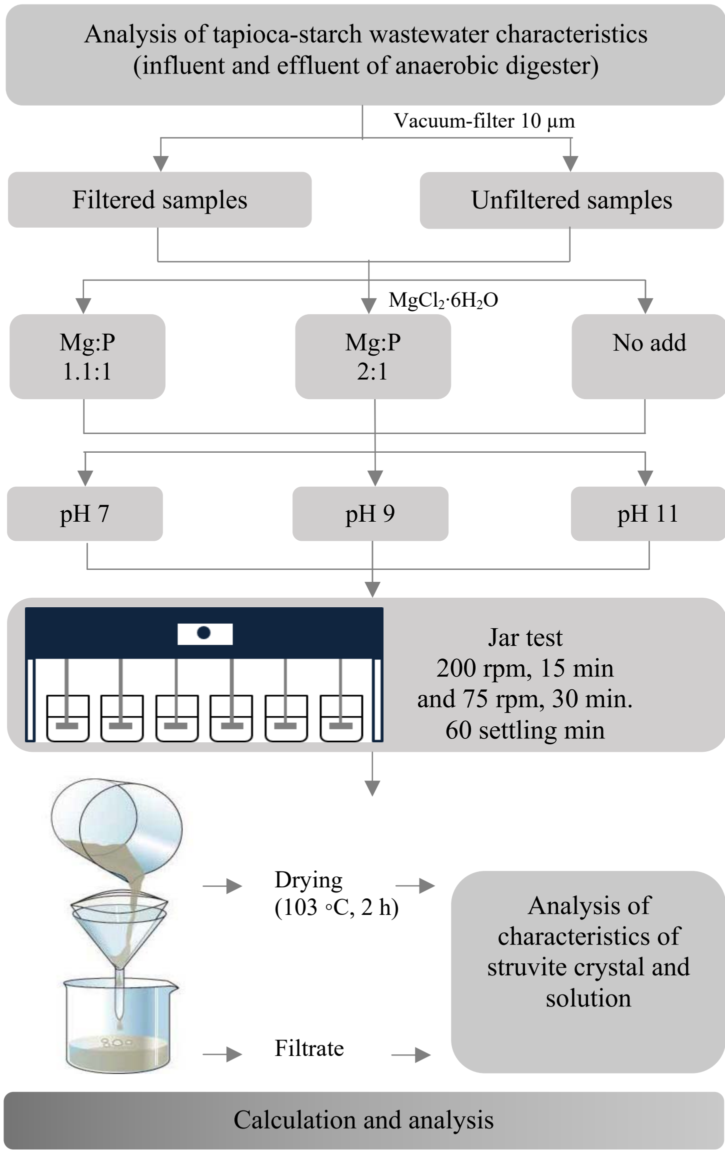

Figure 1 Flowchart of the struvite experiment

of TDS, TKN, NH_4-N, TP, PO_4-P, Mg^{2+}, Ca^{2+}, Fe^{2+}, and COD. Precipitate solids were dried at 103°C for 2 h, prior to analyses for the concentrations of TP, Mg^{2+}, Ca^{2+}, and Fe^{2+}. All parameters were evaluated following the standard Methods [6]. Total phosphorus (TP) was measured using the sulfuric acid-nitric acid digestion method and the resultant orthophosphate was determined with the spectrophotometer using Standard Method 4500-P, vanadomolybdophosphoric acid colorimetric method with UV-visible spectrophotometer. Calcium, ferrous and magnesium ions were analyzed with flame atomic absorption spectroscopy according to Standard Method 3111. NH_4-N was analyzed from filtrate sample; while organic nitrogen plus ammonium nitrogen were determined together as total TKN from unfiltered sample by a digestion and distillation using Standard Methods 4500-N_{org}. Total solids (TS), total suspended solids (TSS) and volatile solids (VS) were determined using Standard Method 2540. The size and morphological characteristics of struvite sample was examined, using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). All experiments were carried out in triplicate -at ambient temperature (25-30°C).

RESULTS AND DISCUSSIONS

Tapioca-starch Wastewater Characterization

Characteristics of the AD’s influent and effluent are shown in Table 1. The AD’s influent (raw tapioca starch wastewater) was characterized by pH being acidic with low P and Mg levels, about 40.3 mg P/L and 12.4 mg Mg/L. During anaerobic digestion, major parts of the organic P and Mg were released as a consequence of decomposition of organic matter [7]. With pH being rather basic, P and Mg concentrations were increased to 68.4 mg /L and 78.4 mg /L respectively. After all, around 58% of the total phosphorus was present as orthophosphate (PO_4^{3-}), having concentration 41% higher than that of influent. AD’s influent and effluent were both filtered so to obtain filtrate samples as to avoid interferences with precipitation reactions and observe purity of struvite solids formed. As illustrated in Table 1, the differences of TSS and VSS concentrations in unfiltered AD’s influent and effluent imply that TSS of AD’s influent was in the form of organics (98%), while 28.5% of effluent TSS belonged to inorganics, indicating that chemical precipitation reactions had occurred in the AD tank. These are consistent with TP concentrations in unfiltered and filtered samples (Table 1) of which organic P was converted to ortho-P and then precipitated, resulting in 44% reduction of TP concentration in AD's effluent samples.

Struvite Precipitation Reaction

From the wastewater’s constituents shown in Table 1, two significant precipitation reactions that would occur are written as follows.

Hydroxyapatite (HAP); log K_{sp} @ 25 °C = -59.63

$$Ca_5(PO_4)_3OH_{(s)} \leftrightarrow 5Ca^{2+} + 3PO_4^{3-} + OH^- \quad (1)$$

Magnesium Ammonium Phosphate (MAP, struvite); log K_{sp} @ 25 °C = -13.26

$$MgNH_4PO_{4\,(s)} \leftrightarrow Mg^{2+} + NH_4^+ + PO_4^{3-} \quad (2)$$

Setting molar concentration of P as 1.0, the molar ratios of constituents pertaining to the above precipitation reactions were computed as summarized in Table 2. Molar concentrations of N were found to be over sufficient to precipitate as MAP. Based on solubility products, however, P will react firstly with Ca to form HAP. After Ca is used up, then it will with Mg and N to form MAP.

AD’s influent samples - filtered and unfiltered - were brought to precipitation experiments at pH = 7, 9, and 11. As illustrated in Figure 2, both cases provided low P recovery with the efficiency ranging between 15 to 40%. This indicates that the precipitating solids would predominantly be HAP as struvite formation was inhibited when molar ratio of Mg:Ca was 1:2 [8-9]. Also previously mentioned in tapioca-starch wastewater characterization, most P and Mg were bound in organic colloids. This resulted in less amounts of reactants to further precipitate after Ca was completely reacted. Percentage of P in solids was thus found to be very low of about 0.3% (Table 3). In case of filtered sample, too low amount of solid precipitate was produced about 20 mg/L as depicted in Table 3, thereby causing the determination of %P in solids not possible.

Table 1 Characteristics of tapioca-starch wastewater

	Influent of AD		Effluent of AD	
	Unfiltered	Filtered	Unfiltered	Filtered
pH	2.9 - 3.5	-	6.8 - 7.5	-
TS (mg/L)	8,773	4,870	7,781	2,797
TSS (mg/L)	4,597	697	5,680	343
TDS (mg/L)	4,176	4,173	2,101	2,454
VS (mg/L)	6,813	3,127	4,343	703
VSS (mg/L)	4,503	-	4,063	-
COD (mg/L)	17,907	14,053	4,181	336
TKN (mg/L)	308.5	-	366.8	-
NH_4-N (mg/L)	-	132.1	-	211.9
TP (mg/L)	40.3	30.7	68.4	42.8
PO_4^{3-} (mg/L)	22.5	22.5	39.6	39.6
Mg^{2+} (mg/L)	12.4	9.8	78.4	62.8
Ca^{2+} (mg/L)	54.1	45.4	32.2	25.8
Fe^{2+} (mg/L)	4.3	2.5	0.1	ND

Table 2 Molar ratio of constituents in AD's influent and effluent

Molar Ratio		Mg	N	P	Ca
Influent of AD	Unfiltered	0.4	16.9	1.0	1.0
	Filtered	0.4	9.5	1.0	1.1
Effluent of AD	Unfiltered	1.5	11.8	1.0	0.4
	Filtered	1.9	10.9	1.0	0.5

Since AD's influent sample showed the deficit of Mg for struvite crystallization, the reagent of $MgCl_2 \cdot 6H_2O$ was added to the filtered samples to reach Mg:P ratios of 1.1:1 and 2:1 in the precipitation experiments at pH = 7, 9, and 11. Figure 3 shows the highest P recovery efficiencies of 71.4% and 75.3% occurred at pH = 11 for Mg:P ratios of 1.1:1 and 2:1, respectively. Compared to that of unfiltered samples, higher P in solids was achieved although solid precipitates were generated low of about 400 mg/L (Table 3). This indicates that removal of organic solids may help improve the quality of P-containing solids harvested [10].

Results of precipitation experiments at pH = 7, 9, and 11 for AD's effluent samples - filtered and unfiltered – were summarily illustrated in Figure 4. AD was found to help liberate P and Mg bound in organic solids contained in the starch wastewater, resulting in Mg:P ratios of 1.5:1 and 1.9:1 for unfiltered and filter samples, respectively. Such these ratios were favorable for struvite formation without any external Mg addition. Moreover, as Ca:P was lower than 1 (Table 2), the low Ca concentrations might be the consequence of calcium carbonate ($CaCO_3$(s)) precipitation, thereby resulting in higher TSS concentration in AD's effluent than that in AD's influent. Comparison of precipitating solids produced from unfiltered and filtered sample shown in Figure 4 and Table 3 reveals that although filtered samples gave much lower solids concentration than did unfiltered samples, %P in solids obtained from filtered samples was found to be much higher, about 8% P, which is comparable to that of commercial single superphosphate fertilizer. Based on cost of chemical addition and maximum % P in solids, the optimum pH for P recovery from AD's effluent was found to be 9, which is consistent with that of previous studies [11-14].

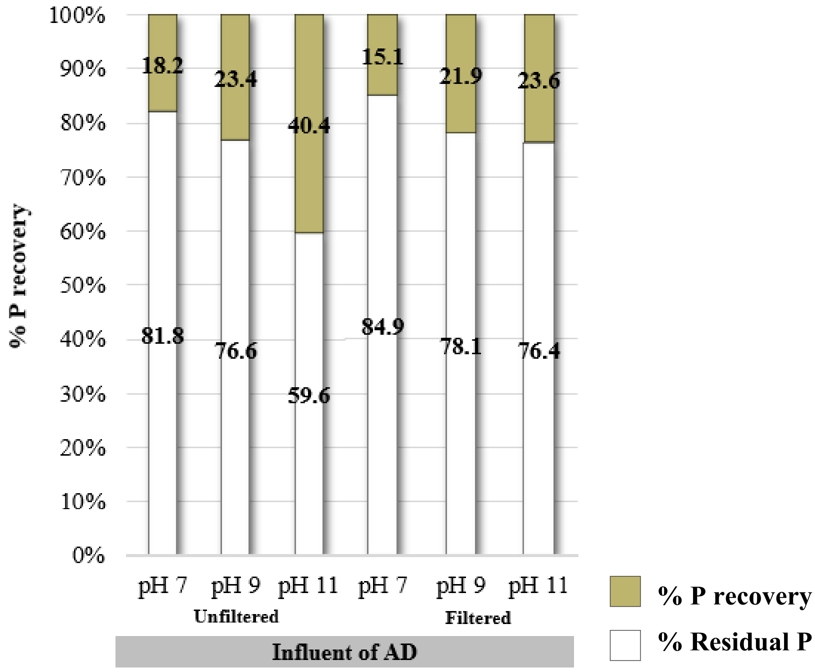

Figure 2 P recovery efficiency from AD's influents (unfiltered and filtered)

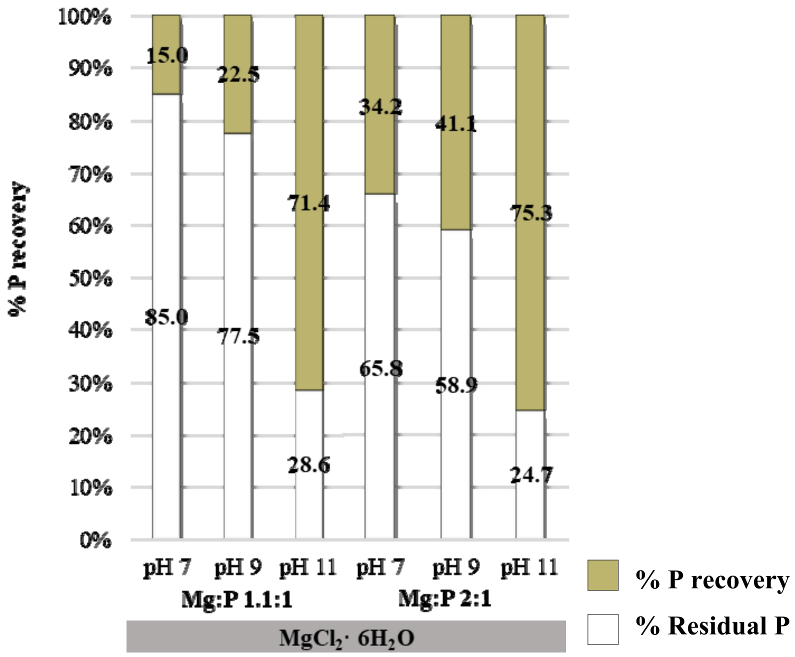

Figure 3 P recovery efficiency from AD's filtered influents with the addition of $MgCl_2 \cdot 6H_2O$

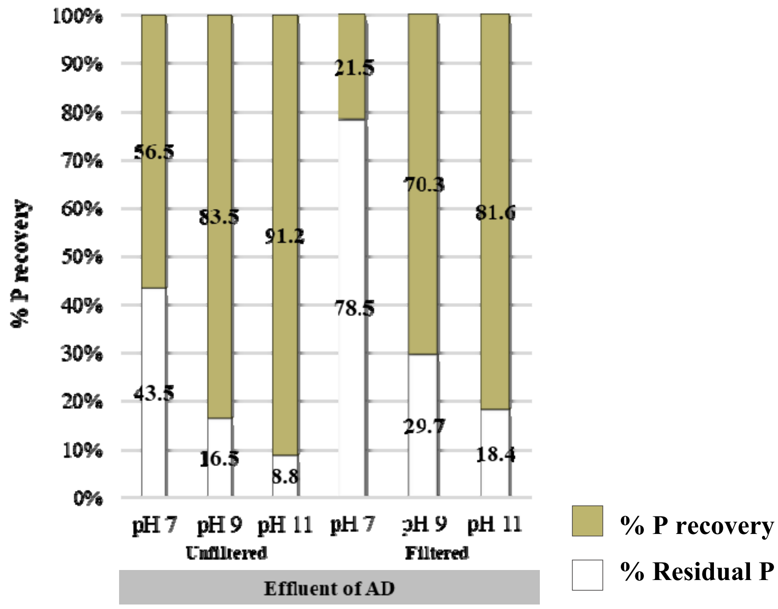

Figure 4 P recovery efficiency from AD's effluents (unfiltered and filtered)

Table 3 Solid precipitates and %P in solids

Sample		$MgCl_2$ added	Solids (g/L)			% P in solids		
			pH 7	pH 9	pH 11	pH 7	pH 9	pH 11
AD's influents	unfiltered	no add	3.44	3.88	3.91	0.31	0.36	0.35
	filtered	no add	0.31	0.36	0.35	-	-	-
	filtered	Mg:P 1.1:1	0.40	0.43	0.47	1.27	2.13	5.06
		Mg:P 2:1	0.35	0.38	0.43	2.58	3.04	5.33
AD's effluents	unfiltered	no add	5.14	5.13	5.48	0.63	1.01	0.97
	filtered	no add	0.07	0.22	0.33	5.68	8.27	6.75

CONCLUSION

AD's influent and effluent of tapioca-starch wastewater were used to study struvite precipitation in laboratory. Characterization of both samples revealed that AD's influent with Mg:P = 0.4:1 was not favored for struvite formation, resulting in low P recovery efficiency. However, AD was found to help liberate P and Mg bound in organic solids, thereby giving the effluent with Mg:P favorable for MAP crystallization and subsequently resulting in higher P recovery efficiency. Overall, results of this study suggest that struvite recovery be carried out from AD's effluent at pH = 9 so as to produce a good-quality slow-release fertilizer with high percentage of P comparable to commercial single superphosphate fertilizer.

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