JARQ 35(4), 271 – 276 (2001) http://www.jircas.affrc.go.jp

Concentrations and Crystallization of Phosphate, Ammonium and Minerals in the Effluents of Bio-Gas Digesters in the Mekong Delta, Vietnam

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Abstract

The concentrations of PO_4-P, NH_4-N and certain minerals (Mg, Ca, K, Cu, Zn) in effluents of bio-gas digesters were determined in 6 swine farms in Tan Phu Thanh and Hoa An villages in Can Tho Province, Vietnam, for the evaluation of water pollution from swine husbandry with the incorporation of a bio-gas digester into the farming system. Phosphate, NH_4-N, Mg and Ca occurred at high concentrations in the effluents. However, the phosphorus and nitrogen balance associated with the cycling of the components in the farming system was considered to be satisfactory, because the total volume of effluents was small compared to the area of the ponds and rivers where the effluents were discharged. It was demonstrated that sludge in a bio-gas digester contains high concentrations of P, Mg and Ca, which are considered to be effective fertilizers. Artificial crystallization reactions (MAP and HAP reactions) were examined for the effluents of the bio-gas digester with the pH adjusted by NaOH to confirm the possibility of removing and recovering PO_4-P, Mg and Ca from the effluent. Because of the high density of crystals, the components could be removed and recovered easily by sedimentation.

Discipline: Animal industry / Agricultural environment
Additional key words: MAP, magnesium ammonium phosphate, struvite, HAP, hydroxyapatite

Introduction

In the Mekong Delta of Vietnam, farming systems combining crop production, animal husbandry, aquaculture and horticulture are being implemented. These systems are linked to each other through the use of by-products from one component to other components, and are considered to exert a beneficial effect on material cycling. Bio-gas digesters have been incorporated into such farming systems to produce bio-gas (methane) as fuel from animal excreta (Fig. 1)[5]. Recently, the economy of Vietnam has markedly improved under the "Doi Moi" policy implemented since 1985, and farming systems in the Mekong Delta have also undergone changes. For example, some swine farmers have increased the number of animals, and fed them with imported concentrates for effective fattening. Therefore, it is necessary to pay more attention to the material flow in order to maintain the sustainability of the farming systems in the Mekong Delta[6, 11, 12]. Especially, analysis of the flow and control of phosphorus are considered to be important, because a large amount of rice bran with high phosphorus content is fed to swine in this area[7] (Table 1).

For controlling the amount of phosphorus in wastewater, 2 phosphate crystallization reactions, MAP (magnesium ammonium phosphate: struvite) reaction (1), and HAP (hydroxyapatite) reaction (2) can be used as follows[4]:

(1) $HPO_4^{2-} + NH_4^+ + Mg^{2+} + OH^- + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O$ (MAP) $\downarrow + H_2O$;

(2) $6HPO_4^{2-} + 10Ca^{2+} + 8OH^- \rightarrow Ca_{10}(OH)_2(PO_4)_6$ (HAP) $\downarrow + 6H_2O$.

The studies reported were conducted in Can Tho University, Vietnam, 20 Feb. 2001 – 6 Mar. 2001 within the framework of the collaborative research project titled, "Development of new technology and their practice for sustainable farming systems in the Mekong Delta" between Can Tho University and JIRCAS.

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Received 2 May 2001, accepted 1 June 2001.

Table 1. Average composition of diet for swine in Vietnam

Ingredients	Composition[a)]	Dry matter[b)]	Content[b)]		
	%	%	P (dry %)	Mg (dry %)	Ca (dry %)
Vietnam[7)]					
Broken rice	43.0	86.2	0.33	0.09	0.03
Rice bran	45.7	88.0	2.34	0.97	0.03
Commercial Protein Concentrate	10.0	88.9	0.97	0.40	3.97
Oyster shell ground	1.0	99.6	0.07	0.30	38.10
Premix	0.3	87.8	0.07	0.09	0.04
Total	100.0	87.43	1.32	0.53	0.86
Japan[10)]					
Total	100.0	87.48	0.66	0.17	0.86

a): Composition is indicated in % on an air dry matter basis.
b): Broken rice, rice bran and oyster shell ground were cited from reference[1)].
Commercial Protein Concentrate and Premix were actually analyzed.

Phosphate in raw swine wastewater[10)] and anaerobic digested swine wastewater[3,13)] could be crystallized with these reactions under alkaline conditions (pH >7.7)[10)].

In the present study, the concentrations of PO_4-P, NH_4-N and minerals (Mg, Ca, K, Cu, Zn) in the effluents of a bio-gas digester were determined in 6 swine farms in Tan Phu Thanh and Hoa An Villages in Can Tho Province, Mekong Delta, for the evaluation of water pollution associated with swine husbandry with the incorporation of a bio-gas digester. Artificial crystallization reactions were then performed in the effluents of the bio-gas digester under high pH conditions, by the addition of NaOH to confirm the possibility of removing and recovering PO_4-P, Mg and Ca from the effluents.

Materials and methods

1) Swine farms for study and sampling

The studies were carried out in 4 swine farms in Tan Phu Thanh Village and 2 swine farms in Hoa An Village, both located in Can Tho Province in the Mekong Delta. As shown in Table 2, all of these farms used a bio-gas digester and produced bio-gas from swine manure. Well water (pumped up from a depth of approximately 90 m) or canal water was used for drinking water of swine and for washing out swine barns. In every farm, a large amount of rice bran was fed to swine. The effluents of the bio-gas digester, the well water or canal water for drinking and washing, and the sludge at the bottom of the bio-gas digester (Fig. 1), were collected in each farm.

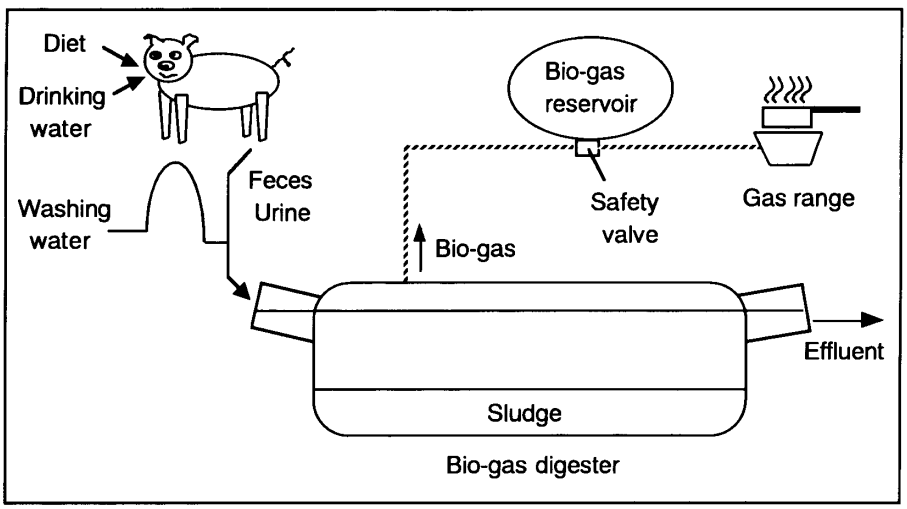

Fig. 1. Bio-gas digester system in Mekong Delta, Vietnam

Table 2. Characteristics of farms for study

Farm No.	1	2	3	4	5	6
Location (village)	Tan Phu Thanh	Tan Phu Thanh	Tan Phu Thanh	Tan Phu Thanh	Hoa An	Hoa An
Date of sampling	26 Feb. 2001	26 Feb. 2001	26 Feb. 2001	26 Feb. 2001	26 Feb. 2001	26 Feb. 2001
Type of bio-gas digester	Plastic	Concrete	Plastic	Concrete	Plastic	Plastic
Gas use	Kitchen	Kitchen	Kitchen	Kitchen	Kitchen	Kitchen
Water for swine	Well water	Well water	Well water	Well water	Canal water	Well water
Depth of well (m)	96	>70	98	No data	–	90
Year of well digging	1996	1995	No data	No data	–	No data
Breed of swine	Large White	Large White	Large White	Large White	Large White	Large White
Number of swine						
Mother sow	2	1	0	4	3	4
Fattening (fat.)	2	5	3	20	5	0
Piglet	8	0	0	0	1	25
Total	12	6	3	24	9	29
Diet for swine (kg/swine/day)						
Rice bran	1.25	0.67	2.0	No data	3.0(sow), 2.0(fat.)	2.5
Broken rice	1.25	0.5	–		–	0.5
Fish meal	–	0.05	–		–	–
Bone meal	–	–	–		–	Small amount
Rice wine waste	–	–	2.0		–	–
Kitchen waste	–	–	–		2.0(fat.)	–
Vitamin-premix	–	–	–		–	Small amount
Concentrate	0.5 (sow and fat.)	0.08 (sow and fat.)	0.2 (sow and fat.)		–	1.0 (sow)
<Feeding>	<3 times/day>	<2 times/day>	<3 times/day>		<2 times/day>	<3 times/day>
Vegetables	Water spinach Sweetpotato	Water spinach	Water spinach		Wild vegetables	Wild vegetables
	0.5(total)	0.5	1.7		2.0	2.5(preg. sow) 5.0(milk. sow)
<Feeding>	<1 time/day>	<1 time/day>	<1 time/day>		<1 time/day>	<2 times/day>

2) Chemical analysis

As a proportion of the PO_4-P, NH_4-N, Mg and Ca in the effluents was considered to be already crystallized naturally, the concentrations in the soluble fraction as well as in the crystallized fraction were determined[10]. The effluent was centrifuged at 3,000 rpm for 10 min, and the supernatant was analyzed for determining the concentrations of the components in the soluble fraction. To determine the concentrations in the crystallized fraction, 5 N HCl was added to the effluent at a final concentration of 0.1 N to dissolve the crystals, and the solution was mixed on a vortex mixer and centrifuged at 3,000 rpm for 10 min after being allowed to stand for 30 min. The supernatant was analyzed for the determination of the concentrations of the components in the soluble and crystallized fractions, and the concentration in the crystallized fraction was calculated as the difference between these amounts. The concentrations of the components in the soluble fraction only were determined in the well and canal water. To determine the concentrations of the components in the sludge of the bio-gas digester, the sludge was digested with nitric acid[2], and then analyzed. The concentrations of PO_4-P, NH_4-N, Mg, Ca, K, Cu and Zn were measured using standard methods[2].

3) Artificial crystallization of effluents

Effluents from farm 1 and farm 5 were used for the artificial crystallization experiment. Ten percent NaOH solution was added to the effluents to adjust the pH to 8.5. Samples were collected 15 min after pH adjustment, and then the concentrations of the soluble and crystallized forms of PO_4-P, NH_4-N, Mg and Ca were deter-

Table 3. Concentrations of components in effluent of bio-gas digester

(mg/L)

Components	Farm 1	Farm 2	Farm 3	Farm 4	Farm 5	Farm 6
Crystallized PO_4-P	3	0	0	0	11	1
Soluble PO_4-P	116	114	33	93	153	68
Total PO_4-P	119	114	33	93	164	69
Crystallized NH_4-N	20	9	1	9	5	3
Soluble NH_4-N	447	262	36	339	319	459
Total NH_4-N	467	271	37	348	324	462
Crystallized Mg	1	2	1	1	5	2
Soluble Mg	72	92	62	59	98	175
Total Mg	73	94	63	60	103	177
Crystallized Ca	4	0	0	0	3	0
Soluble Ca	68	57	56	62	75	147
Total Ca	72	57	56	62	78	147
Soluble K	271	166	64	215	401	546
Soluble Cu	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
Soluble Zn	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
pH	6.9	7.0	6.9	7.2	6.8	6.9

mined using the methods described above.

Results and discussion

1) Effluent of bio-gas digester

As shown in Table 3, the effluents contained high concentrations of PO_4-P, NH_4-N, Mg and Ca, and most of the components occurred in a soluble form. All the 6 farmers fed swine on a large amount of rice bran (Table 2) that contained high concentrations of P (2.34% dry matter) and Mg (0.97% dry matter)[1)](Table 1), which may account for the high concentrations of PO_4-P and Mg in the effluents. High concentrations of Mg and Ca were considered to be derived from well water. Most of the swine farmers used well water for drinking water for swine and washing out swine barns (Table 2). This well water contained high concentrations of Mg and Ca (Table 4). The high concentrations of NH_4-N were considered to be due to the presence of NH_4-N in the urine excreted by the swine and to the production of NH_4-N resulting from organic matter decomposition during methane fermentation under anaerobic conditions. The K concentrations were also high, whereas Cu and Zn could not be detected in the effluents. The pH of the effluents ranged between 6.8 and 7.2.

As described above, the concentrations of PO_4-P, NH_4-N, Mg and Ca in the effluents of the bio-gas digester were high, but the total volume of effluents was small.

Table 4. Concentrations of components in water for swine

(mg/L)

Components	Farm 1 Well water	Farm 2 Well water	Farm 3 Well water	Farm 4 Well water	Farm 5 Canal water	Farm 6 Well water
Soluble PO_4-P	0.10	0.12	0.07	0.18	0.18	0.04
Soluble NH_4-N	1.19	0.95	1.22	1.26	0.12	2.94
Soluble Mg	24	33	36	23	11	64
Soluble Ca	31	50	48	31	6.5	203
Soluble K	5.6	6.8	8.9	6.6	4.2	17
Soluble Cu	<1.0	<1.0	<1.0	<1.0	<1.0	1.2
Soluble Zn	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
pH	6.8	7.2	6.8	6.9	6.3	6.6

Table 5. Concentrations of components in sludge of bio-gas digester
(mg/g dry matter)

Components	Farm 1	Farm 2	Farm 3	Farm 4	Farm 5	Farm 6
Total P	17.6	18.4	15.5	10.8	5.9	16.9
Total Mg	12.1	7.4	3.7	3.7	5.5	9.3
Total Ca	36.2	39.7	29.3	25.3	7.2	26.8
Total K	4.7	1.8	1.5	1.8	5.1	5.9
Total Cu	0.64	0.12	0.24	0.11	0.03	0.39
Total Zn	1.52	0.42	0.65	0.32	0.20	0.93

The ponds and rivers where the effluents were discharged are so large[6,12], that the phosphorus and nitrogen balance associated with the cycling of the components in the farming systems was considered to be satisfactory presently. However, in future, should the number of swine increase considerably, the balance may not be maintained and it will be necessary to implement measures to maintain the sustainability of the farming systems in the Mekong Delta.

2) Sludge in bio-gas digester

Some farmers in the Mekong Delta utilize the sludge in the bio-gas digester for farmland fertilizer after drying. Therefore, the concentrations of P, Mg, Ca, K, Cu and Zn in the sludge were determined. As shown in Table 5, the sludge in the bio-gas digester contained high concentrations of P, Mg and Ca, and was considered to be an effective fertilizer. The concentrations of Cu and Zn were not appreciably high. Cu and Zn included in the commercial concentrate diet to comply with swine nutritional requirements are known to be pollutants when discharged into the environment. This aspect should be kept in mind, should the amount of commercial concentrate diet for swine increase in future.

3) Artificial crystallization reaction

Effluents of the bio-gas digester contained high concentrations of soluble forms of PO_4-P, NH_4-N, Mg and Ca, and the mole ratio of these components was deemed suitable for the MAP and HAP crystallization reactions. For example, in the case of the effluent from farm 5, mole concentrations of soluble PO_4-P, NH_4-N, Mg and Ca were 4.8, 22.8, 4.1 and 1.9 mmol/L, respectively, and the mole ratio was 1.0 : 4.8 : 0.9 : 0.5. Since MAP crystal, for example, was formed by the reaction of PO_4-P, NH_4-N and Mg[4] at equal molarity, the effluents were assumed to be suitable for crystallization. Merely by increasing the pH of the effluents, most of the soluble forms of PO_4-P, Mg and Ca can become crystallized, since crystallization reactions occur under alkaline conditions[3,10]. Attempts were made to develop an artificial crystallization reaction in the effluents of the bio-gas digester from farm 1 and farm 5 by the addition of NaOH to increase the pH to 8.5. The changes in the concentrations of soluble and crystallized forms of PO_4-P, Mg and Ca before and after pH adjustment are indicated in Fig. 2a,b. Most of the components which occurred in a soluble form before pH adjustment, were converted into a crystallized form.

These results indicated that crystallization of PO_4-P, Mg and Ca in effluents of a bio-gas digester could be achieved. Due to the high density of the crystals (density of MAP was 1.71 g/cm^3 [8]), they could be removed and

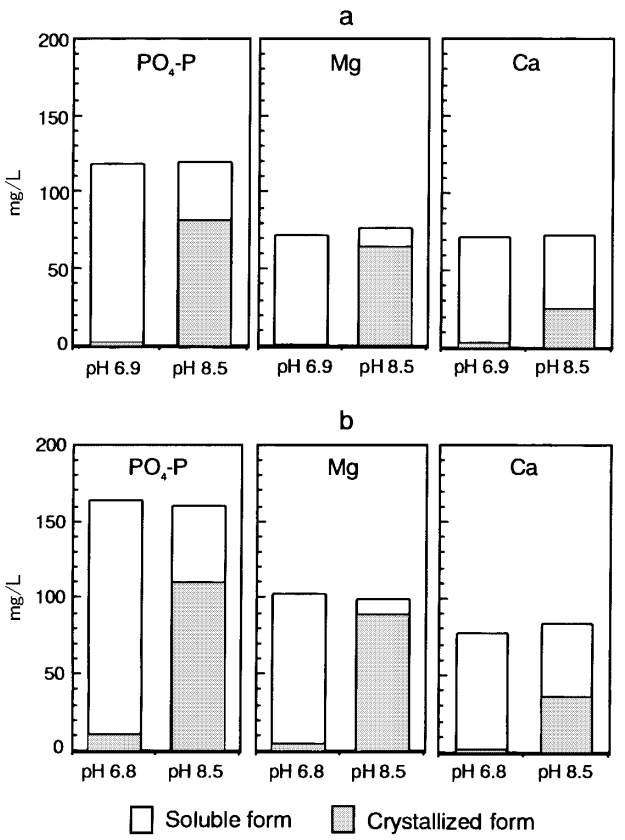

Fig. 2. Crystallization of PO_4-P, Mg and Ca in the effluent of a bio-gas digester in farm 1 (a) and farm 5 (b), by the addition of 10% NaOH solution for adjusting pH to 8.5

recovered easily by sedimentation. The crystals could then be used on farmland as fertilizer after drying, since MAP is known to be a fertilizer[9]. In the present studies, alkali was added to adjust the pH, but other methods could be used for pH adjustment as well. If the crystallization technology were to be applied in Vietnam, most suitable methods for pH adjustment for that country should be selected. Since Vietnam imports all of the phosphorus required, if phosphorus could be recovered from the effluents of bio-gas digesters, a small amount of phosphorus could be imported. Although presently, the phosphorus balance in the farming systems is satisfactory, in future, the balance may not be maintained. In that case, the phosphate crystallization method could become one of the technologies that may enable to maintain the sustainability of the farming systems in the Mekong Delta.

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