REVIEW

The Technology of Phosphorous Removal and Recovery from Swine Wastewater by Struvite Crystallization Reaction

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Abstract

Swine wastewater has a high potential for phosphorous recovery in Japan. The pH of swine wastewater increased up to approximately 8.5 with continuous aeration, and a large part of the soluble PO_4-P, Mg and Ca was crystallized. A reactor for removing and recovering phosphorous from swine wastewater was designed with a dual function i.e., crystallization through aeration, and separation of formed struvite by settling. However, a dehydration, composting and characterization process was first needed before using sediment sludge, including struvite, on farmland, since it will settle along with huge amounts of other suspended solids (organic matter). For the recovery of pure struvite, an accumulation device was designed and its efficiency was examined. During submergence in the aeration column of the demonstration reactor, struvite cross-bridged and it accumulated on the face of the device. The struvite could be scraped off easily with only a light brushing, and was found to be approximately 95% pure. Because this device is made of a very simple structure, it should be acceptable to swine farmers.

Introduction

All the phosphate rock Japan needs must currently be imported from abroad, because it has no subterranean phosphorous resources. Recently, the amount of imported phosphate rock has been decreasing because the United States, which accounted for approximately 40% of Japan's imports in 1990, stopped exporting it in 1995 (Fig. 1). Since this phosphorous shortage has become increasingly serious, we need to accelerate the development and establishment of the technologies for phosphorous recovery from waste and wastewater.

Phosphorous in swine wastewater within Japan

In many swine husbandry facilities in Japan, the feces, urine and washing water from piggeries are separated into solid and liquid fractions by mechanical solid-liquid separation[6]. The solid fraction is composted and utilized for farmland fertilizer. The law requires the liquid fraction (swine wastewater) to be purified through a treatment process before being discharged into public waters.

In addition to PO_4^{3-} and NH_4^+, swine wastewater also contains high concentrations of Mg^{2+} and Ca^{2+} [10, 11]. According to our estimation, approximately 13, 24 and 17% of given P, Mg and Ca amounts, respectively, were separated into liquid fractions (swine wastewater) following solid-liquid separation, when 30% of excreted feces became mixed with urine and washing water (Fig. 2). In this case, concentrations of P, Mg and Ca in liquid fractions (swine wastewater) were calculated to be 120, 63 and 210 mg/L, respectively[13].

To confirm such high concentrations of P, Mg and Ca, swine wastewater from 9 piggeries in Japan was analyzed. The above components were determined according to the standard methods[1]. Crystallized and
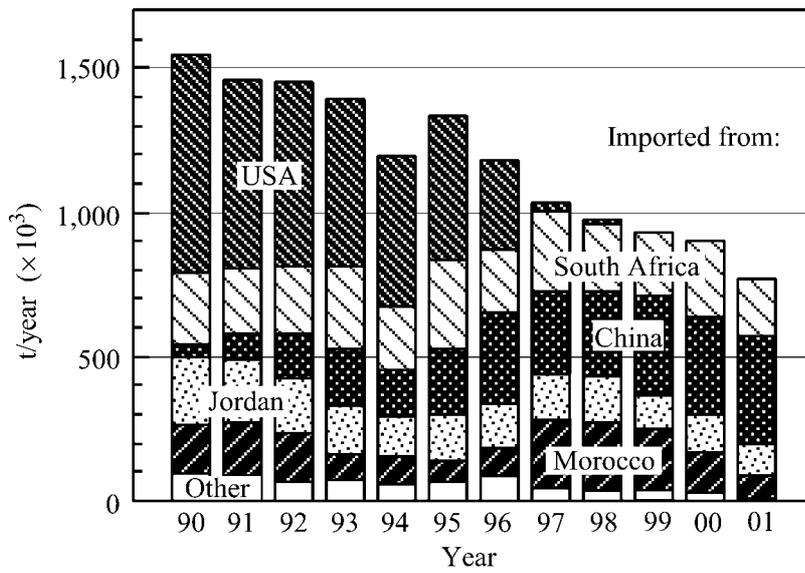
Fig. 1. Change of phosphate rock amount imported into Japan
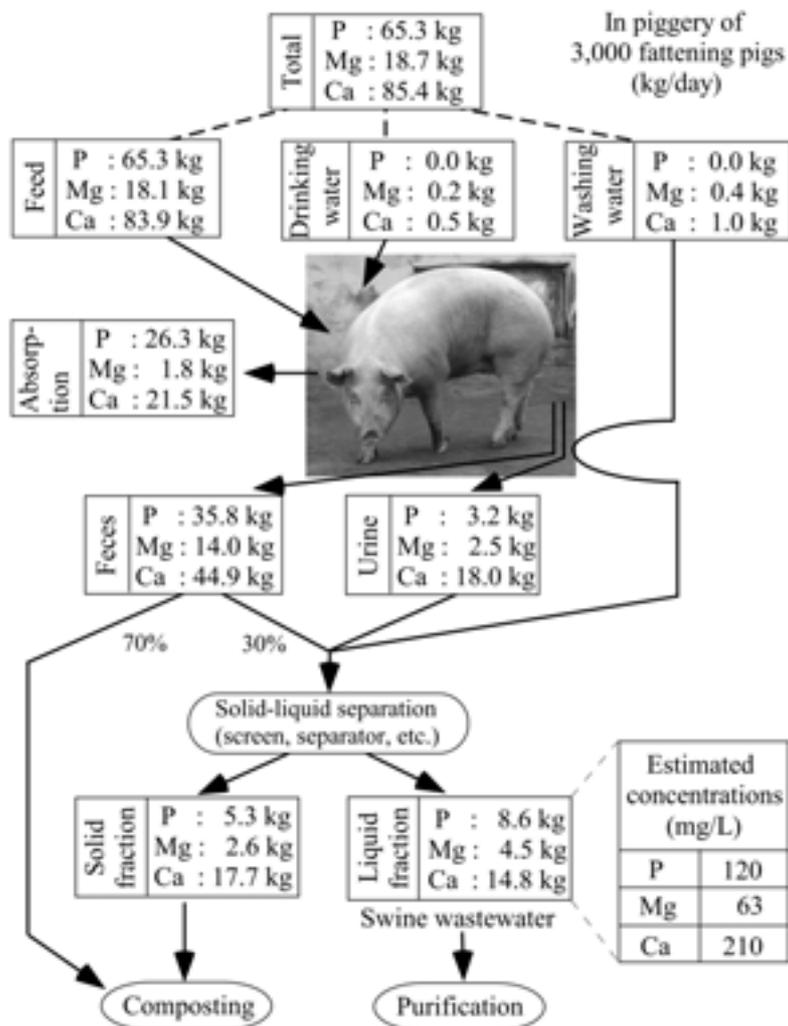
Fig. 2. Estimation of P, Mg and Ca flows in an average swine husbandry system in Japan
In this case, 30% of excreted feces became mixed with urine and washing water.

soluble components were determined by the method of Suzuki et al.[10]. As shown in Table 1, each sample of swine wastewater contains high concentrations of P, Mg and Ca with pH variations between 5.7 and 8.7. There was a tendency for much PO_4-P, NH_4-N, Mg, and Ca to exist in soluble form in swine wastewater at a relatively low pH range (5.7–7.4). Therefore, PO_4, Mg and NH_4 became crystallized, forming struvite (MAP: magnesium ammonium phosphate) when the pH of swine wastewater rose (Fig. 3). Struvite is known as a valuable slow-release fertilizer. Ca also crystallizes with PO_4 and forms, for example, hydroxyapatite (HAP)[13]. These phosphate crystallization reactions are accelerated when the pH of wastewater is between 8 and 9.

According to our estimation, if 30% of excreted feces would be mixed with urine and washing water, approximately 10,000 t of phosphorous would be discharged in swine wastewater every year in Japan. This amount corresponds to 7.4% of the total phosphorous in waste and wastewater (135,000 t), and 1.46% of the total

phosphorous imported (683,000 t) in 1998. Since the Kyushu and Kanto areas of Japan are home to large herds of swine, we also found the total phosphorous amount in swine wastewater to be high in both these areas (Fig. 4), confirming that they have a particularly high potential for phosphorous recovery in Japan[13].

These properties of swine wastewater lead to problems of scale in wastewater treatment plants, where crystallization reactions occur under natural conditions[3]. Scale accumulating in pipes and pumps sometimes causes serious problems at such treatment plants[4]. However, these properties of swine wastewater and crystallization reactions can also provide the technology for phosphorous removal and recovery when they are made to occur under controlled conditions.

The removal and recovery of phosphorous with crystallization reactions should be conducted during the very first stage of wastewater treatment so as to reduce the concentration of phosphorous to approximately a 50 mg/L level, thus minimizing the risk of scaling (Fig. 5).

Table 1. P, N, Mg, and Ca concentrations (mg/L) in swine wastewater from 9 piggeries in Japan

Components		Swine wastewater from 9 piggeries (a-i)								
		a	b	c	d	e	f	g	h	i
P	Crystallized PO_4-P	25	12	12	22	31	19	208	273	149
	Soluble PO_4-P	112	217	121	161	68	34	158	40	87
	Total P	177	–	146	195	102	65	365	316	263
N	Soluble NH_4-N	90	3,780	373	543	779	153	2,722	1,430	3,026
	Total N	497	3,947	415	682	852	241	–	2,055	3,745
Mg	Soluble Mg	63	83	68	119	63	46	12	22	5
	Total Mg	80	97	75	129	66	56	187	226	156
Ca	Soluble Ca	148	88	156	136	128	84	120	84	64
	Total Ca	369	633	200	188	313	172	381	569	224
	pH	5.7	5.7	6.2	6.7	7.0	7.4	7.7	8.1	8.7

Struvite crystallization reaction
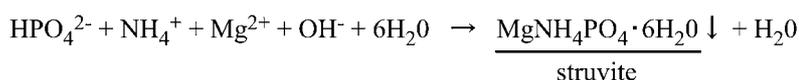
$$HPO_4^{2-} + NH_4^+ + Mg^{2+} + OH^- + 6H_2O \;\rightarrow\; \underline{MgNH_4PO_4 \cdot 6H_2O} \downarrow + H_2O$$
$$\text{struvite}$$
(MAP: magnesium ammonium phosphate)

Hydroxyapatite crystallization reaction

$$10Ca^{2+} + 2OH^- + 6PO_4^{3-} \;\rightarrow\; \underline{Ca_{10}(OH)_2(PO_4)_6} \downarrow$$
$$\text{hydroxyapatite}$$
(HAP)

Fig. 3. Phosphate crystallization reactions

Estimated total P amount
in swine wastewater
for each prefecture
(t/year)

0 - 100

100 - 200

200 - 400

400 - 800

800 -

Total 9,875 t/year

Hokkaido

553

381

244 398

Tohoku

176 224

230

220

343

651 627

39 39

Kinki 103 158 Kanto

5 22 562

Chugoku 111

74 5

39 17 14 397 171 5

32 27 98

65 43 126 Chubu

30 50 15 5

22 40 10

83

85 134 Shikoku Okinawa

196 296

Kyushu 881 300

1,335
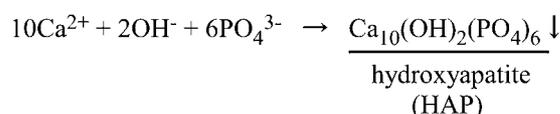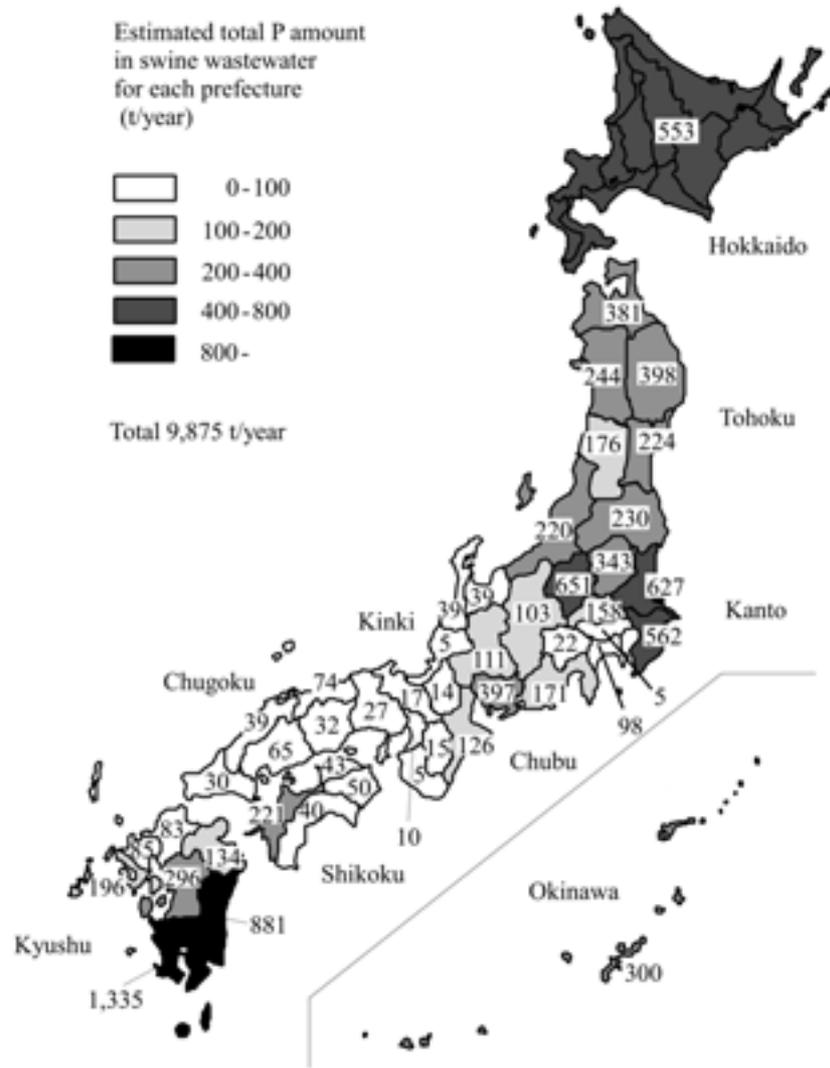
Fig. 4. Estimated total phosphorous amounts in swine wastewater for each prefecture in Japan

Crude removal of phosphorus
to decrease risk of scaling

Strict removal of phosphorus
in conformity with law

P(mg/L)
100-400

Pre-treatment

P(mg/L)
< 50

Main-treatment

Advanced treatment
(Post-treatment)

P(mg/L)
< 8

Crystallization
process

Swine
wastewater

Activated sludge
process,
UASB, etc.

Coagulation
Crystallization
Electrodialysis, etc.

Treated
water

Recovery of phosphorus
as a resource

Obtained phosphorus
(struvite, etc.)

Utilization as fertilizer
on farmland

**Fig. 5. Proposed procedures for swine wastewater treatment including phosphorous removal and recovery
(from the standpoint of phosphorus handling)**

In this case, strict removal (and recovery) of phosphorous is required after the main treatment of swine wastewater mandated by law prior to being discharged into public waters[13].

Crystallization reactor for struvite formation in swine wastewater

A reactor for removing and recovering phosphorous from swine wastewater was designed with a dual function i.e., crystallization through aeration, and separation of formed struvite by settling[12]. The pH of wastewater increases with aeration because of CO_2 stripping[2,18]. As shown in Figs. 6A and 6B, by aeration with 0.45 m³/h, the pH of swine wastewater increased from 7.0 to 8.0 in 0.5 h, and reached 8.5 at the end of the period. The concentrations of soluble PO_4-P, Mg and Ca in swine wastewater were decreased remarkably with the rise in pH. This decrease was caused by the crystallization of soluble PO_4-P, Mg and Ca. Two hours are thought to be enough of an aeration period for crystallization in swine wastewater, because the concentrations of soluble PO_4-P, Mg and Ca in swine wastewater were decreased remarkably for the 2 h after beginning aeration, but there were only minimal changes in the concentrations of these compo-

nents after 2 h. As shown in Fig. 6C, reduced aeration of 0.23 m³/h was not enough to either raise pH or crystallize PO_4-P. On the other hand, aeration as high as 1.11 m³/h would induce high pH (8.7), but the efficiency of PO_4-P crystallization was almost the same as for the case of aeration with 0.45 m³/h. Therefore, aeration with 1.11 m³/h would be too much for efficient PO_4-P crystallization[12].

This reactor, which is incorporated into the first stage of the swine-wastewater treatment process mainly to decrease the risk of scaling, can be adapted with only minor modifications to an existing primary settling tank, thus making it more readily acceptable to swine farmers.

The demonstration reactor (Fig. 7) has been operated continuously for 2 years in National Institute of Livestock and Grassland Science (NILGS: Tsukuba, Japan) using swine wastewater. Oil has been added to decrease foam formation at the aeration column. The equipment for the $MgCl_2$ additive used to increase the efficiency of struvite crystallization is optional. Figure 8 shows the transition of pH as well as the concentrations of suspended solids (SS) and phosphorous (P) during the 2-year operation of the demonstration reactor[13].

This reactor is incorporated into the pre-treatment stage of the swine-wastewater treatment process (Fig. 5), and the struvite formed will settle with other organic sus-
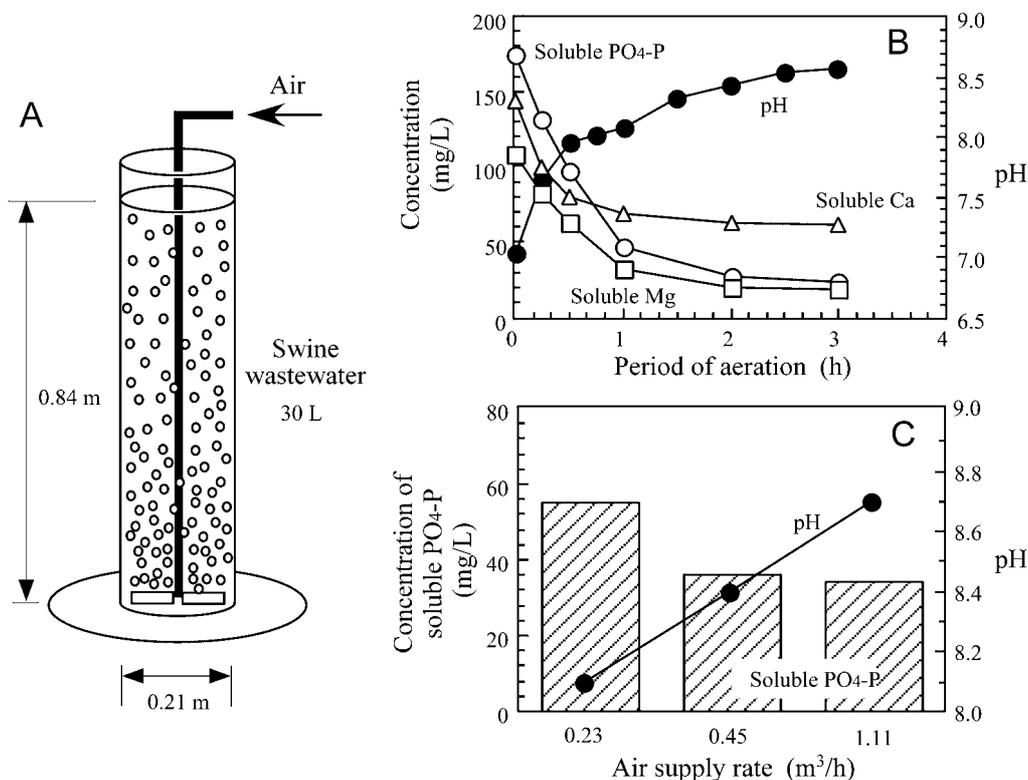
Fig. 6. Batch experiment for crystallization by aeration
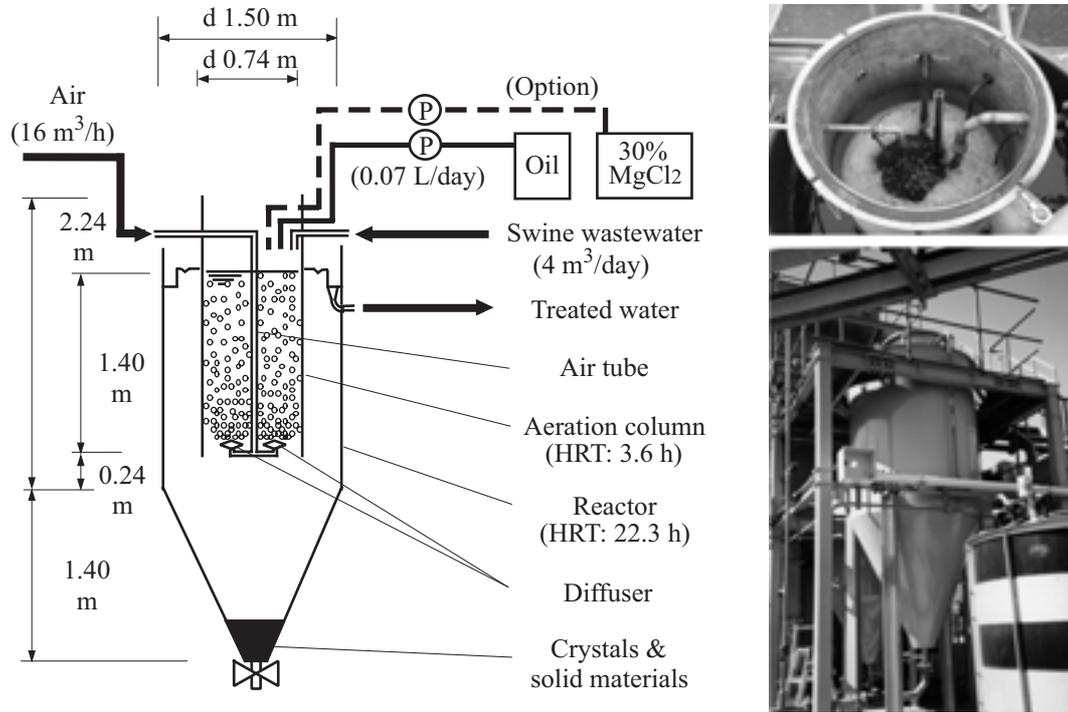
Fig. 7. Layout and photographs of NILGS demonstration crystallization reactor
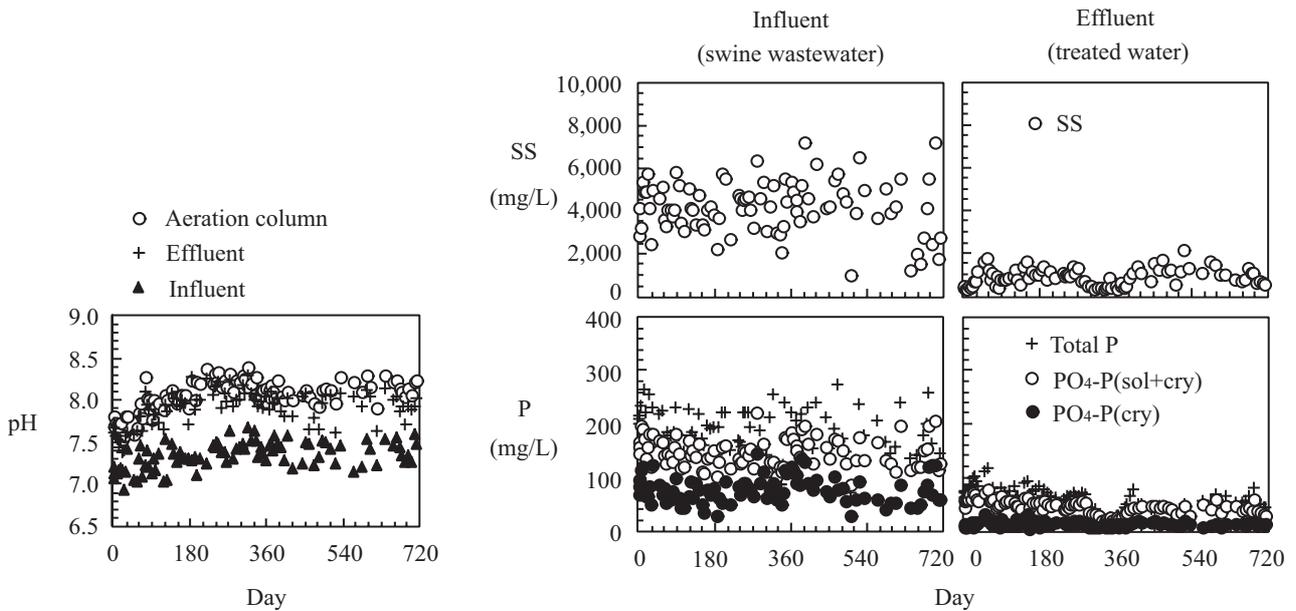
Fig. 8. Transition of parameters during a 2-year operation of demonstration reactor

Table 2. Chemical characteristics of accumulated crystals

Fractions	Components	Accumulated struvite			Struvite (theoretical)	
		mg/kg	mg/kg	mole ratio	mg/kg	mole ratio
1N HCl-insoluble (Organic matter)		47,900				
1N HCl-soluble (Struvite)		952,100				
	PO_4		366,058	1.000	388,000	1.000
	NH_4		73,800	1.064	73,000	1.000
	Mg		96,870	1.047	98,000	1.000
	Ca		167	0.001	0	0.000
	K		1,880	0.013	0	0.000
	Cu		37	0.000	0	0.000
	Zn		69	0.000	0	0.000
	Other(H_2O)		413,219		441,000	

pended solids. Therefore, a dehydration, composting and characterization process is first needed prior to applying sediment sludge, including struvite, to farmland. If struvite could be recovered as a pure, ready-to-use material, it would be advantageous for immediate application to farmland[13].

Accumulation of struvite on the surface of submerged material in the reactor aeration column

In the operation of the demonstration reactor, crystal accumulations were observed on the surface of the air tube and the inside walls of the aeration column. According to chemical analysis, these crystals were confirmed to be struvite, and were almost completely free of organic materials (Table 2). They could then be scraped off easily by merely a light brushing. This presented the possibility of recovering unadulterated struvite for beneficial application to farmland[14].

In our previous study, we reported that not only struvite, but also hydroxyapatite was formed in the aeration column[12]. Because of the low Ca concentration in accumulated crystals, the formed hydroxyapatite did not accumulate on the surface of submerged materials in the aeration column, and was thought to settle to the bottom of the reactor with organic materials. Since concentrations of K, Cu and Zn in the accumulated crystals were not all that high, there was little need to be concerned about these minerals when accumulated struvite was used on farmland[14].

To evaluate the struvite accumulation rates of each material, test specimens (plates) of aluminium, stainless
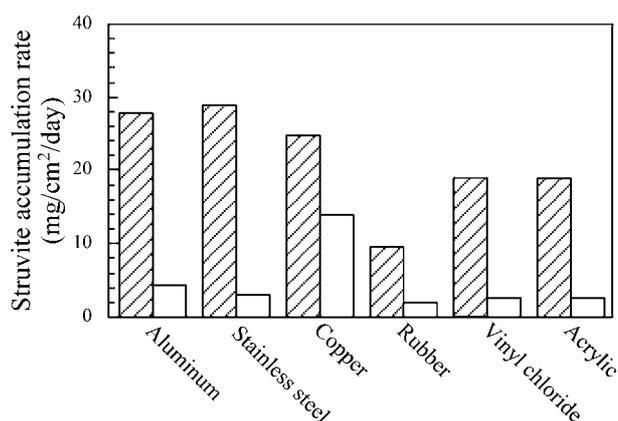
Fig. 9. Struvite accumulation rates on each material
⊞: Coarse face, ☐: Smooth face.

steel, copper, rubber, polyvinyl chloride, and acrylic were submerged in the aeration column of the demonstration reactor. To test the specimens, both coarse and smooth plates (10 cm × 10 cm × 0.3–0.5 cm each) were used, so that the difference in the struvite-accumulation rates between the two plate materials could be reported[5]. These test specimens were fixed to the inside wall of the aeration column, and removed after 34 days' submersion. As shown in Fig. 9, struvite accumulation rates on the coarse plates were higher than those on the smooth plates for every material. Higher struvite accumulation rates were observed on the coarse specimens of aluminium, stainless steel and copper than on those of polyvinyl chloride and acrylic[14]. This same accumulation tendency was also reported by Ohlinger et al.[8].
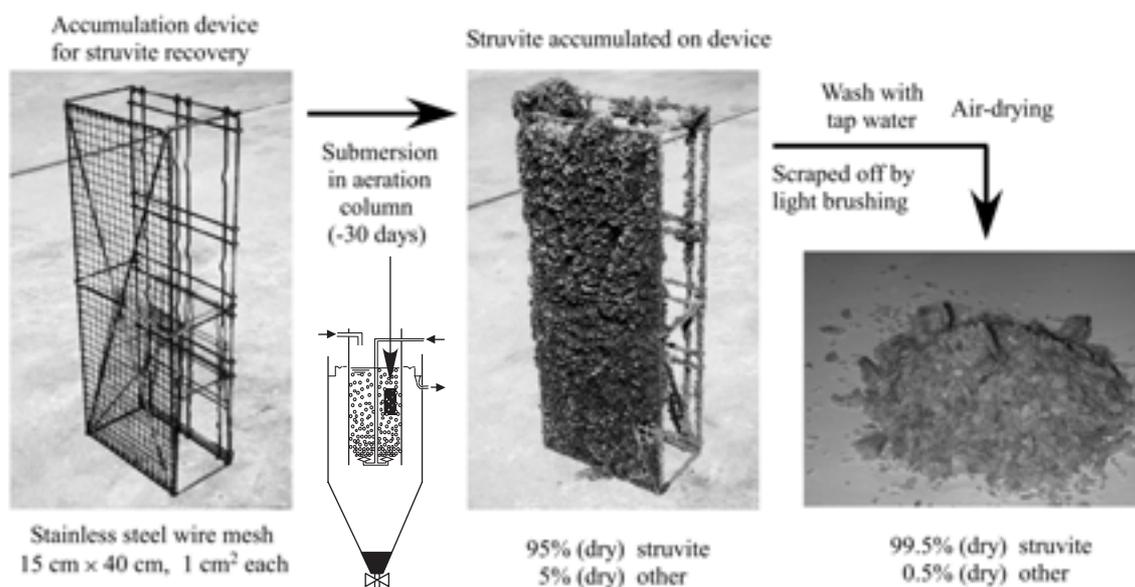
Fig. 10. Struvite recovery with experimental accumulation device

Accumulation device for struvite recovery

For the recovery of pure struvite, a customized accumulation device was designed and its efficiency examined. The experimental device has a struvite-accumulation face (15 × 40 cm) made of stainless steel wire mesh (1 mm diameter wire; 1 cm² mesh) to reduce the total weight of the device.

During the 30-day submersion in the aeration column of the demonstration reactor, 1,037 g of struvite cross-bridged on the struvite accumulation face (Fig. 10). The struvite could be scraped off easily with only a light brushing. The purity of that struvite was 95%, and it was increased to 99.5% by washing with tap water before air-drying. The recovered struvite needs only air-drying, but no dehydration, composting or characterization before use since it is approximately 95% pure even without washing. Therefore, it is ready for immediate application to farmland[14]. Experiments with a demonstration struvite-recovery device are ongoing in NILGS.

Conclusion

According to our estimation, approximately 10,000 t of phosphorous are annually discharged in swine wastewater, establishing its high potential for phosphorous recovery in our country. A reactor for removing and recovering phosphorous from swine wastewater was designed with the dual functions of crystallization through aeration, and of separation of formed struvite by settling. However, a dehydration, composting and characterization process is first needed before applying sediment sludge, including struvite, directly to farmland. For the recovery of pure struvite, a specialized accumulation device was designed and its efficiency examined. During submersion in the aeration column of the demonstration reactor, 95%-pure struvite cross-bridged to the device's accumulation face, and could be scraped off easily with only a light brushing. Since this device (stainless steel wire mesh) has a very simple structure, it should be readily acceptable to swine farmers. Recovered struvite can be used as a valuable slow-release fertilizer.

This phosphorous (P) handling technology including the suspended solids (SS) reduction effect is incorporated into the pre-treatment stage of the swine-wastewater treatment process, and can be combined with anaerobic and aerobic biochemical oxygen demand (BOD) reducing technologies such as intermittent aeration activated sludge technology[9] or UASB plus trickling filtration technology[15, 16] at the main treatment stage, it also can be combined with nitrogen (N) reducing technologies such as sulfur utilizing denitrification technology[7] or methane utilizing denitrification technology[17] at the post-treatment (advanced-treatment) stage. The concentrations of the main environmental pollution materials such as BOD, SS, P, and N in swine wastewater can be reduced by sequential combination of these treatment technologies for discharging into public water bodies.

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