



## NITROGEN AND PHOSPHORUS REMOVAL FOR SWINE WASTEWATER USING INTERMITTENT AERATION BATCH REACTOR FOLLOWED BY AMMONIUM CRYSTALLIZATION PROCESS

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**Abstract**—A process for the crystallized precipitation of ammonium by adding magnesium salt and phosphate were carried out in order to remove nitrogen and phosphorus as well as to improve the C/N ratio in swine wastewater. The optimal operation conditions were obtained as follows: reaction temperature (25°C), reaction time (1 h), pH (7.5) and the molar ratio of NH<sub>4</sub>-N:PO<sub>4</sub>-P:Mg = 1.0:0.9:0.9. Under these conditions, the maximum quantity of the crystallized precipitation occurred, the removal ratio of NH<sub>4</sub>-N increased to more than 90% and the C/N ratio increased from 1.98 to more than 8, but phosphorus was not removed. On the other hand, when the molar ratio of NH<sub>4</sub>-N:PO<sub>4</sub>-P:Mg = 1.0:0.6:0.9, the ammonium and phosphorus removal ratio would be 79.32–87.45% and 40.3–88.5%, respectively. After completion of the crystallized precipitation of ammonium, an intermittent aeration process with an aeration to anaerobic time ratio of 1:1 h is used for this improved swine wastewater (T-N/BOD = 0.14, in which BOD = 8200 mg/l, T-N = 1166 mg/l, and NH<sub>4</sub>-N = 519 mg/l). The results obtained from these experiments showed that the removal ratio of T-N and NH<sub>4</sub>-N are 91 and 99%, respectively. T-P is not removed, while the removal ratio of PO<sub>4</sub>-P is 60% when 3% CaCl<sub>2</sub> liquid is added.

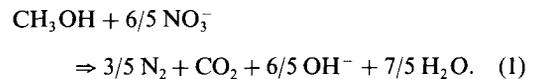
**Key words**—Swine wastewater, nitrification, ammonium crystallization, denitrification, intermittent aeration

### INTRODUCTION

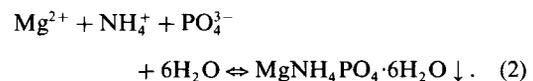
The standards of discharged livestock wastewater have been strictly set to prevent eutrophication of rivers, lakes and marshes in Japan and Taiwan. Nitrogen and phosphorus will be included among these values which are controlled by these standards in the near future. Therefore, pig farms will be forced to purify wastewater while keeping within very strict limits imposed by the law. Based on this prospect, treatment plants for swine wastewater using activated sludge after methane fermentation will be disseminated in Japan and Taiwan. These methods are effective for the removal of BOD and COD but not for nitrogen and phosphorus (Liao *et al.*, 1992). So an intermittent aeration process has been extensively studied for the treatment of swine wastewater in which the C/N ratio is low (Liao *et al.*, 1992, 1993; Liao and Maekawa, 1994).

The intermittent aeration process is a batch treatment; aerobic and anaerobic conditions are alternately repeated over a certain period. This method is especially effective for gasification of ammonium

nitrogen. But the C/N ratio of swine wastewater is generally so low that it causes a carbon source shortage requirement for denitrification. In general, methanol can serve as a carbon source in the denitrification process (Timmermans and Van Haute, 1983)



This method is very expensive. So to improve the C/N ratio, another method of removing ammonium by adding magnesium salt and phosphate to allow MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O crystallization was used. The stoichiometric equation is as follows (Shinjikken kagaku koza, 1977)



The crystallized precipitation may be dependent on the pH range of the solution, and is either acid soluble (pH < 6) or becomes Mg<sub>3</sub>(PO<sub>4</sub>) in basic solution (pH > 10). Through the crystallized treatment, the effluent was also treated by an intermittent aeration process in a batch reactor.

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## MATERIALS AND METHODS

## Synthetic wastewater

**Materials.** Potassium hydric phosphate ( $\text{KH}_2\text{PO}_4$ ) was dried for 3 h at  $105^\circ\text{C}$  in an electric dryer, and after that, a 0.1 mol./l solution is made. In addition, 0.1 mol./l solutions of  $\text{NH}_4\text{Cl}$  and  $\text{MgCl}_2$  are also separately made.

**Experimental operation.** After adjusting the pH of the  $\text{KH}_2\text{PO}_4$  and the  $\text{NH}_4\text{Cl}$  solutions using 1% NaOH solution at a selected concentration, 50 ml of each solution is added to a 500 ml flat-bottom flask and the experiments are began. The pH of the  $\text{MgCl}_2$  could not be adjusted at the selected level because of  $\text{Mg}(\text{OH})_2$  sediment while NaOH was added. Each control factor and selected level are shown in Table 1.

Experiment design of  $L_{27}(3^{13})$  is used to analyze these factors (Taguchi, 1976). Linear graphs in the orthogonal array table are used for setting each factor and the positions of their levels, and the order of the experimental operation is determined by using the method of partial execution and a table of random numbers.

## Wastewater from pig housing

**Materials.** Raw swine wastewater was obtained from the pig farm of Tokyo Yoton Agricultural Cooperative located in Iwai city, Ibaraki, Japan. After scooping up the supernatant after centrifuging the raw swine wastewater at 3000 rpm for 3 min, it was stored at  $4^\circ\text{C}$  in a refrigerator. A 100 ml sample of supernatant liquid was sampled, then 10% (mol./l)  $\text{KH}_2\text{PO}_4$  and  $\text{MgCl}_2$  solutions were separately prepared.

**Experimental operation conditions.** (a) Temperature,  $25^\circ\text{C}$ , (b) stirring speed, 165 rpm, (c) reaction time, 1 h and (d) supernatant liquid quantity, 100 ml (composition:  $\text{NH}_4\text{-N} = 2500\text{--}2600$  mg/l, and  $\text{PO}_4\text{-P} = 200\text{--}450$  mg/l).

The concentration of phosphorus ions and magnesium ions were set at 0.9, 0.8, 0.7, and 0.6 times the molar numbers with which it can completely react with ammonium in the raw swine wastewater (including the concentration of phosphorus ions in the raw swine wastewater). The pH for the entire reaction liquid was set at 7.5, 8.0, 8.5, and 9.0. An experimental design of  $L_{16}(4^5)$  was used (Taguchi, 1976). Table 2 shows the factors and the experimental levels.

**Analytical method.** Each crystallized solution of the synthetic wastewater and the swine wastewater were filtered through filter paper ( $\text{NO}_{0.5}$  Toyo Filter Paper) soon after the reaction. The concentrations of  $\text{PO}_4\text{-P}$ , Mg, and  $\text{NH}_4\text{-N}$  were measured in the solution using standard methods (APHA, 1985). The weight of the crystallized sediment on the filter paper was measured using an electronic balance (Mettler PE300) after drying at  $35^\circ\text{C}$  in an electric dryer for 24 h. The crystallized sediment from the raw swine wastewater was again dried at  $600^\circ\text{C}$  in an electric oven for 3 h, then gradually cooled it for 24 h in a desiccator. The weight was then measured to confirm the purity of the crystallized precipitate.

The chemical reaction at high temperature is shown as follows:

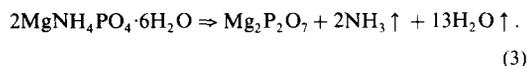


Table 1. Factors and levels set up for the crystallization of synthetic wastewater

Factor	Level		
	1	2	3
(A) Temperature ( $^\circ\text{C}$ )	15	25	35
(B) Stirring speed (rpm)	125	145	165
(C) pH (—)	9.5	10	10.5
(D) Reaction time (min)	20	40	60

Table 2. Factors and levels set up for the crystallization of ammonium in the swine wastewater

Factor	Levels			
	1	2	3	4
$\text{PO}_4\text{-P}^a$	0.9	0.8	0.7	0.6
Mg <sup>a</sup>	0.9	0.8	0.7	0.6
pH	7.5	8	8.5	9

<sup>a</sup>Stoichiometric ratio for the ammonium nitrogen.

## Intermittent aeration experiments using four types of swine wastewater

**Material and experimental operation.** Activated sludge was brought from the activated sludge plant of Tokyo Yoton Agricultural Cooperative and was incubated in a 5 l of a cylinder type reactor (Fig. 1) using a raw swine wastewater for one month at  $20^\circ\text{C}$ . Raw swine wastewater was also brought from the same place and divided into 4 samples by dilution and crystallization: (a) raw swine wastewater, (b) 3-times diluted swine wastewater diluted with pure water, (c) 6-times diluted swine wastewater diluted with pure water, and (d) supernatant liquid obtained from filtering after crystallized treatment of the raw swine wastewater. These liquids were used when the molar ratio of  $\text{NH}_4\text{:PO}_4\text{:Mg} = 1\text{:}0.6\text{:}0.9$ , and the pH of the whole liquid was 7.5. The characteristics of the swine wastewater used are shown in Table 3.

Four operations were performed in the same reactor (Fig. 1) for the working volume of 3 l. The air was supplied by a sparger at the bottom of the reactor through an intermittent air pump at the rate of 2.0 l/min controlled by an electric timer. Excess sludge was adjusted and MLSS concentration was measured once a week. The intermittent aeration time ratios of *aerobic/anaerobic* were 1/1 h and 1.25/0.75 h. 2.5 l of the supernatant was scooped out from the reactor every day at 9:45 am, and the same quantity of the swine wastewater was added into the reactor. The reactor was operated at the same conditions for one week.

**Analytical method.** The sampled effluent from the reactor was centrifuged at 3000 rpm for 3 min.  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4\text{-P}$  of the supernatant were measured every day. pH, DO and oxidation-reduction potential (ORP) were monitored throughout the experiment.  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ ,  $\text{NO}_2\text{-N}$ ,  $\text{PO}_4\text{-P}$ , T-N, T-P were analyzed by an ion chromatography (TRACCS800 Analytical Console).  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ ,  $\text{NO}_2\text{-N}$ ,  $\text{PO}_4\text{-P}$  were also checked by standard methods

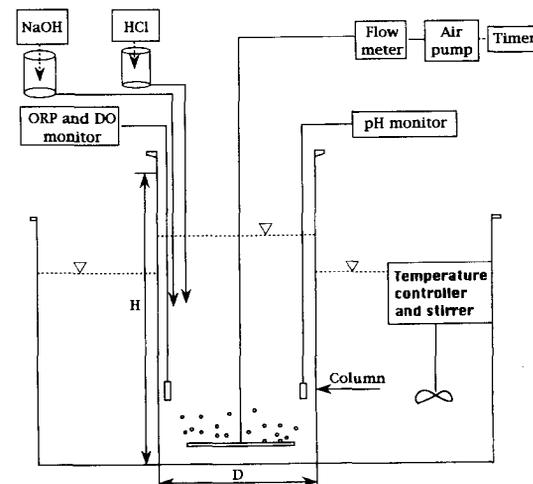


Fig. 1. Monitoring and control system of bench-scale experiment for the intermittent aeration process ( $H = 290$  mm,  $D = 165$  mm).

Table 3. The quality of swine wastewater

Items	Units	Swine wastewater (SWW)	3-times diluted SWW	6-times diluted SWW	Crystallized SWW
pH	---	8.48	8.42	8.45	7.51
BOD	mg/l	9500	3200	1600	8200
TOC	mg/l	4540	1648	866	3923
T-N	mg/l	5930	2864	2583	1166
NH <sub>4</sub> -N	mg/l	2500	830	290	519
NO <sub>x</sub> -N	mg/l	7.02	2.34	1.2	6
T-P	mg/l	360	138	158	108
PO <sub>4</sub> -P	mg/l	302	112	115	91

(APHA, 1985). TOC was measured using a TOC Analyzer (TOC-5000 Analyzer, Meishinkogyo).

### RESULTS AND DISCUSSION

The analysis results of variance for the residual NH<sub>4</sub>-N concentration of the crystallized synthetic wastewater are shown in Table 4. From Table 4, it is obvious that the reaction time (D), reaction temperature (A) and interaction among temperature (A) and pH (C) have a great influence on the residual concentration of ammonium and its removal ratio. The residual ammonium concentration has the lowest value when the temperature, time and pH were 25°C, 60 min and 10, respectively.

The longer the reaction time, the more crystallized sediment, the lower residual ammonium and phosphate concentrations were obtained, so the crystallization needs a longer reaction time than that of the operation.

Table 5 shows the analysis results of variance for the residual NH<sub>4</sub>-N concentration of the crystallized swine wastewater. From Table 5, it is clear that the initial phosphate concentration, magnesium ion and pH in the whole liquid during the reaction have a great influence on the residual ammonium ion. When the concentration ratios of the initial phosphate,

magnesium ion and pH were 0.9, 0.9, and 7.5, respectively, the residual ammonium concentration has a minimum value, and the ammonium removal ratio was 91.42–91.98% (significant level: 5%). But phosphorus could not be removed. This would occur in the raw swine wastewater, since it contains various ions, it is necessary to consider how to make those ions interact effectively, i.e. there are general rules such as the complex ion effect, common ion effect and rule of Paneth–Fajans–Hahn (Day and Underwood, 1982), and some negative ions among those in the raw swine wastewater that make insoluble ammonium magnesium phosphate more adhesive.

So, for the crystallized influent of the following intermittent aeration experiments, the molar concentration ratio of the initial phosphate to ammonium diminished from 0.9 to 0.6, that is to say, while the initial molar ratio of NH<sub>4</sub>-N:PO<sub>4</sub>-P:Mg = 1.0:0.6:0.9, and pH is 7.5, the ammonium and phosphorus removal ratio was 79.32–87.45% (significant level: 5%) and 40.3–88.5% (significant level: 5%), respectively. The T-N concentration in the crystallized swine wastewater decreased from 5930 to 1166 mg/l.

Through microscopic inspection, it was found that the diameter of the crystal grains from swine waste-

Table 4. Analysis results of variance for the residual NH<sub>4</sub>-N concentration of the crystallized Synthetic wastewater

Factor	<i>S</i>	<i>f</i>	<i>V</i>	<i>F</i>
A: Temperature	4121	2	2065.5	4.71 <sup>a</sup>
B: Stirring speed	1968.8	2	984.4	2.25
<i>e</i> <sub>1</sub>	1147.7	2	573.5	1.03 < 6.94(0.05)
C: pH	647	2	323.5	
D: Reaction time	5446	2	2723	6.224 <sup>a</sup>
A*C: Interaction of A & C	7020.5	4	1755.1	4.01 <sup>a</sup>
B*C: Interaction of B & C	5538	4	1385	3.16
C*D: Interaction of C & D	1244.6	4	311.15	
<i>e</i> <sub>2</sub>	2210.6	4	552.5	
Pooled ( <i>e</i> <sub>3</sub> )	(5249.9)	12	437.49	

<sup>a</sup> $F_{12}^2(0.05) = 3.98$ ,  $F_{12}^4(0.05) = 3.26$ .

<sup>b</sup> $F_{12}^2(0.01) = 6.93$ ,  $F_{12}^4(0.01) = 5.41$ .

Table 5. Analysis results of variance for the residual NH<sub>4</sub>-N concentration of the crystallized swine wastewater

Factor	<i>S</i>	<i>f</i>	<i>V</i>	<i>F</i>
A: concentration of phosphate ion	14181.5	3	4727.17	42.6 <sup>b</sup>
B: concentration of magnesium ion	52435.2	3	17478.4	157.6 <sup>b</sup>
C: pH	2460.2	3	820.1	7.39 <sup>a</sup>
<i>e</i>	665.4	6	110.9	
Total	69742.3	15		

<sup>a</sup> $F_3^3(0.05) = 4.76$ .

<sup>b</sup> $F_3^3(0.01) = 9.78$ .

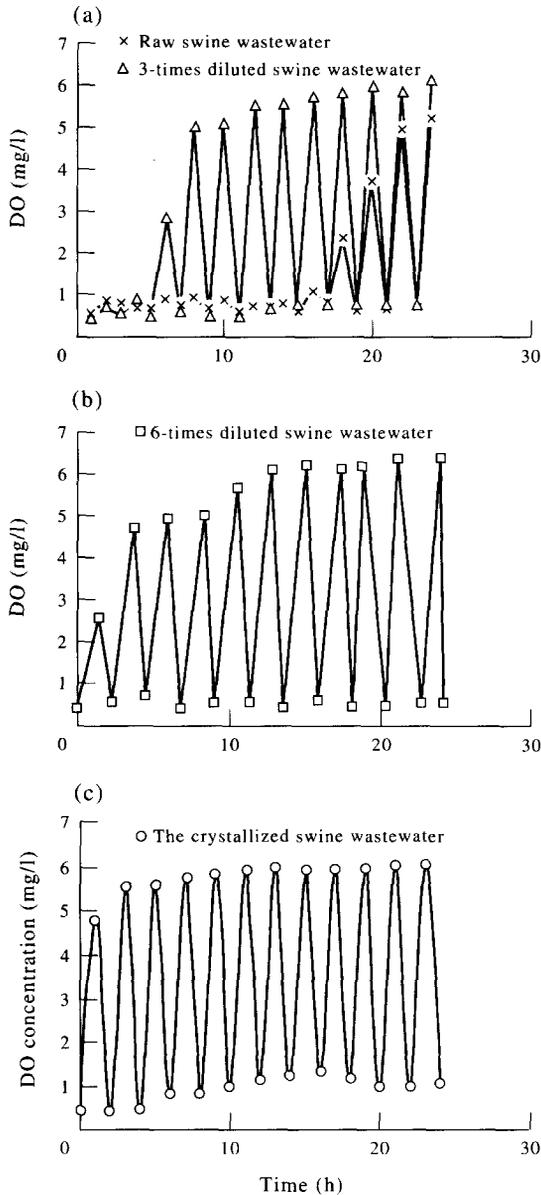


Fig. 2. The time-course changes of the DO concentrations at the intermittent time ratio of 1/1 h for the influent of (a), (c), and 1.25/0.75 h for the influent of (b).

water was smaller than that of synthetic wastewater. The reason is that swine wastewater contains various kinds of organic matter and break them into smaller pieces during stirring, such that the organic grains in the wastewater were drawn into the precipitate of the crystallized ammonium.

In these experiments, since the diameter of the precipitation obtained from raw swine wastewater were from 10 to 100  $\mu\text{m}$ , so in practice, they could be filtered by an oscillating sieve, and could be used as fertilizer.

Figure 2 shows the time-course change of the DO in the four types of swine wastewater. The time ratio of aerobic and anaerobic was 1/1 h for swine wastewater, 3-times diluted swine wastewater and crystal-

lized swine wastewater, and 1.25/0.75 h for 6-times diluted swine wastewater.

The initial DO concentration under aerobic conditions reached 1.00 mg/l after 16 h in the raw swine wastewater, but for the 3-times diluted swine wastewater, the DO concentration reached 2.00 mg/l after only 3 h. Under anaerobic conditions, the DO concentration could not reach 1.00 mg/l even after 24 h for both the raw and 3-times swine wastewater.

In the crystallized swine wastewater, the initial DO concentration under aerobic conditions was 4.79 mg/l, and then reached 6.05 mg/l after 24 h. Under anaerobic conditions, the DO concentration started at 0.43 mg/l and increased to 1.00 mg/l after 10 h, then remained at the same level. Both initial and final DO concentrations for crystallized swine

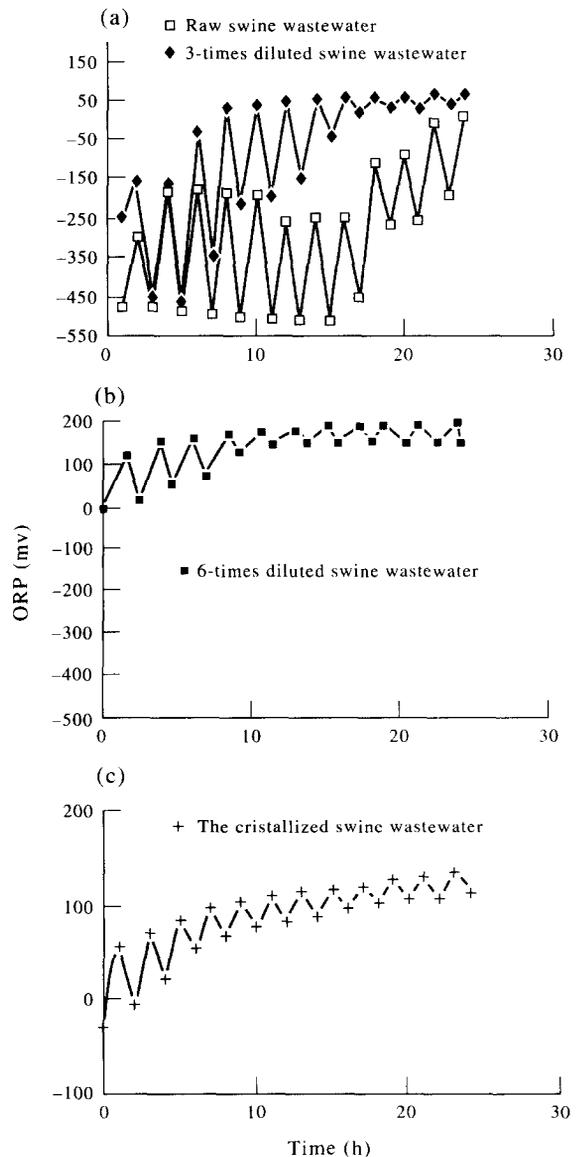


Fig. 3. The time-course changes of ORP in the four types of swine wastewater at the intermittent time ratio of 1/1 h for (a), (c), and 1.25/0.75 h for (b).

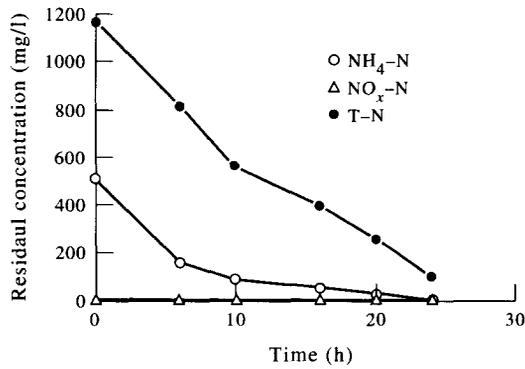


Fig. 4. The transition of the residual concentrations of T-N, NH<sub>4</sub>-N, NO<sub>x</sub>-N for the influent of crystallized swine wastewater at the intermittent time ratio of 1/1 h.

wastewater under aerobic and anaerobic conditions were higher than that of raw swine wastewater and 3-times diluted swine wastewater, that is to say, the crystallization process improved the C/N ratio of the raw wastewater increase to higher than 8 and makes the wastewater treated easy.

In the 6-times diluted swine wastewater, the initial DO concentration under aerobic conditions was 2.55 mg/l, and then reached 6.30 mg/l after 24 h. Under anaerobic conditions, the DO concentration started at 0.41 mg/l and increased to 0.53 mg/l after 5 h, then remained at the same level.

Figure 3 shows the time-course of ORP in the four types of swine wastewater. The ratio of aerobic and anaerobic time was 1/1 h for swine wastewater, the 3-times diluted swine wastewater and crystallized swine wastewater, and 1.25/0.75 h for the 6-times diluted swine wastewater.

For swine wastewater, the voltage of the ORP (using hydrogen standard electrode) started increasing to 0 mV after 20 h under aerobic conditions. Under anaerobic conditions, it increased to -158 mV after 24 h.

For the 3-times diluted swine wastewater, the voltage of the ORP started increasing to 34 mV after 8 h under aerobic conditions. Under anaerobic conditions, it increased to 44 mV after 24 h.

For the 6-times diluted swine wastewater, the voltage of the ORP started increasing from 118 mV up to 196 mV under aerobic conditions and started at -9 mV and increased to 151 mV under anaerobic conditions after 24 h respectively.

For crystallized swine wastewater, the voltage of the ORP started increasing from 57 mV up to 133 mV under aerobic conditions. Under anaerobic conditions, it started at -29 mV and increased to 113 mV, and the change was smaller than that for the 6-times diluted swine wastewater. After 10 h of treatment, the change in ORP under aerobic and anaerobic conditions was maintained between 20 and 33 mV.

From Fig. 3, it is clearly that since the crystallization process improved the C/N ratio of the raw wastewater and decrease the organic loading of

treatment, so that both initial and final ORP value for crystallized swine wastewater under aerobic and anaerobic conditions were higher than that of raw swine wastewater and 3-times diluted swine wastewater.

Figure 4 shows the transition of the residual concentrations of T-N, NH<sub>4</sub>-N, and NO<sub>x</sub>-N in the crystallized swine wastewater. The ratio of aerobic and anaerobic time was 1/1 h. The initial residual T-N concentration was 1166 mg/l, which then decreased to 103 mg/l after 24 h. The average removal rate and ratio of T-N was 44.3 mg/l·h and 91.2%, respectively. The NH<sub>4</sub>-N concentration started with 519 mg/l then decreased to 2 mg/l after 24 h. The average removal rate and ratio was 21.2 mg/l·h and 99.6%, respectively. The NO<sub>x</sub>-N concentration decreased from 7.75 to 1.32 mg/l, and it showed that denitrification was successful. This result was the same as the best result in the references concerning the nitrification/denitrification of livestock wastewater under similar condition.

Figure 5 shows the transition of the T-P and PO<sub>4</sub>-P concentrations in the crystallized swine wastewater. The ratio of aerobic and anaerobic time was 1/1 h. T-P decreased from 109 to 98.5 mg/l after 7 h, but gradually increased until it reached 142 mg/l after 24 h. PO<sub>4</sub>-P decreased from 91.0 to 51 mg/l after 7 h, and gradually increased to 112 mg/l after 24 h. Under anaerobic conditions, when phosphorus in the sludge dissolved into the treated water and the DO increased to more than 1.00 mg/l, denitrifying bacteria used the oxygen and directly consumed the carbon source, and then the NO<sub>x</sub>-N concentration in the effluent increased. At the same time, due to excessive uptake of phosphorus by phosphate-accumulated bacteria, phosphoric acid remains in the treated wastewater by these bacteria autolysis. By adding 45 ml of CaCl<sub>2</sub> (3%) into the treated water, the phosphoric acid decreased to 41 mg/l. This reaction was caused by sedimentation of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

Figure 6 shows the time course of the TOC/T-N ratio and removal ratios of T-N and NH<sub>4</sub>-N in the crystallized swine wastewater. TOC quickly

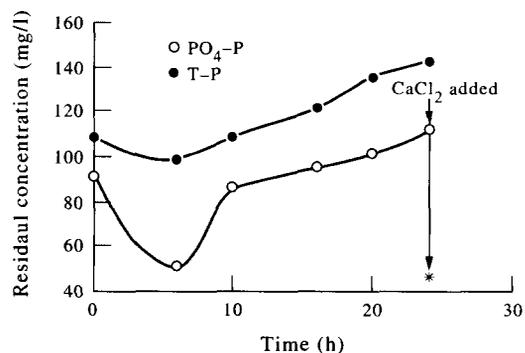


Fig. 5. The transition of the residual T-P, PO<sub>4</sub>-P concentrations in the crystallized swine wastewater at the intermittent time ratio of 1/1 h (added CaCl<sub>2</sub> conc. and volume are 3% and 45 ml, respectively).

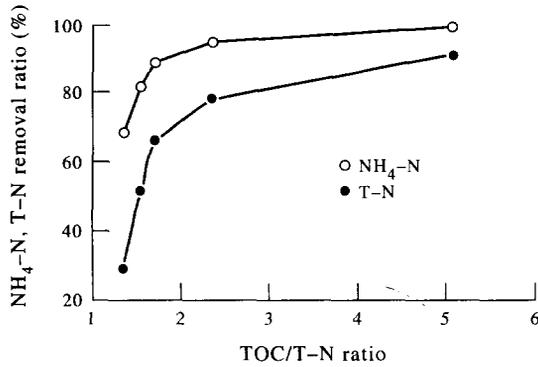


Fig. 6. The relationship of NH<sub>4</sub>-N, T-N removal ratio to TOC/T-N ratio in the crystallized swine wastewater at the intermittent time ratio of 1/1 h (initial quality of the wastewater was shown in Table 3).

decreased in the first 6 h from 3923 to 1105 mg/l, and the TOC/T-N ratios in the whole treated wastewater temporarily decreased to 1.35, then TOC slowed down, and TOC/T-N ratio began to increase to 5.05 because T-N decreased, therefore the T-N, and NH<sub>4</sub>-N removal ratio were also both increased.

Figure 7 shows the relation between the change in the TOC/NH<sub>4</sub>-N ratio in each wastewater sample and removal ratios of T-N and NH<sub>4</sub>-N after intermittent aeration treatment. The TOC/NH<sub>4</sub>-N ratio in raw swine wastewater, the 3-times diluted swine wastewater, the 6-times diluted swine wastewater, and the crystallized swine wastewater were 1.86, 1.98, 2.98, 8.76, respectively. Accordingly, the removal ratios of T-N were 28.63, 31.2, 48.7 and 91.2%, respectively, while for NH<sub>4</sub>-N they were 32, 45, 57 and 99%, respectively.

Figure 8 shows the relation between the kinds of influent wastewater and their most optimum treatment time for attaining the maximum T-P, PO<sub>4</sub>-P removal ratio. For raw swine wastewater, the 3-times diluted swine wastewater, the 6-times diluted swine wastewater and the crystallized swine wastewater, the most optimum treatment time is 24, 11, 4.5 and 6 h, respectively. From these results, it is clear that for

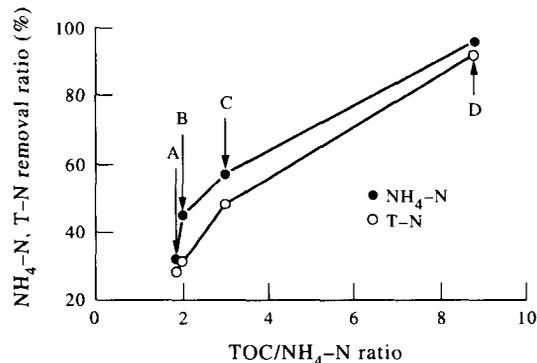


Fig. 7. The relationship between the change in the TOC/NH<sub>4</sub>-N ratio and T-N, NH<sub>4</sub>-N removal ratios for the four types of swine wastewater. A: Raw swine wastewater. B: 3-times diluted swine wastewater. C: 6-times diluted swine wastewater. D: The crystallized swine wastewater.

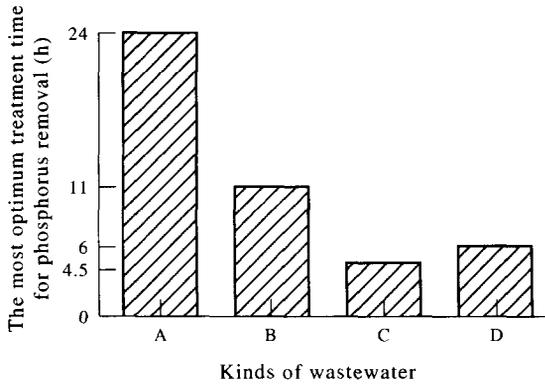


Fig. 8. The relationship between the kinds of influent wastewater and their most optimum treatment time for attaining the maximum T-P, PO<sub>4</sub>-P removal value. A: Raw swine wastewater. B: 3-times diluted swine wastewater. C: 6-times diluted swine wastewater. D: The crystallized swine wastewater.

phosphorus and nitrogen removal, the most optimum treatment time is not the same if only depending on the biological reaction. In theory, during the nitrification process, for obtaining high nitrogen removal efficiency, the sludge residence time (SRT) has to be longer and longer, but for phosphorus removal, since it depends on the amount of excess sludge, so that the SRT would be shortened, if possible.

Based on these results, the following points have to be considered for the removal of nitrogen and phosphorus from swine wastewater using the intermittent aeration process.

(1) pH: it is very important to fix the pH value during the treatment because bacteria for nitrification and denitrification have their own suitable pH value (Murata *et al.*, 1977a, b); for common *Nitrosomonas*, it is 8.0–8.5, and for *Nitrobacteria*, it is 6.5–8.3. The change in pH influences not only nitrate and nitrite bacteria, but also the reduction of nitrogen. When the pH value increases to more than 9, denitrification efficiency significantly decreases. Delwiche (1956) indicates that the best pH value is more than 7.3, but when less than 7.3, more N<sub>2</sub>O is generated. Warner

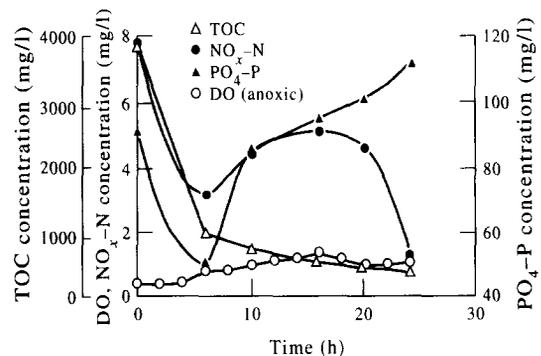


Fig. 9. The time-course changes of the residual TOC, NO<sub>x</sub>-N, DO(anoxic), PO<sub>4</sub>-P concentrations for the crystallized swine wastewater at the intermittent time ratio of 1/1 h (initial quality of the swine wastewater was shown in Table 3).

*et al.* (1986) and Osada *et al.* (1991) point out the importance of stabilizing the pH and alkalinity for aerobic/anaerobic digestion of excess sludge. In an experiment using intermittent aeration treatment after the crystallizing treatment, the pH in the liquid had the similar value.

(2) DO: it is very important to monitor the changes in DO concentration. Dowing *et al.* (1964) indicates that at least 0.5 mg/l of DO is required for the nitrification process. Toya (1970) indicates that DO has to be maintained at 3–4 mg/l to achieve a nitrification rate of 90% or more during nitrification. The results obtained from the experiment meet these requirements. As Fig. 9 shows, the removal ratio of ammonium nitrogen increased as the DO increased.

(3) Removal of nitrogen: by intermittent aeration treatment (the time ratio of aerobic/anaerobic time was 1/1 h) of swine wastewater in which the C/N ratio has been improved, the highest removal ratios of T-N and NH<sub>4</sub>-N were 91%, and 99%, respectively. This result is similar to that of Liao and Maekawa (1994), and Osada *et al.* (1991).

(4) Inhibited phosphorus removal during the intermittent aeration treatment of crystallized swine wastewater: in the intermittently activated sludge method, the phosphoric acid concentration in the liquid decreases because the phosphate bacteria excessively consumes phosphoric acid in the wastewater while aerobic and anaerobic conditions are maintained. This phosphorus is stored in the activated sludge, and is finally removed as excess sludge. Thus, organic matters such as glucose or acetic acid must not be contained in the wastewater. Similarly, under anaerobic conditions, DO, NO<sub>3</sub>-N, and NO<sub>2</sub>-N must not be contained in the wastewater. When wastewater does not meet these requirements, removal of phosphorus is inhibited.

Figure 9 shows the time course changes of the PO<sub>4</sub>-P concentration of the crystallized influent in the intermittent aeration process, and DO and NO<sub>x</sub>-N concentration under anaerobic conditions. For the first 6 h, DO was as low as 1 mg/l and denitrification occurred. As the NO<sub>x</sub>-N concentration decreased, the PO<sub>4</sub>-P concentration also decreased. The DO then increased as the TOC decreased and the consumption of DO decreased. Because denitrifying bacteria consume part of the DO, denitrification is proceeded slowly and the NO<sub>x</sub>-N concentration increased. These results might explain why phosphate-accumulated bacteria consumed PO<sub>4</sub>-P in the liquid to inhibit the denitrification.

#### CONCLUSIONS

The obtained results are summarized as follows:

(1) In the synthetic wastewater: the results makes it clear that the reaction temperature (25°C), reaction time (1 h), and interaction between temperature and pH have a great influence on the quantity of the

crystallized precipitate and the removal ratio of NH<sub>4</sub>-N.

(2) In the swine wastewater: the case of the reaction temperature (25°C), reaction time (1 h) and pH (7.5), as well as the molar ratio of NH<sub>4</sub>-N:PO<sub>4</sub>-P:Mg = 1.0:0.9:0.9, the quantity of the crystallized precipitate is a maximum value, the removal ratio of NH<sub>4</sub>-N increases to more than 90% and the C/N ratio increases from 1.98 to more than 8, except for phosphorus which could not be removed. For the molar ratio of NH<sub>4</sub>-N:PO<sub>4</sub>-P:Mg = 1.0:0.6:0.9, the ammonium and phosphorus removal ratio would be 79.32–87.45% and 40.3–88.5%, respectively.

(3) When crystallized effluent is treated by the intermittent aeration process, the NH<sub>4</sub>-N concentration decreases from 519 to 2 mg/l, and the removal ratio increases to 99%. The T-N concentration decreases from 1166 to 102 mg/l, and the removal ratio increases to 91%.

(4) For the intermittent aeration process, during phosphorus and nitrogen removal, the most optimum treatment time is not the same if only depending on the biological reaction. The removal ratios of PO<sub>4</sub>-P and T-P decrease in the order of raw wastewater, 3-times diluted swine wastewater, 6-times diluted swine wastewater, and crystallized swine wastewater. Phosphorus is not removed when crystallized swine wastewater is treated by the intermittent aeration process. The removal ratio of PO<sub>4</sub>-P reaches 60% due to the flocculation and precipitation by adding CaCl<sub>2</sub>.

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