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Effectiveness of Oxidation-Reduction Potential and pH as Monitoring and Control Parameters for Nitrogen Removal in Swine Wastewater Treatment by Sequencing Batch Reactors

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Two bench-scale sequencing batch reactors (SBRs) were operated in a fixed hydraulic retention time study to investigate the effectiveness of oxidation-reduction potential (ORP), pH and dissolved oxygen as parameters for indicating denitrification followed by nitrification in SBRs for swine wastewater treatment. The ORP and pH profiles were monitored and evaluated under different denitrification and nitrification conditions with and without a supplemental carbon source. With a low C/N ratio, and using a suitable C/N ratio adjustment control, ORP and pH could be used as monitoring and control parameters in both the anoxic and oxic phases for practical swine wastewater treatment. High-level accumulation of nitrate was observed without any C/N ratio adjustment. In this case, ORP and pH were not useful for monitoring denitrification followed by nitrification in SBRs. According to our research, with regard to N removal, it would be better to use pH as a parameter during the oxic phase and ORP as a parameter during the anoxic phase. Using a suitable adjustment of a C/N ratio in the influent by adding swine slurry, a high total nitrogen removal efficiency of up to 95.5% was reached. It was found that, in this case, the use of ORP and pH as parameters for real-time control processes was possible in swine wastewater treatment.

[**Key words:** oxidation-reduction potential (ORP), pH, real-time control, sequencing batch reactor (SBR), nitrogen removal, swine wastewater]

Animal manure is widely used as a fertilizer in many countries, since animal waste contains nutrients such as nitrogen and phosphorus (1, 2). While land application of swine manure may be an economical and easy method to manage waste, this treatment causes many environmental problems such as contamination of groundwater and eutrophication of surface waters (3). In addition, with the present trend toward raising large herds of livestock in smaller areas, it is becoming difficult to apply all of the waste to cropland (4). Therefore, it is necessary to develop an alternative cost-effective waste treatment system and an enhanced treatment system for nutrient removal.

In recent years, real-time control processes using oxidation-reduction potential (ORP), pH and dissolved oxygen (DO) as parameters to control the oxic and anoxic cycles of sequencing batch reactor (SBR) systems, have received much attention (5–9). Many researchers have shown that the ORP and pH pattern in a given wastewater treatment process can be used successfully to identify specific control points. In particular, in biological nitrogen removal processes, several investigators have identified the “nitrate knee” in ORP profiles and the “nitrate apex” in pH profiles which indicate the end of denitrification (5, 6), and the “nitrogen break point” or the “DO elbow” in ORP profiles and the “ammonia valley” in pH profiles, which indicate the end of nitrification (7–9). According to these control points, the flexible hydraulic retention time (HRT) from cycle to cycle was obtained and a high and stable removal rate of nitrogen and energy saving were achieved using a real-time control strategy. Although online control using pH and ORP profiles can be implemented easily, there is a problem associated with anoxic cycle control for extremely low C/N ratios (10). In some cases, the “nitrate knee” in ORP profiles and the “nitrate apex” in pH profiles were not observed during anoxic cycles.

Although several authors indicated that real-time control using ORP and pH as parameters could be successfully applied to swine wastewater treatment (3, 7), in practice the water quality of swine wastewater fluctuates markedly due to the use of various waste management and pretreatment technologies. In particular, the denitrification efficiency is directly affected by the C/N ratio of the influent. More often, there is no sufficient source of carbon for the com-

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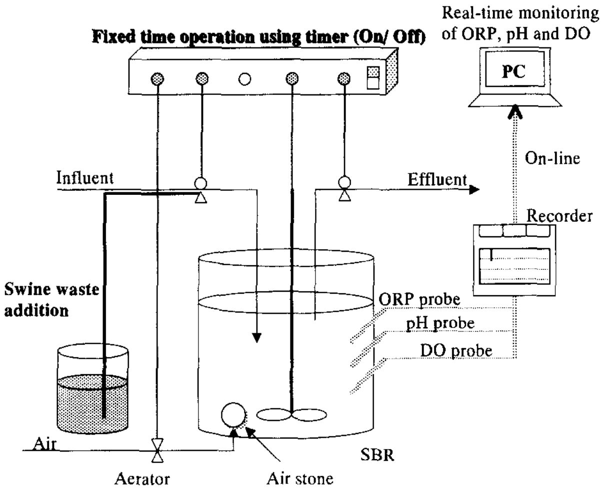

FIG. 1. Schematic of single batch reactors with fixed time operation.

plete denitrification of swine wastewater discharged from large-scale farms using solid-separation processes. Therefore, it is necessary to investigate the ORP and pH profiles under different denitrification and nitrification conditions and establish a more effective real-time control strategy using ORP and pH as parameters for swine wastewater treatment.

The specific objective of this study was to investigate the effectiveness of ORP, pH and DO as parameters for indicating denitrification followed by nitrification in SBRs for swine wastewater treatment. For this purpose, a bench-scale SBR system for use in fixed HRT study using ORP, pH and DO monitors was designed and evaluated for practical swine wastewater treatment. Using fixed HRT operation, it was determined whether the above-mentioned control points are consistently present under different denitrification/nitrification conditions. Because of an insufficient source of carbon in the swine wastewater, swine slurry as an external carbon source was added for complete denitrification.

MATERIALS AND METHODS

Sequencing batch reactors and operation Two bench-scale SBRs were operated in parallel as shown in Fig. 1. The effective volume of each SBR was 9 *l*. The ORP (Ag/AgCl as a reference), pH and DO were continuously monitored and recorded. The operational parameters are shown in Table 1, while the operational strategy applied in runs 1 and 2 is shown in Fig. 2. The volume of the influent loaded into reactors was measured daily. The HRT was set at 10 d and the water temperature was maintained at 23±2°C.

TABLE 1. Operating conditions of SBRs

Parameters	Run 1	Run 2
Volume (*l*)	9	9
HRT (d)	10	10
Sludge retention time (d)	46	560
MLSS ($\mathrm{mg}\cdot l^{-1}$)	8860	5730
MLVSS/MLSS (–)	0.78	0.77
Water temperature (°C)	23±2	23±2
Swine slurry	Addition from cycle-46	No addition

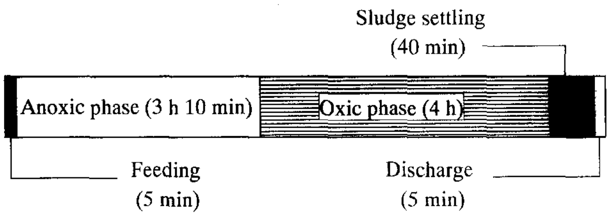

FIG. 2. Operational mode of runs 1 and 2.

Runs 1 and 2 differed only with respect to the C/N ratio of the influent. Swine slurry was added to run 1 to adjust the C/N ratio from cycle-46 when the accumulation of nitrate was observed, and then run 1 was maintained under complete denitrification conditions. Swine slurry was pumped into the reactor in run 1 by a pulse-metering pump with influent feeding, and the average amount of swine slurry added was 8 g per cycle. Run 2 was operated without any swine slurry addition. Consequently, after the cycle-46, the influent $\mathrm{BOD_5}$/total nitrogen (T-N) ratio of runs 1 and 2 was 4.5 and 2.6, respectively.

Feed swine wastewater and activated sludge The swine slurry composed mainly of feces and the swine wastewater composed mainly of urine used in this study were obtained from a local pig farm in Saitama, Japan. Swine wastewater treated by screening and coagulation was collected from an influent tank located in the farm. Swine slurry was also directly collected from the piggery floor. The collected swine slurry and wastewater were stored at 4°C, and their characteristics are listed in Tables 2 and 3, respectively.

Seed sludge taken from a sewage plant in Saitama was used for the SBR setup. Before the start of the experiment, the activated sludge was acclimated for six months using swine wastewater with a relatively high $\mathrm{BOD_5}$/T-N ratio ($\mathrm{BOD_5}$/T-N=4–6).

Analytical methods Parameters routinely assayed included T-N, $\mathrm{NH_4}$-N, $\mathrm{NO_3}$-N, $\mathrm{NO_2}$-N, total-phosphorus (T-P), $\mathrm{PO_4}$-P, carbonaceous biological oxygen demand ($\mathrm{CBOD_5}$), nitrogenous biological oxygen demand ($\mathrm{NBOD_5}$), total organic carbon (TOC), total suspended solids (TSS), pH, mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS). Track analyses that covered the entire cycle were done three times

TABLE 2. Characteristics of the swine slurry

Parameters	Average
$\mathrm{BOD_5}$ ($\mathrm{mg}\cdot l^{-1}$)	97260
TSS ($\mathrm{mg}\cdot l^{-1}$)	115700
T-N ($\mathrm{mg}\cdot l^{-1}$)	3660
T-P ($\mathrm{mg}\cdot l^{-1}$)	2780
BOD/T-N ratio (–)	26.6

TABLE 3. Characteristics of the swine wastewater

Parameters	Average	SD	N
$\mathrm{BOD_5}$ ($\mathrm{mg}\cdot l^{-1}$)	2960	545	7
TOC ($\mathrm{mg}\cdot l^{-1}$)	1230	251	19
TSS ($\mathrm{mg}\cdot l^{-1}$)	306	58	7
T-N ($\mathrm{mg}\cdot l^{-1}$)	1130	33.2	13
$\mathrm{NH_4}$-N ($\mathrm{mg}\cdot l^{-1}$)	1120	72.8	19
$\mathrm{NO_3}$-N ($\mathrm{mg}\cdot l^{-1}$)	<0.1	–	19
$\mathrm{NO_2}$-N ($\mathrm{mg}\cdot l^{-1}$)	<0.1	–	19
T-P ($\mathrm{mg}\cdot l^{-1}$)	20.8	3.2	13
$\mathrm{PO_4}$-P ($\mathrm{mg}\cdot l^{-1}$)	4.6	4.0	19
pH (–)	8.87	0.03	7

SD, Standard deviation; N, number of samples.

under different accumulation levels of nitrate and ammonia (cycle-25, cycle-84 and cycle-160). Mixed-liquor samples from reactors 1 and 2 were taken at fixed intervals during track studies. Most analytical methods were performed in accordance with standard methods (11). NH_4-N, NO_3-N, NO_2-N and PO_4-P were analyzed with an ion chromatograph (IC 7000; Yokogawa Analytical Systems, Tokyo). TOC was detected with a total organic carbon analyzer (TOC-5000; Shimadzu, Kyoto). T-N and T-P were analyzed with a total nitrogen/phosphorus analyzer (T-N30, T-P30; Mitsubishi Chemical Corporation, Tokyo).

RESULTS AND DISCUSSION

C/N ratio adjustment and nitrogen removal in runs 1 and 2 The T-N, NO_3-N and NH_4-N concentrations of the effluent in both reactors are shown in Fig. 3. Since the low C/N ratio of the influent caused incomplete denitrification, the accumulation of nitrate was observed in both reactors from the start of monitoring to cycle-46. At the same time, the ammonia concentration in the mixed liquor also increased and reached approximately 100 mg·l^{-1} due to the decrease in pH and activity of nitrifying bacteria. After cycle-46, ammonia and nitrate levels apparently decreased in run 1 following a C/N ratio adjustment using swine slurry, and accumulation of ammonia and nitrate stopped completely after cycle-93. However, the accumulation of ammonia and nitrate of high rates was continuous in run 2.

ORP, pH and DO profiles under conditions of complete denitrification and nitrification Figure 4 shows the track analysis data in run 1 at cycle-160, in which neither nitrate nor ammonia accumulated. Firstly, in the ORP profile, real-time control points (RCPs), which can be used for real-time operation in biological nitrogen removal processes, appeared in both the oxic and anoxic phases. In particular, RCP_{anoxic}, which indicates the end of denitrification, appeared very clearly in the anoxic phase. After denitrification, the ORP value suddenly decreased. It was previously reported (12) that the commencement of sulfate-reducting activity that produces sulfides caused this sudden decrease. The dORP/dt just after the RCP_{anoxic} markedly changed and reached approximately −12 mV·min^{-1}. Thus, because the RCP_{anoxic} appeared so clearly, the ORP profile is very effective for anoxic phase control. Secondly, in the pH profile, RCPs also appeared in both the anoxic and oxic phases. However, in the anoxic phase, the RCP_{anoxic} was not clear as shown in Fig. 4. It was previously reported (10) that the RCP_{anoxic} in the pH profile cannot be effectively used as an RCP in some cases, and we also found that this point is ineffective for anoxic phase control in swine wastewater treatment. Thirdly, in the DO profile, an RCP was observed only in the oxic phase because of the inability to monitor DO in the anoxic phase. Consequently, the ORP is the most useful parameter for monitoring the anoxic phase during swine wastewater treatment.

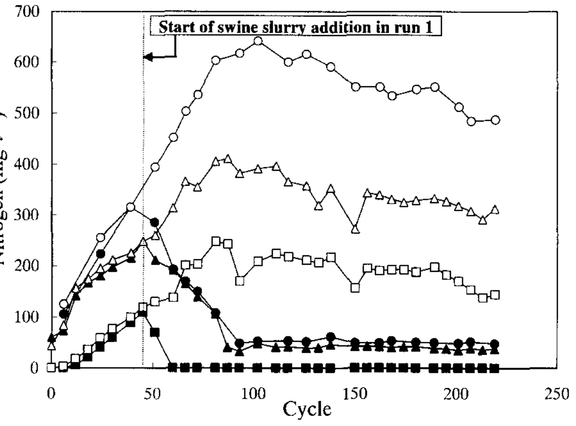

FIG. 3. Nitrogen removal in runs 1 and 2. Symbols: closed circles, T-N effluent concentration (run 1); closed triangles, NO_3-N effluent concentration (run 1); closed squares, NH_4-N effluent concentration (run 1); open circles, T-N effluent concentration (run 2); open triangles, NO_3-N effluent concentration (run 2); open squares, NH_4-N effluent concentration (run 2).

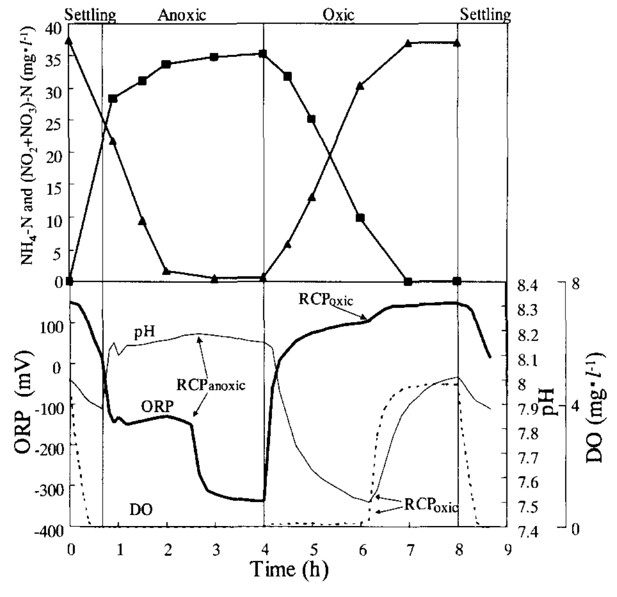

FIG. 4. ORP, pH and DO profiles under complete denitrification and nitrification conditions. Symbols: squares, NH_4-N concentration; triangles, (NO_2+NO_3)-N concentration.

ORP, pH and DO profiles during accumulation of nitrate Figure 5 shows the track analysis data in run 1 at cycle-84, in which only low nitrate accumulation was observed. The effluent nitrate concentration was approximately 65 mg·l^{-1}. Firstly, in the ORP profile, the RCP_{oxic} that indicates the end of nitrification appeared. This point corresponded to the dissolved oxygen break point and resulted in another abrupt change in the ORP profile. The increase in the DO level at this point could have resulted from the lowered oxygen uptake rate (OUR) of the bacteria. Since the ammonia concentration decreased in the reactor, the OUR of nitrifying bacteria decreased, and the DO level increased. Aeration can be terminated at this point when the targeted nutrient is ammonia (13). Secondly, in the pH profile, the RCP_{oxic} appeared clearly. After complete nitrification, the pH value immediately increased due to air stripping of carbon dioxide (13). Finally, in the DO profile, the RCP appeared very clearly, but this profile was unstable compared with the ORP and pH profiles. In particular, the DO value was unstable when a large amount of scum was produced in the reactor.

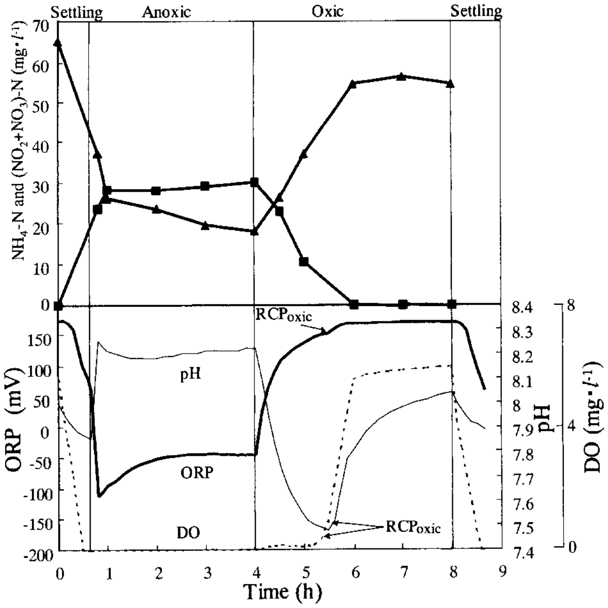

FIG. 5. ORP, pH and DO profiles under nitrate accumulation condition. Symbols: squares, NH_4-N concentration; triangles, (NO_2+NO_3)-N concentration.

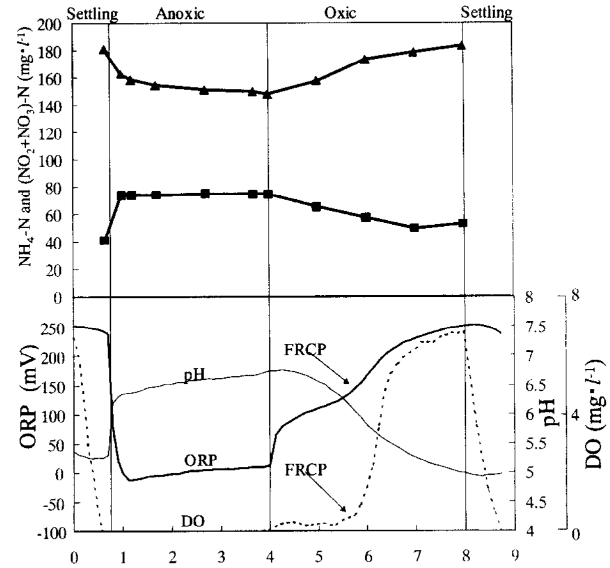

FIG. 6. ORP, pH and DO profiles under ammonia and nitrate accumulations condition. Symbols: squares, NH_4-N concentration; triangles, (NO_2+NO_3)-N concentration.

ORP, pH and DO profiles during accumulation of ammonia and nitrate Figure 6 shows the track analysis data in run 1 at cycle-25, in which both of ammonia and nitrate accumulated simultaneously. The effluent concentrations of ammonia and nitrate were approximately 40 mg·l^{-1} and 180 mg·l^{-1}, respectively. Firstly, in the ORP profile, RCPs did not appear because of incomplete nitrification. However, in the oxic phase, a false real-time control point (FRCP), which is similar to RCP but does not indicate the end of nitrification and denitrification, appeared despite incomplete nitrification. Secondly, in the pH profile, neither RCP nor FRCP was detected in the anoxic and oxic phases, respectively. Finally, in the DO profile of the oxic phase, the FRCP appeared as in the ORP profile. This is because nitrification was inhibited by the pH decrease, and the decrease in the OUR increased the DO concentration markedly so that the FRCP appeared in the DO profile. Since it was reported (14, 15) that the ORP value is correlated to the logarithm of the DO concentration in a linear relationship, the increase in the ORP value as a result of the increase in the DO concentration causes the FRCP to appear on the ORP curve. Thus, the ORP value was greatly dependent on the fluctuations of the DO concentration, which contraindicates the use of an ORP profile for oxic phase control in this case. On the other hand, in a pH profile, the pH value continuously decreased with nitrification so that the FRCP did not appear. Consequently, based on track analysis data at cycle-25 and cycle-84 in run 1, the pH is the most useful parameter for controlling the oxic phase in swine wastewater treatment.

In run 2, since the low C/N ratio load caused incomplete denitrification and nitrification, ammonia and nitrate accumulated at high levels. The effluent concentrations of ammonia and nitrate were approximately 170 mg·l^{-1} and 360 mg·l^{-1}, respectively. In this case, RCPs did not appear in the ORP, pH and DO profiles. Although it was reported (16) that a low C/N ratio of the influent was a limiting factor in the removal of nitrogen from swine wastewater, it was found that a low C/N ratio also makes real-time control impossible in this study. Thus, the C/N ratio of the influent was a very important determinant for real-time control.

Effectiveness of ORP, pH and DO as real-time parameters for the denitrification and nitrification processes Based on track analysis data, the effectiveness of parameters for real-time control under several conditions is summarized in Table 4. In the oxic phase, although the relevant RCP appeared in the pH profile only when complete nitrification was accomplished, in the ORP and DO profiles, FRCPs appeared despite incomplete nitrification when ammonia and nitrate accumulation was observed. In the anoxic phase, although the RCP appeared in both the ORP and pH profiles only when complete denitrification was accom-

TABLE 4. Effectiveness of parameters for real-time control under several conditions

Accumulation	ORP profile		pH profile		DO profile
	Anoxic	Oxic	Anoxic	Oxic	Oxic
Ammonia and nitrate	NA	FRCP	NA	NA	FRCP
Nitrate only	NA	RCP	NA	RCP	RCP
No accumulation	RCP	RCP	RCP[a]	RCP	RCP

NA, No appearance; RCP, real-time control point; FRCP, false real-time control point.

[a] Not clear.

TABLE 5. Nutrient removal in runs 1 and 2

Parameters	Run 1		Run 2		N
	Average in effluent	SD	Average in effluent	SD	
BOD_5 (mg·l^{-1})	21.7	6.9	68.6	35.4	7
TSS (mg·l^{-1})	70	29	111	24	7
T-N (mg·l^{-1})	51.5	3.5	560.4	47.9	13
NH_4-N (mg·l^{-1})	<0.1	–	187.1	25.6	19
NO_3-N (mg·l^{-1})	40.5	3.7	337.0	31.5	19
NO_2-N (mg·l^{-1})	<0.1	–	<0.1	–	19
T-P (mg·l^{-1})	23.1	2.6	19.5	4.6	13
PO_4-P (mg·l^{-1})	17.3	1.9	14.7	2.2	19
pH (–)	7.85	0.06	4.36	0.43	7

SD, Standard deviation; N, number of samples.

plished, the RCP in the ORP profile was much clearer than that in the pH profile.

In this study, RCPs appeared stably and continuously in run 1 in more than 200 cycles, as shown in Fig. 7. In addition, this fixed time study shows that real-time control using ORP and pH is possible using the optimum C/N ratio load condition for swine wastewater treatment.

Performance of two reactors The characteristics of the effluent in both reactors are listed in Table 5. As compared with run 2, the high removal rate of nitrogen was mainly achieved in run 1 due to swine slurry addition to the influent, with the BOD_5/T-N ratio of the influent being approximately 4.5. Average T-N removal efficiency was 95.5% in run 1. With regard to N removal, the swine slurry addition resulted in enhanced denitrification and constant effluent as listed in Table 5. On the other hand, in run 2, the average effluent concentration of nitrogen compounds was too high because of long-term operation with a low C/N ratio, with the BOD_5/T-N ratio of the influent being approximately 2.6. The T-N removal efficiency was only 50.5% in run 2. In addition, the BOD_5 concentration of the effluent in run 2 was relatively high (average=68.6 mg·l^{-1}). This is because the oxygen demand by nitrifying bacteria increased the total BOD_5. In fact, the NH_4-N concentration of the effluent in run 2 was too high (average=187.1 mg·l^{-1}), and the $NBOD_5$ accounted for approximately 60% of the total BOD_5. The CBOD concentrations of runs 1 and 2 were similar.

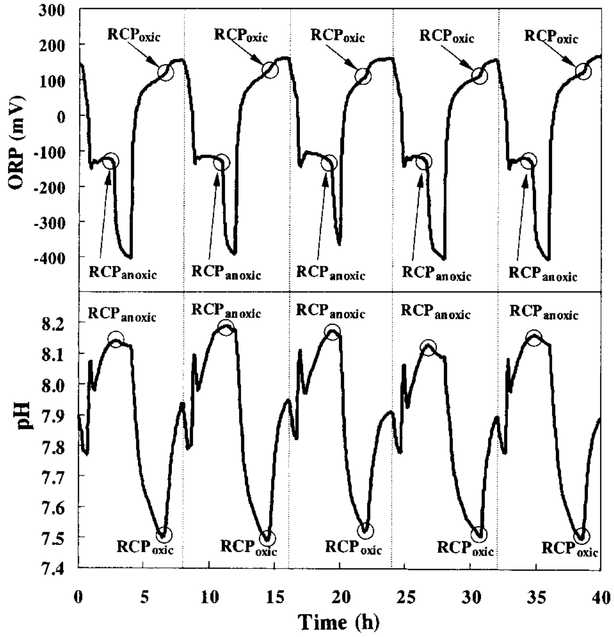

FIG. 7. Real-time control points in ORP and pH profiles observed from run 1 operation (cycles 169–173).

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