ORP control for nitrogen removal from sewage with low C/N ratio in a hybrid biofilm pilot plant

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Abstract

An oxidation reduction potential (ORP) control system, which adjusted amount of external carbon source for denitrification based on ORP values, was applied to a hybrid biofilm pilot plant for cost-effective removal of nitrogen from sewage with low C/N ratio. The pilot plant consisted of serially anoxic-, aerobic-, anoxic-, aerobic-reactor and both aerobic reactors were separated two parts with a baffle. Influent BOD and total nitrogen (T-N) concentrations were varied in the rage of 25.0-140.5 mg/L and 15.5-46.5 mg/L, respectively. Because the C/N ratio (1.6-3.0) of the influent was too low to complete denitrification, an external carbon source of methanol was added to the second anoxic reactor to meet the regulation limit of effluent T-N, 10.0 mg/L. The effluent T-N concentration was directly affected by methanol addition in the tested concentration range, 50 to 100 mg/L as final concentration in the second anoxic reactor. An empirical equation decided from the ORP values according to added methanol amount was $\mathrm{ORP} = 0.0055[\mathrm{methanol}]^2 - 2.2733[\mathrm{methanol}] + 37.402$. The concentration of methanol addition was decided from an empirical equation according to the ORP value measured in the second anoxic reactor. As a result of applying the ORP automatic control system, 20% of the amount of methanol addition was reduced comparing with the fixed amount addition of methanol as final concentration as 75 mg/L without ORP control system. These results suggested that ORP auto-control system would be applied to efficient and cost effective removal of nitrogen from sewage with low C/N ratio.

Keywords
Denitrification; external carbon source; low C/N ratio; nitrogen removal; ORP control

INTRODUCTION

The conventional activated sludge process is the most typical bioprocess for removal of nitrogen from sewage but this system demands long hydraulic retention time (HRT) to retain slow growing microorganisms for nitrification and has drawbacks such as sludge bulking and excess sludge treatment. To meet more stringent requirements for the removal of the nutrient chemicals, the attached growth system (i.e., biofilm process) has been applied to wastewater treatment because this system can maintain large amount of biomass and can be operated at a significantly reduced HRT and reactor volume (Nam *et al.*, 2000). Recently, hybrid biofilm systems containing both suspended and attached biomass have been also used and found that the hybrid processes enhanced BOD and nutrient removal even at low temperature conditions (Müller, 1998; Gebara, 1999).

The sewage in Korea has low C/N ratio due to dilution of sewage by rainfall water (Choi, *et al.*, 1998). The characteristic of sewage leads to demand an additional carbon source for enhancing denitrification. However, too much addition of the external carbon without control system will bring an excessive sludge production and increase of operating cost. The oxidation reduction potential (ORP) value has been widely used as sensitive and rapid on-line method to monitor denitrification in biological nutrient removal (BNR) processes. The ORP control system was mostly applied in sequencing batch reactor (SBR) system or operated at on-off control systems in other BNR systems.

The objectives of this study were to operate the hybrid biofilm pilot plant for satisfying the effluent regulation limit of total nitrogen (T-N), 10.0 mg/L and to apply an ORP auto control system for minimizing amount of external carbon source for denitrification.

MATERIAL AND METHODS

Hybrid biofilm pilot plant

A pilot hybrid biofilm pilot plant with ORP control system was placed in Suyoung sewage treatment plant in Busan, Korea. A schematic diagram of the pilot plant with the control system is shown in Fig. 1.The pilot plant was consisted of rectangular type six reactors; serially the first anoxic-, first aerobic-, second aerobic-, second anoxic-, third aerobic-, and fourth aerobic reactor and volumes of the reactors were 0.83, 0.69, 0.69, 0.65, 0.65, and 0.74 m^3, respectively (Fig. 1). The plant had an external recycle flow from the clarifier to the first anoxic reactor for sludge supplement. Aquatic Media®, a fiber type media made of polypropylene, was placed in the aerobic reactors with packing ratios 2.4-2.9. Methanol was added to the second anoxic reactor as an external carbon source. The concentration of methanol addition was decided based the on the ORP value measured in the second anoxic reactor. The measured ORP value was transferred to the concentration of methanol and the rpm of pump for methanol addition was controlled to maintain the ORP set value by PID controller.

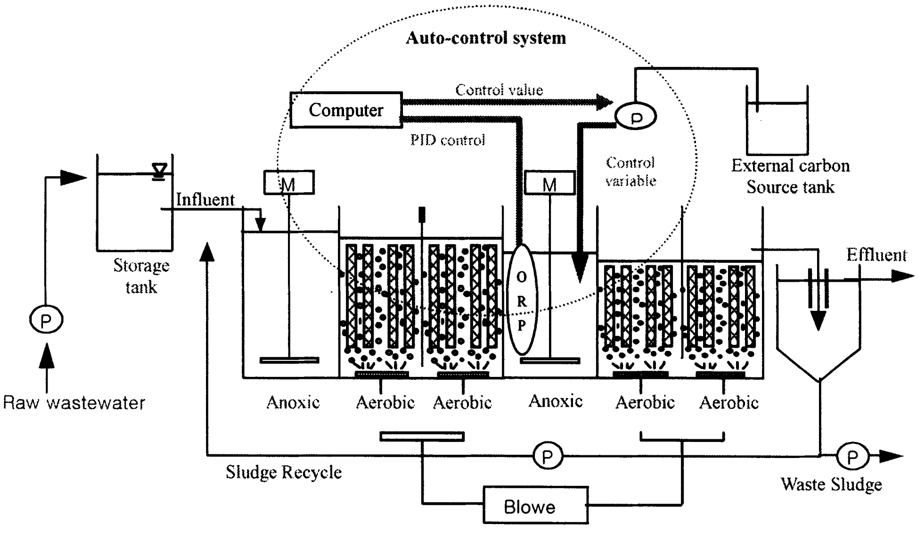

Fig. 1. A schematic diagram of a hybrid biofilm pilot plant with an ORP auto control system.

Operating conditions

The pilot plant was operated with two modes, controlled and uncontrolled mode, during winter season and the hydraulic retention time (HRT) was 6 hr at both two modes. DO and MLVSS concentrations were kept over 2.5 mg/L and 2,000 mg/L in aerobic reactors, respectively. The other operation conditions of the pilot plant are shown in tab. 1.

Tab. 1. Operating conditions of the hybrid biofilm pilot plant

	Without control	With control
Average temp. (℃)	15	15
HRT (hr)	6	6
Sludge recycle rate (%)	150	150
Media packing ratio (%)	2.4-2.9	2.4-2.9
Carbon source dosage (mg/L)	50-100	controlled

The primary clarifier effluent of the municipal sewage treatment plant, which treated 738,800 population equivalents (PE, 1 PE = 60g of biological oxygen demand day^{-1}), was used as influent of the pilot plant. The concentrations of chemicals in the influent sewage were TCOD of 95.5mg/L, BOD of 80.5mg/L, T-N of 35.4mg/L and T-P of 2.5mg/L. The concentrations in the influent for the pilot plant are shown in tab. 2.

Tab. 2. Influent characteristics of the pilot plant

Item	Unit	Concentrations (average)
pH	-	6.4 - 8.7 (7.5)
BOD	mg/L	25.0 - 140.5 (80.5)
$TCOD_{Cr}$	mg/L	24.0 - 180.0 (95.5)
T-N	mg/L	15.5 - 46.5 (35.4)
NH_4^+-N	mg/L	13.4 - 43.9 (31.8)
SS	mg/L	25.0 - 120.4 (62.3)
PO_4-P	mg/L	0.34 - 1.96 (0.98)

Sample analysis methods

Influent samples were collected twice a week and effluent samples every 2 days. Samples for the determination of soluble components were immediately filtered using 0.45 ㎛ filter paper to determine soluble compounds and cooled to prevent further reaction after sampling. All the samples, except NOx-N measured by HPLC (Waters, USA), were performed according to Standard Methods.

RESULTS & DISCUSSION

Pilot plant performance

During operating days, the range of influent NH_4^+-N concentrations were 13.4 to 43.9 mg/L and the effluent NH_4^+-N concentration was 0.1 to 5.4 mg/L. In order to obtain complete nitrification in the aerobic reactor, the total biomass concentration should be maintained over 1,500mg/L. The biomass concentration in the second anoxic reactor was needed to maintain over 2,500 mg/L to obtain over 90% of denitrification efficiency. The NH_4^+-N removal rate in winter season was 0.16 kg NH_4^+-N /m^3/day and the NH_4^+-N removal rate in summer was 0.29kg NH_4^+-N /m^3/day (even at HRT of 3.0hr, data not shown). These results showed that the hybrid biofilm system could get the higher NH_4^+-N removal rate.

Total nitrogen removal according to external carbon dosage

In order to enhance the denitrification performance, methanol was added to the second anoxic reactor as an external carbon source. The effect of methanol dosage as an external carbon on the effluent T-N concentration and T-N removal efficiency was tested (Fig. 2). Increasing the external carbon dosage, the T-N removal efficiency was also increased. When the external carbon was not added, the effluent T-N concentration was over 10 mg/L according to increasing T-N concentration in the influent above 15 mg/L. While the case of adding 50 mg COD/L of methanol showed that the effluent T-N concentration was not often satisfied the regulation limit of 10 mg/L, In most cases of adding 75 and 100 mg COD/L of methanol, the effluent T-N concentrations could be maintained below 10 mg/L even at the influent T-N concentration above 40 mg/L. The result suggested that at least 75 mg COD/L of methanol addition was necessary to keep the stable effluent quality below T-N 10mg/L. Therefore, the external carbon dosage was fixed as 75 mg COD/L of methanol in the operation without control mode.

Determination carbon dosage by ORP response

In the fixed external carbon dosage operation without the ORP control, as the influent NH_4^+-N concentration was changed, NOx-N concentration and ORP value in the second anoxic reactor was also dramatically changed and sometimes the added amount of methanol was excess the amount of methanol to be needed for complete denitrification when low concentrations of NOx-N entered into the second anoxic reactor. This would be cause of an excessive sludge production and operating cost.

In the ORP control operation, the concentration of methanol addition was decided based the on the ORP value measured in the second anoxic reactor. The measured ORP value was transferred to the concentration of methanol by using an empirical equation, $ORP = 0.0055[methanol]^2 - 2.2733[methanol] + 37.402$ (where, [methanol] means the concentration of methanol added) and the rpm of pump for methanol addition controlled to maintain the ORP set value by PID controller. As a result of applying the automatic control system with the ORP set point of -120mV for optimizing the methanol addition, 20% of the methanol dosage was decreased comparing with the operation without the ORP control system and the denitrification efficiency was maintained above 90% (data not shown).

In the rainy season, the ORP control operation with set-value of −120 mV led to an excess increase of methanol dosage. This problem could be resolved with modifications of ORP set-value and control parameter. In Fig. 3, the ORP responses and COD dosage are shown when the change of ORP set point from -120 mV to -80 mV. The variation of ORP value was decreased and converged to the new set point -80 mV and the methanol dosage was also decreased comparing with that of ORP set value -120 mV. These results suggest that ORP control system in nitrogen removal process is one of the cost-effective solutions for reducing external carbon source dosage.

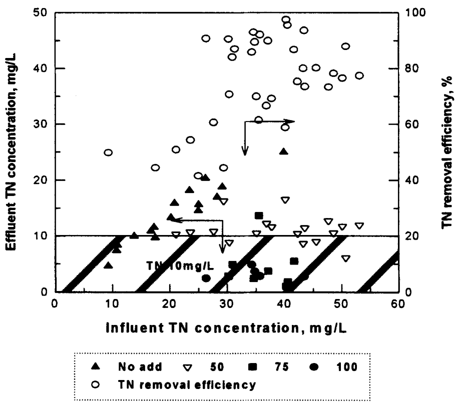

Fig. 2. Effluent T-N concentration and T-N removal efficiency according to external carbon dosage.

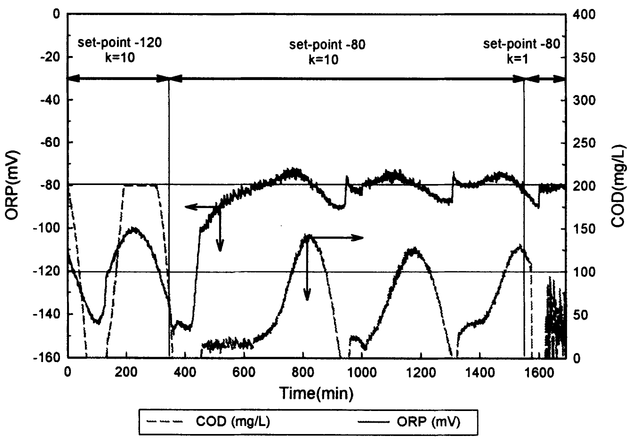

Fig. 3. ORP response and COD dosage when the change of ORP set point from -120 mV to -80 mV.

CONCLUSIONS

An ORP control system, which adjusted amount of external carbon source for denitrification based on ORP values, was applied to a hybrid biofilm pilot plant for cost-effective removal of nitrogen from sewage with low C/N ratio. During operating days, the range of influent NH_4^+-N concentration was 13.4 to 43.9 mg/L and the effluent NH_4^+-N concentration was 0.1 to 5.4mg/L. The NH_4^+-N removal rate in winter was 0.16 kg NH_4^+-N /m^3/day and the NH_4^+-N removal rate in summer was 0.29kg NH_4^+-N /m^3/day.

As a result of applying the automatic control system with the ORP set point of -120mV for optimizing the methanol addition, 20% of the methanol dosage was decreased comparing with the operation without the ORP control system and the denitrification efficiency was maintained above 90%. These results suggested that ORP auto-control system would be applied to efficient and cost effective removal of nitrogen from sewage with low C/N ratio.

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Parameter estimation of ASM3+Bio-P Module for step-feed EBPR process by batch tests and CSTR operation data

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Abstract

Various parameter optimization approaches of ASM3+Bio-P Module were examined for five-stage step-feed EBPR process. Optimization approaches could be classified to the data sources from batch experiments or CSTR operation data and the number of target variables for calculating objective function. Optimized parameters values by each approach were validated with CSTR operation data which were not used for parameter optimization step. Results showed that the parameters optimization only with batch experimental results could not be directly applied to CSTR operation data. ASM3+Bio-P Module parameters could be finely optimized only with CSTR operation data when enough target variables for objective function calculation were applied. When increased the number of target variables, prediction performance was significantly improved. Optimized parameters values could present the characteristic of five-stage step-feed process; high PAO yield, fast PAO growth, fast X_{PP} storage and slow X_{STO} and X_{PHA} storage.

Keywords : dPAO, EBPR, five-stage step-feed process, parameter estimation, sensitivity analysis

INTRODUCTION

A five-stage step-feed EBPR process was developed to get the effective nitrogen and phosphorus removal from wastewater which had low C/N and C/P ratio with minimum external carbon. These were made possible by employing denitrifying phosphorus accumulating organisms (dPAOs) which could accumulate phosphate under anoxic condition by utilizing nitrate as a final electron acceptor (Barker and Dold, 1996; Kuba *et al.*, 1993). ASM2d (Henze *et al.*, 1999) and ASM3 (Gujer *et al.*, 1999) with EAWAG Bio-P Module (Rieger *et al.*, 2001) were compared for their applicability to this process, and ASM3+Bio-P Module was proved to be a proper model (Lee *et al.*, 2004). Many researchers have often used batch test data for the parameter estimation (Ekama *et al.*, 1986; Sollfrank and Gujer, 1991; Ko *et al.*, 2001). In these cases, the batch experiments were usually designed and operated under restricted experimental conditions. Therefore, it was difficult to convince that the estimated parameters found from the batch experimental results would be valid to predict the behavior of continuous flow reactors; commonly expressed as CSTR (Completely Stirred Tanks Reactor).

The purpose of this paper was to find a proper approach for parameter estimation with minimum calibration efforts for the application of ASM3+Bio-P Module to five-stage step-feed EBPR process. Five different approaches were examined which could be classified to the data sources from batch experiments or CSTR operation data and the number of target variables for calculating objective function. Optimized parameters values by each approach were validated with CSTR operation data which were not used for parameter optimization step. Consequently, the most proper approach was selected and validated using operation data of the field scale five-stage step-feed EBPR process.

METHODS

Five-stage step-feed EBPR process & Batch experiments

Total working volume of the lab-scale reactor was 39.4 L. The volume ratio of pre-anoxic, anaerobic, anoxic1, anoxic2, and aerobic was 1:2:1:4:7 approximately. The sludge recycle flow and the nitrate recycle flow were 0.3Q and 2Q, respectively as showed in Fig. 1. SRT and temperature was maintained as 15 days and 20℃, respectively.

Two sets of batch experiments were performed using sludge from the CSTR after 80 days of operation. Fig. 2 shows the operating conditions of the batch experiments. Experimental set #1 was designed to identify the phosphate accumulation under anoxic condition by utilizing nitrate as a final electron acceptor. Experimental set #2 was done as control experiments. Initial PO_4^{3-}-P and NO_3^--N concentration at anaerobic and anoxic period were adjusted as 25 and 50 mg/L by the addition of H_3PO_4 and KNO_3, respectively. Each set had four different runs according to various initial SCOD concentrations such as 40, 55, 75, and 105 mg/L which were adjusted by addition of ethanol. Because the supernatant of mixture contained 40 mg COD/L of inert organic, the biodegradable SCOD was 0, 15, 35 and 65 mg/L. Initial VSS was 2000±200 mg/L. Temperature and pH was adjusted as 20±2 °C and 7.5±0.1, respectively.

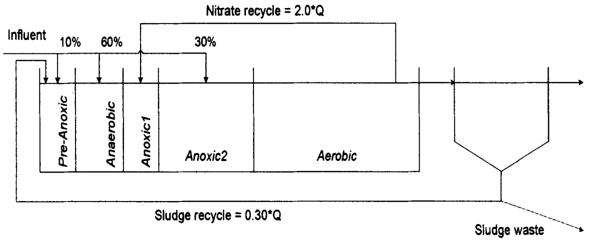


Fig. 1. Schematic diagram of five-stage step-feed EBPR process.

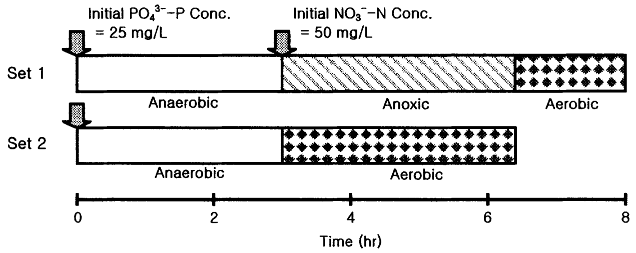


Fig. 2. Operating conditions of batch experiments.

Parameter estimation approaches

Sensitive ASM3+Bio-P Module parameters were selected according to the previous work which aimed at same process (Lee *et al.*, 2004); five stoichiometric; $Y_{STO,NO}$, $Y_{H,O2}$, $Y_{H,NO}$, $Y_{PAO,O2}$, Y_{PO4} and seven kinetic parameters; k_{STO}, η_{NO}, b_H, $\mu_{max,PAO}$, q_{PHA}, q_{PP}, $\mu_{max,A}$. Only these sensitive parameters were optimized experimentally or mathematically, while others were fixed as model defaults suggested by Rieger *et al.* (2001).

1) *For the case of using only batch experimental results:* Two approaches of Opti.B1 and Opti.B2 were proposed. In both cases, Y_{PO4} and $\eta_{NO,PAO}$ were directly calculated from batch experimental results. For Opti.B1, only four parameters related with PAO reactions were optimized mathematically, whereas rest of them were adopted from the default values. For Opti.B2, eleven sensitive parameters except $\mu_{max,A}$ were optimized mathematically. However, $\mu_{max,A}$ could not be optimized experimentally nor mathematically, because nitrification was inhibited, therefore it was assumed as default.
2) *For the case of using both batch and CSTR operation data:* This approach was expressed as Opti.B+C. As it was done for the cases of using only batch experimental results, Y_{PO4} and $\eta_{NO,PAO}$ were calculated with batch results. Other sensitive parameters were mathematically optimized with CSTR operation data during 10-45 days. Data 1-10 days were ignored, because operation was unstable. Estimated parameters were validated with the operation data during 46-87 days.
3) *For the case of using only CSTR operation data:* In these cases, all sensitive parameters were mathematically optimized only with CSTR operation data. The parameter estimation was conducted using two different approaches such as Opti.C1 and Opti.C2 that were different in objective function and the number of target variables.

Objective functions

The objective function was to minimize the sum of relative squared error on TSS, COD, PO_4^{3-}-P, NH_4^+-N and NO_3^--N. Most of parameter estimation was conducted using Optimizer in GPS-X (Hydromantis Inc.) except Opti.C2, because it had 24 target variables while Optimizer in GPS-X can handle the maximum 10 target variables at a time. The objective function of Opti.C2 was to find parameter set minimizing WSSNE (Weighted Sum of Squared Normalized Error).

Validation of parameter estimation approach using data from field-scale plant

The operation data of field plant were used for the validation of parameter estimation approach. Data were collected at J. sewage treatment plant consists of nine serial reactors with total working volume of 1,036m^3 that treats 80,000 p.e. of sewage.

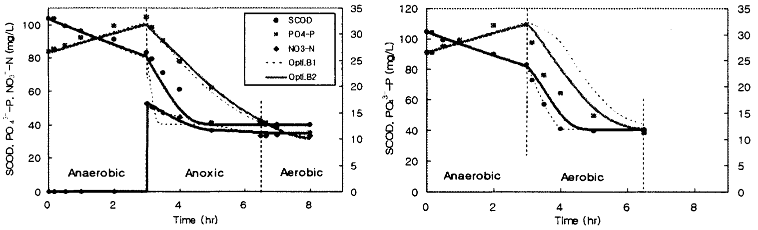
RESULTS AND DISCUSSTION

Parameter estimation and validation with batch results

Sensitive parameters were optimized with batch experimental results at initial COD of 75 mg/L and validated with those at initial COD of 55 and 105 mg /L in this cases. Fig. 3 shows the measured COD, NO_3^--N and PO_4^{3-}-P concentrations at initial COD of 105 mg/L together with simulation results using optimized parameters by Opti.B1 and Opti.B2. Y_{PO4} and $\eta_{NO,PAO}$ were calculated based on the experimental results as 0.38P/gCOD and 0.60. Model prediction showed too fast COD removal at anoxic period of set #1 and too slow PO_4^{3-}-P uptake at aerobic period of set #2 compared with measured data (Fig. 3). It meant that the optimization of only PAO related parameters, Opti.B1, was not the proper approach to explain the bath experimental results, even though experiments were designed to identify phosphate release and accumulation. The simulation using parameters optimized with Opti.B2 could explain the batch results more accurately. However, it underestimated the PO_4^{3-}-P variation in CSTR as shown in Fig. 4. Based on the prediction results which Opti.B2 shown, it could be said as that the parameters optimized with batch results could not be directly applied to CSTR, because the batch experiments were operated under restricted conditions which were quite different from CSTR.

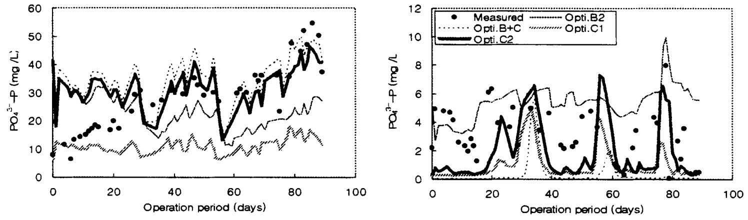
Parameter optimization and validation with CSTR operation data

The parameters optimized by Opti.B+C could successfully predict PO_4^{3-}-P variation in anaerobic reactor, while inconsistency between the experimental data and model prediction was observed in PO_4^{3-}-P variation of effluent (Fig. 4). WSSNE was significantly decreased from 3,186 to 513 compared to Opti.B2 (Tab. 1). It meant that parameter optimization performance could be considerably increased by using both of batch and CSTR operation results. The difference between Opti.B+C and Opti.C1 was the selection method of Y_{PO4} value. At Opti.B+C, Y_{PO4} was experimentally estimated while mathematically optimized at Opti.C1. The value of Y_{PO4} in Opti.C1 was over-estimated to 0.43, but resulted in improved WSSNE at validation. It did not mean that Opti.C1 was better approach than Opti.B+C, but implied Opti.B+C approach was not fully optimized. However, the reliability of parameters optimization only with CSTR operation data was confirmed, and need for strict optimization was arisen, such as Opti.C2. Opti.C2 had the largest numbers of target variables such as COD, PO_4^{3-}-P, NH_4^+-N & NO_3^--N in each reactor and effluent. Validation of Opti.C2 presented the lowest WSSNE of 298. It was concluded as that parameters optimization only with CSTR operation data could produce reliable results when enough target variables were applied.



(a)　(b)

Fig. 3. Validation of optimized parameters with batch results; Initial COD of 105 mg/L. (a) Set #1, (b) Set #2



(a)　(b)

Fig. 4. Prediction of PO_4^{3-}-P concentration with optimized parameters by each approach (a) in anaerobic reactor and (b) in effluent.

Tab. 1. Optimized values of sensitive parameters by each approach.

	Default	Opti.B1		Opti.B2		Opti.B+C		Opti.C1		Opti.C2	
		Value	%Diff.*	Value	%Diff.*	Value	%Diff.*	Value	%Diff.*	Value	%Diff.*
$Y_{STO,NO}$	0.70	0.70	0.0	0.73	4.3	*0.40*	*-42.9*	0.71	1.4	0.71	1.4
$Y_{H,O2}$	0.80	0.80	0.0	*0.98*	*22.5*	0.96	20.0	0.85	6.2	0.91	13.8
$Y_{H,NO}$	0.65	0.65	0.0	0.77	18.5	*0.28*	*-56.9*	*0.26*	*-60.0*	0.52	-20.0
$Y_{PAO,O2}$	0.60	*0.99*	*65.0*	*0.86*	*43.3*	*0.82*	*36.7*	*0.94*	*56.7*	*0.83*	*38.3*
Y_{PO4}	0.35	0.38	8.6	0.38	8.6	0.38	8.6	*0.43*	*22.9*	0.34	-2.9
K_{STO}	12.50	12.50	0.0	*16.55*	*32.4*	*16.39*	*31.1*	*15.17*	*21.4*	*16.83*	*34.6*
η_{NO}	0.80	0.80	0.0	*0.44*	*-45.0*	0.84	5.0	0.91	13.8	0.93	16.3
b_H	0.30	0.30	0.0	0.30	0.0	*0.18*	*-40.0*	0.28	-6.7	*0.22*	*-26.7*
$\mu_{max,A}$	1.80	1.80	0.0	1.80	0.0	*3.00*	*66.7*	*2.67*	*48.3*	1.66	-7.8
q_{PHA}	6.00	*1.65*	*-72.6*	*1.28*	*-78.7*	*2.32*	*-61.3*	*2.22*	*-63.0*	*3.32*	*-44.7*
q_{PP}	1.50	*3.18*	*111.9*	*3.41*	*127.3*	*4.67*	*211.3*	*3.67*	*144.7*	*3.03*	*102.0*
$\mu_{max,PAO}$	1.00	*1.41*	*40.5*	*2.00*	*100.0*	*1.64*	*64.0*	*2.81*	*181.0*	*2.31*	*131.0*
WSSNE**				3,186		513		408		298	

* : % difference compared with default value,　** : when applied to 46-87 days of CSTR operation data,

italic : parameter has over than 20% of difference

Discussion on optimized parameters values

Parameters determined by each optimization approach were quite different from model defaults as shown in Tab. 1. Parameters which shown more than 20% of difference between defaults and optimized by Opti.C2 were $Y_{PAO,O2}$, K_{STO}, b_H, q_{PHA}, q_{PP} and $\mu_{max,PAO}$. It should be emphasized that all of them except b_H, also exhibited high differences at any other approach. This phenomenon could present the characteristic of five-stage step-feed EBPR process such as high PAO yield, fast PAO growth, fast X_{PP} storage and slow X_{STO} and X_{PHA} storage.

Validation of parameter estimation approach using data from field-scale plant

Opti.C2 approach was applied to J. sewage treatment plant in T. city for the validation. Parameters values were optimized with 100 days of pilot plant operation data and employed without additional tuning. The effluent T-N and T-P concentrations were successfully predicted as shown in Fig. 5. Temperature and sludge recycle flowrate was changed in high degree during simulation period, and their effects were excellently explained.

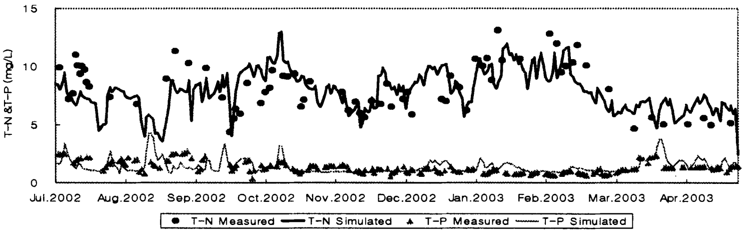


Fig. 5. Measured and simulated effluent T-P and T-N concentrations at J. sewage treatment plant.

CONCLUSIONS

From the comparison of five parameters optimization approaches for ASM3+Bio-P Module, it could be concluded that:

- Optimizing only PAO related parameters was not sufficient to analyze batch experimental results. Phosphate release and uptake is closely related with biodegradable COD in anaerobic phase and stored PHA in anoxic/aerobic phase, therefore other heterotrophic processes take serious effect on phosphate removal. Consequently, other sensitive parameters of heterotrophic processes should be estimated simultaneously.
- Parameters which were optimized only with batch experimental results could not directly be applied to CSTR. For this, parameters should be validated with CSTR operation data.
- Parameters of ASM3+Bio-P Module could be finely optimized only with CSTR operation data when enough target variables were applied. Number of target variables was 24 at Opti.C2, while same or less than 10 at other approaches. It resulted in best effluent quality prediction performance and reliable parameters values.
- Optimized parameters values by Opti.C2 could present the characteristic of five-stage step-feed process; high PAO yield, fast PAO growth, fast X_{PP} storage and slow X_{STO} and X_{PHA} storage.

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