

ผลของอายุตะกอนต่อการบำบัดฟอสฟอรัสโดยใช้ออกซิเจนหรือไนเตรด

เฉลิมราช วันทวิน¹ และ วาสนา พิธรรมนงค์สิน²

สถาบันเทคโนโลยีพระจอมเกล้าธนบุรี

บทคัดย่อ

ในการทดลองนี้ได้ใช้ปฏิกรณ์แบบซีควนซ์แบทช์ (sequencing batch reactor, SBR) 2 ชุด เพื่อศึกษาผลของการควบคุมอายุตะกอนที่เวลาต่างๆ (solids residence time, SRT) และชนิดของตัวรับอิเล็กตรอนตัวสุดท้ายในการกำจัดฟอสฟอรัส โดยที่ชุดหนึ่งใช้ในเตรดเป็นตัวรับอิเล็กตรอน เรียก แอนแอโรบิก-อะน็อกซิด (anaerobic-anoxic SBR) และอีกชุดใช้ออกซิเจน เรียก แอนแอโรบิก-แอโรบิก (anaerobic-aerobic SBR) ทำการทดลองขนานกันโดยแปรเปลี่ยน SRT ที่ 5, 10 และ 15 วัน ดำเนินงานที่หนึ่งวัฏจักรเท่ากับ 8 ชั่วโมง ใช้น้ำเสียสังเคราะห์ที่มีอะซิเตตเป็นแหล่งคาร์บอนวิเคราะห์ COD ได้ 400 มก./ล. มีฟอสฟอรัส 20 มก./ล. คงที่ทุกการทดลอง ผลการทดลองพบว่าความเข้มข้น COD ในน้ำออกจากระบบมีค่าใกล้เคียงกันในทุกการทดลอง แต่การออกซิเดชันสารอินทรีย์ใน anaerobic-aerobic SBR เกิดขึ้นได้ดีกว่าใน anaerobic-anoxic SBR ประสิทธิภาพการกำจัด COD เมื่อใช้ออกซิเจนเท่ากับร้อยละ 96 - 97.9 ในขณะที่ใช้ในเตรดเท่ากับร้อยละ 92.4 - 96 ส่วนในการกำจัดฟอสฟอรัสพบว่า การแปรเปลี่ยน SRT จะให้ผลแตกต่างกันค่อนข้างชัดเจน ซึ่งใน anaerobic - aerobic SBR กำจัดฟอสฟอรัสได้ร้อยละ 47.5, 84 และ 75 ขณะที่ anaerobic - anoxic SBR กำจัดได้ร้อยละ 28.5, 76.6 และ 67.5 ที่การดำเนินงาน SRT 5 วัน, 10 วัน และ 15 วัน ตามลำดับ การวิเคราะห์ความเข้มข้นที่เหลือต่อเวลาในหนึ่งวัฏจักรหลังจากระบบเข้าสู่สภาวะคงที่พบว่า การดำเนินงานที่ SRT ต่ำ ทำให้มีปริมาณสารอินทรีย์ในช่วงการเกิดออกซิเดชัน (aerobic หรือ anoxic) เหลืออยู่ในปริมาณที่มากพอที่จะทำให้ความสามารถในการใช้ฟอสฟอรัสในช่วงดังกล่าวลดลง

¹ ผู้ช่วยศาสตราจารย์ ภาควิชาวิศวกรรมเคมี

² นักศึกษามัธยมศึกษา สาขาวิชาเทคโนโลยีสิ่งแวดล้อม

Effects of Solids Residence Time on Phosphorus Removal with Oxygen or Nitrate

Chalermraj Wantawin¹ and Vasana Peetamnongsin²

King Mongkut's Institute of Technology Thonburi

Abstract

Two sets of experiments were conducted by sequencing batch reactors (**SBRs**) to study the effects of solids residence time (**SRT**) and type of electron acceptor on the removal of phosphorus Nitrate was applied in one set while oxygen in the other and each set was conducted in parallel by varying **SRT** operations that were 5 days, 10 days and 15 days and maintaining cycle time at 8 hours. When tested with synthetic wastewater having acetate as sole carbon source with COD 400 mg/l and phosphorus of 20mg/l, the effluent COD concentrations in all runs were in the same level and slightly higher oxidation were obtained at anaerobic-aerobic **SBRs** (98% - 97.9%) than those at anaerobic-anoxic **SBRs** (92.4% - 98%). However varying **SRTs** results in significant difference on phosphorus removal. At the **SRT** of 5 days, 10 days and 15 days, the phosphorus removal efficiencies were **47.5%**, 84%. and 75% respectively, in the anaerobic aerobic process and **28.5%**, 76.6% and 67.5%. respectively, in the anaerobic anoxic one. Cycle measurement showed that low **SRT** operating gave high remaining COD in external electron acceptor phase and therefore can reduce the capability on phosphorus uptake.

¹ Assistant Professor, **Department** of Chemical Engineering

² Graduate Student, Division of Environmental Technology

Introduction

In biological phosphorus removal process, two different environmental conditions are required : anaerobic and aerobic (or anoxic). The amount of phosphorus uptake in aerobic (or anoxic) phase was related to that released in anaerobic phase which depended highly on the remaining concentration of volatile fatty acids, VFAs (Somiya et al 1988, [1]). The VFAs existing in aerobic period caused by short operation SRT could reduce bacterial ability in phosphorus uptake but too long operating SRT was also objected due to high sludge with phosphorus content accumulated in reactors. Barnard (1984) [2] reported that high efficiencies of phosphorus removal were obtained at low operating SRT. Lin (1988) [3] found that phosphorus removal was decrease when increasing SRT more than 15 days.

Nitrate has been studied by Viekke et al 1988 [4], Wanner et al 1992 [5], and Kuba et al 1993 [6] which concluded that it could be used as a sole electron acceptor, instead of oxygen but less activity.

Same level of high phosphorus removal can be obtained between processes applying nitrate and oxygen if properly parameters be operated. Kinetics and reactor model were also considered in this study in order to investigate the above mentioned condition.

Materials and Methods

Apparatus and Start Up Period

The studies were carried out in two 8 l (5 l working volume) lab-scale reactors. One was operated under cyclic of anaerobic-aerobic while the other anaerobic-anoxic at room temperature ($\approx 28^{\circ}\text{C}$). The reactor contents were agitated continuously by impellers except in the settling period. Inoculated sludge was obtained from leachate treatment plant at Nongkaem in Bangkok. At start up period, mixed liquor suspended solids (MLSS) were maintained to 1500 mg/l and gradually adjusted by sludge volume taken off calculated from following equation

$$Q_w = \frac{V}{\theta_c} \quad (1)$$

where θ_c = solids residence time (d), V = volume of reactor (l), Q_w = volume of drained mixed liquor before settling period (l/d).

Synthetic Wastewater

Acetic acid and phosphate were fed to both of reactors with the concentrations of 400 mg COD/l and 20 mg P/l respectively. Synthetic wastewater with the compositions shown in Table 1 was prepared daily. Sodium nitrate was applied in anoxic period of anaerobic anoxic SBR.

Experimental Procedure

The volumes of sludge were drained, before settling period, 207 ml, 133 ml and 90 ml per cycle in order to control SRTs at 5 days, 10 days and 15 days respectively.

Each SBR was operated in a cycle of 8 hours in which it was consisted of three phases

Table 1 Composition of Synthetic Wastewater

<u>Carbon Source</u>		<u>Comuosition of Trace Mineral</u>	
CH ₃ COONa 3H ₂ O	0.85 g / l	FeCl ₃ 6H ₂ O	1.5 g / l
		H ₃ BO ₃	0.15 g / l
		CuSO ₄ 5H ₂ O	0.03 g / l
		KI	0.03 g / l
		MnCl ₂ 4H ₂ O	0.12 g / l
		Na ₂ MoO ₄ H ₂ O	0.06 g / l
		ZnSO ₄ 7H ₂ O	0.12 g / l
		CoCl ₂ 6H ₂ O	0.15 g / l
<u>Phosphorus Source</u>			
K ₂ HPO ₄	0.065 g / l		
KH ₂ PO ₄	0.037 g / l		
<u>Basic medium</u>			
MgSO ₄ 7H ₂ O	0.6 g / l		
CaCl ₂ 2H ₂ O	0.07 g / l		
NH ₄ Cl	0.227 g / l		
EDTA	0.01 g / l		
Trace mineral	2 ml/l		

as shown in Table 2. The synthetic wastewater was pumped 2 l to the reactors within first 1 hr in Fill & Anaerobic period with the constant rate of 33.33 ml/min. Nitrogen gas was purged in the reactors to assure the anaerobic condition in this phase. Air was supplied through air-diffusers in aerobic phase for anaerobic-aerobic SBR while the other SBR, nitrate was fed with concentration of 692 mg-N/l and constant flow rate of 0.95 ml/min. throughout the period of anoxic phase.

Table 2 SBRs Process Cycle

Time (h)	Reaction	
	Anaerobic-aerobic SBR	Anaerobic-anoxic SBR
4	Fill* & Anaerobic	
	Mixing no aeration	Mixing no nitrate addition
3.5	React	
	aeration and mixing	Continuous nitrate addition and mixing
0.50	Settle & Draw	

* Synthetic wastewater will pump into the reactor with in first 1 h. of the Fill & Anaerobic

Both SBRs were cyclically operating under each SRT until steady state was reached by monitoring MLSS, phosphate, nitrate and COD. At steady state condition, periodical samplings in a cycle were done to examine the changes of phosphate, COD and nitrate or dissolved oxygen. The analytical procedures, including filtrate COD, phosphate, MLSS, MLVSS etc. were as outlined in the Standard Methods for the Examination of Water and Wastewater (1991) [7].

Results and Discussion

Effects of SRT on Substrate Removal.

Steady states of effluent phosphorus concentration in either the experiments on anaerobic-aerobic SBR or those on anaerobic anoxic SBR were reached within 30 days as shown in Figures 1 and 2. The steady state operating parameters as well as removal efficiencies of COD, phosphorus from both sets of SBRs were summarized in Table 3. Even there were no essential differences of organic carbon oxidation determining in term of COD removal percentages, remarkable reduction of COD effluent concentration can be observed as SRT was increased. Phosphorus removal at SRT 5 days was about 50% less than that at SRT 10 days in both SBRs and slightly decreased when SRT changed from 10 days to 15 days. Acetate was sole carbon source applied in this study which was analyzed as COD. Accumulated volatile fatty acid implied by higher concentration of COD effluent at SRT 5 days than that at SRT 10 days results in less phosphorus uptake which can

be shown clearly by cycle measurement in Figures 3 (3.1+3.2) and 4 (4.1+4.2) for anaerobic-aerobic SBR and anaerobic-anoxic SBR respectively. Less sludge taken out at higher operating SRT also reduced phosphorus removal efficiencies and volume of sludge wasted together with MLSS concentration were shown also in Table 3.

Table 3 Summary of operation parameters and qualities of effluent in Anaerobic-aerobic SBR and Anaerobic-anoxic SBR.

Influent COD = 400 mg/l
 PO_4^{3-} - P = 20 mg/l
 Cycle time = 8 hrs.

Process	Anaerobic-aerobic SBR			Anaerobic-anoxic SBR		
	SRT (day)	5	10	15	5	10
MLSS (mg/l)	1480	2580	3432	988	1880	2711
MLVSS (mg/l)	1138	1795	2843	788	1428	2100
Volume of Sludge Waste (ml/d)	800	400	288	800	400	288
COD effluent (mg/l)	16	12	Q	31	22	18
COD removal eff. (%)	82.4	94.5	96	96	97.1	97.8
PO_4^{3-} - P effluent (mg/l)	10.5	3.2	5	14.3	4.7	6.5
PO ₄ ³⁻ - P removal eff. (%)	47.5	84.0	75.0	28.5	76.8	67.5

The rate of phosphorus uptake can be expressed in first order kinetics which was interpreted by linearized plotting between $\ln P$ and t from Figure 5.6 and equation (2)

$$\frac{dp}{dt} = k_p [P][X] \quad (2)$$

where p = concentration of phosphorus in liquid phase (mg/l), k_p = specific P-uptake rate constant (l/mg.h), X = concentration of bacterial MLSS (mg/l). The calculated results were summarized in Table 4 by assuming constant MLSS.

The specific uptake rate constants! k_p , were in the range of $2.13 \times 10^{-4} \sim 3.28 \times 10^{-4}$ l/mg.h for anaerobic-aerobic SBR and $2.09 \times 10^{-4} \sim 3.19 \times 10^{-4}$ l/mg.h for anaerobic-anoxic SBR. Distinctness of k_p values among variation of SRTs could not be promised because the amount of active cells can not be identified by MLSS measurement.

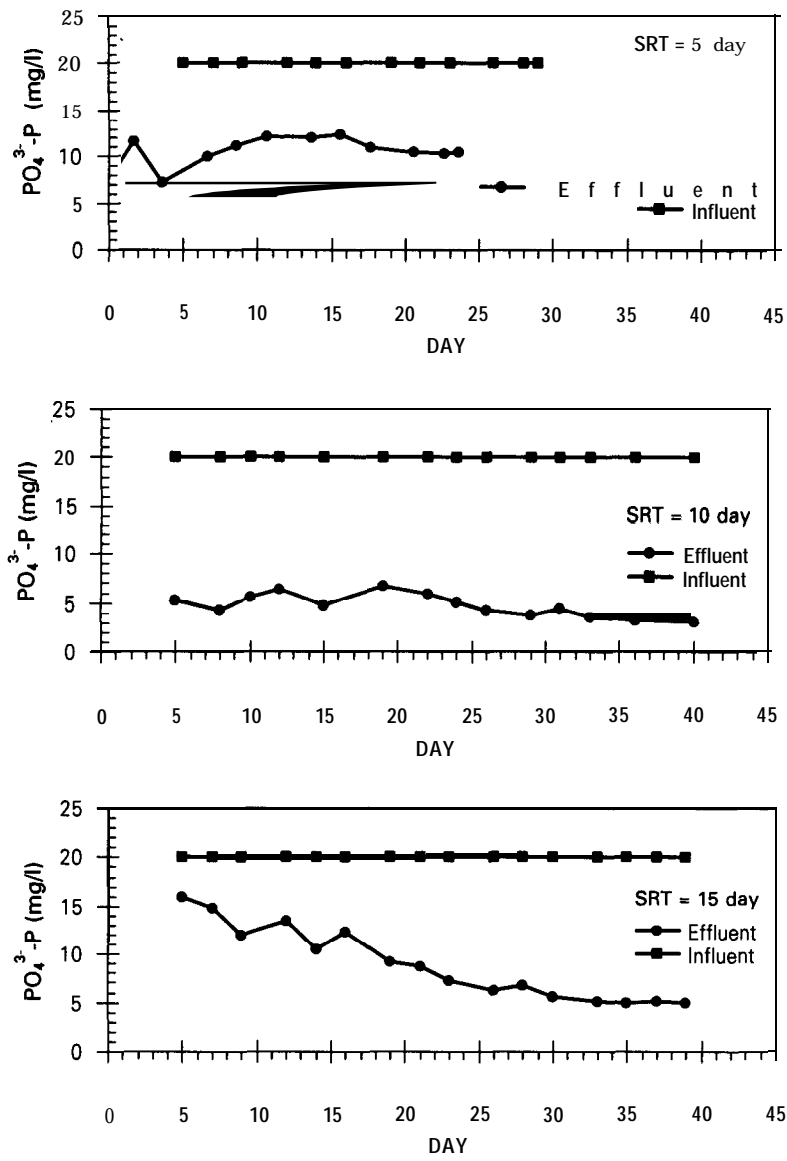


Fig. 1 Effluent Phosphorus variation with time of different SRT in Anaerobic - Aerobic SBR

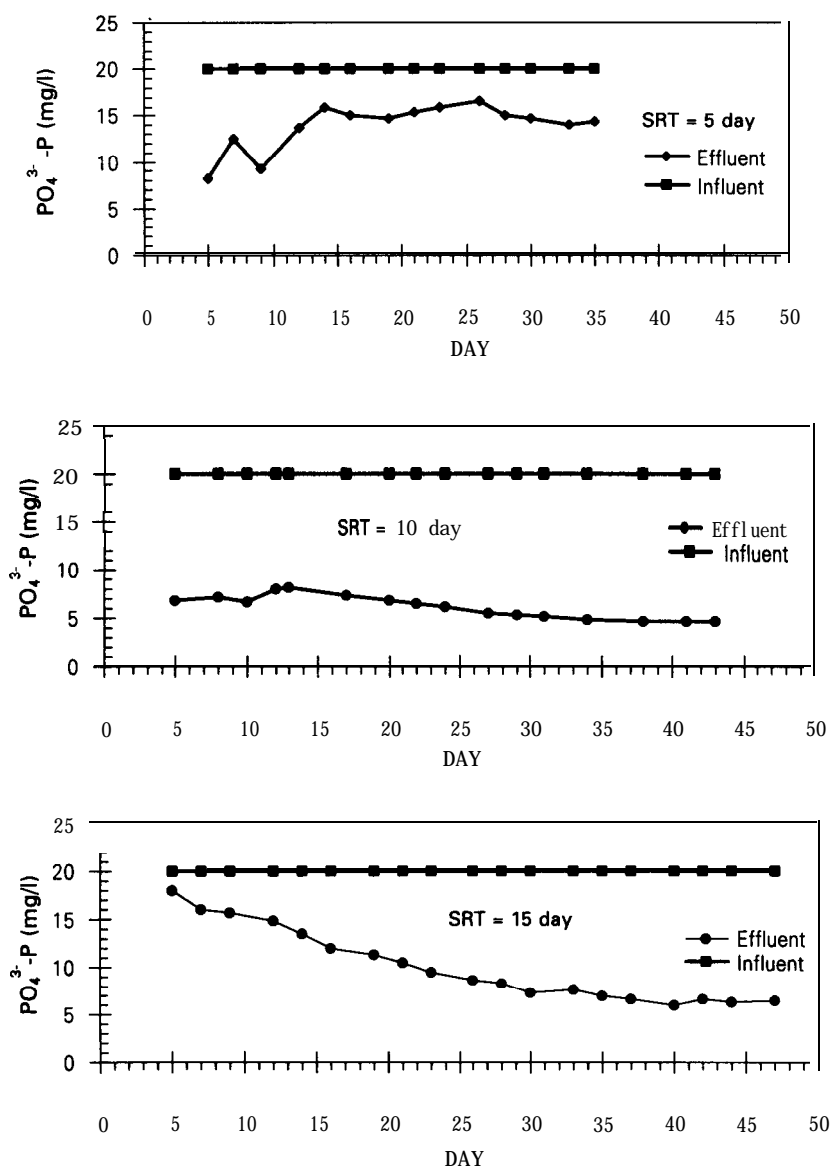


Fig. 2 Effluent Phosphorus variation with time of different SRT in Anaerobic-Anoxic SBR

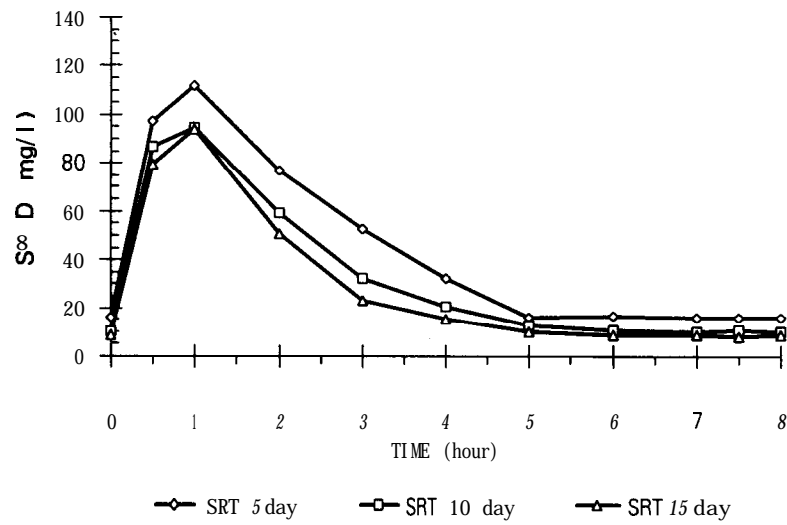


Fig. 3.1 Compare of concentration SCOD variation during a cycle in Anaerobic-Aerobic SBR

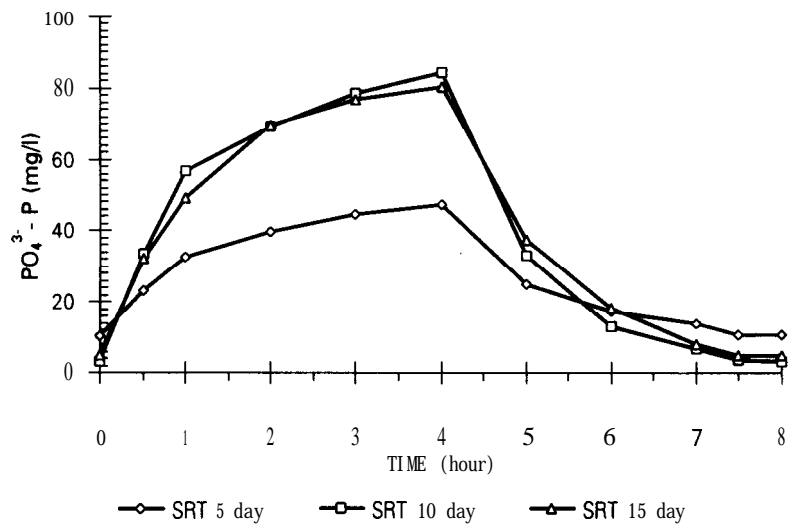


Fig. 3.2 Compare of concentration Phosphorus variation during a cycle in Anaerobic-Aerobic SBR

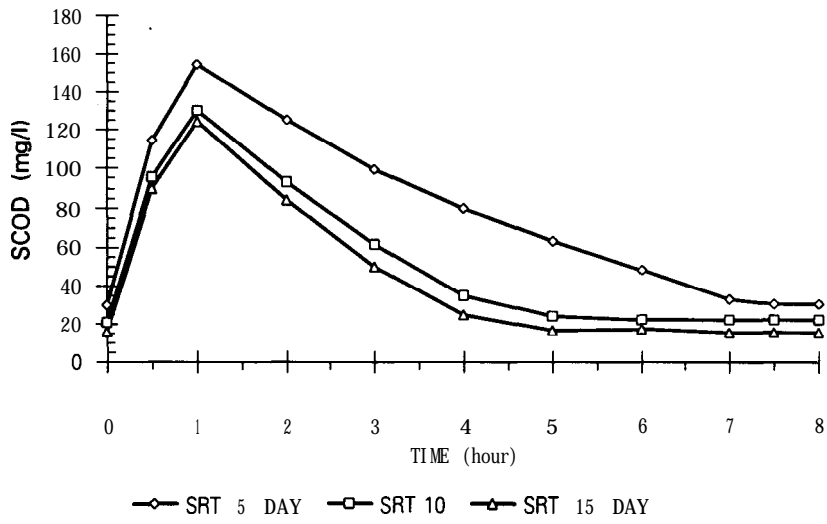


Fig. 4.1 Compare of concentration SCOD variation during a cycle in Anaerobic-Anoxic SBR

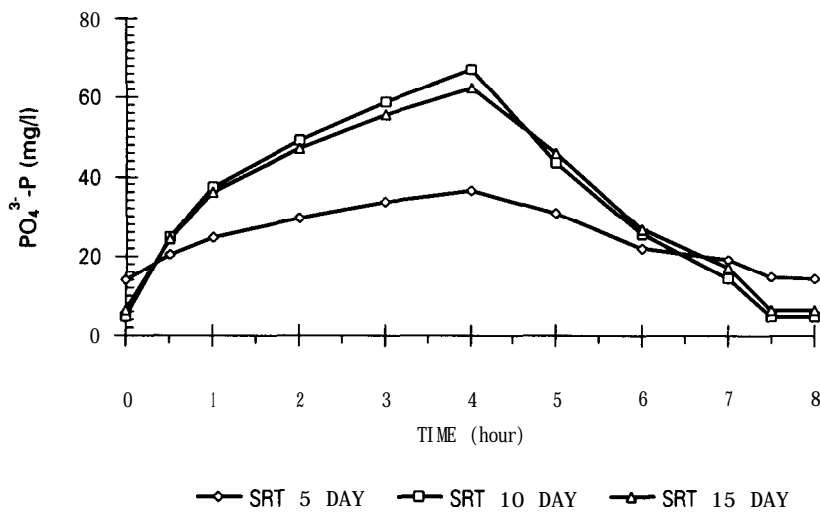


Fig. 4.2 Compare of concentration Phosphorus variation during a cycle in Anaerobic-Anoxic SBR

Table 4 Phosphorus uptake in Anaerobic-aerobic and Anaerobic-anoxic SBRs

Process	Anaerobic-aerobic SBR			Anaerobic-anoxic SBR			
	SRT (day)	5	10	15	5	10	15
MLSS (mg/l)		1460	2500	3432	986	1880	2711
<u>Anaerobic phase</u>							
P released (mg.P/l)		32.3	72.9	68	19.8	55.3	49.4
<u>Aerobic or Anoxic phase</u>							
P uptake (mg.P/l)		37	81.3	75.5	22.3	62.53	55.85
P uptake rate (l/h)		0.37	0.84	0.73	0.25	0.6	0.57
Specific P uptake rate (l/mg.h)		2.53×10^{-4}	3.28×10^{-4}	2.13×10^{-4}	2.49×10^{-4}	3.19×10^{-4}	2.09×10^{-4}
P uptake/ P release		1.14	1.11	1.11	1.13	1.13	1.13

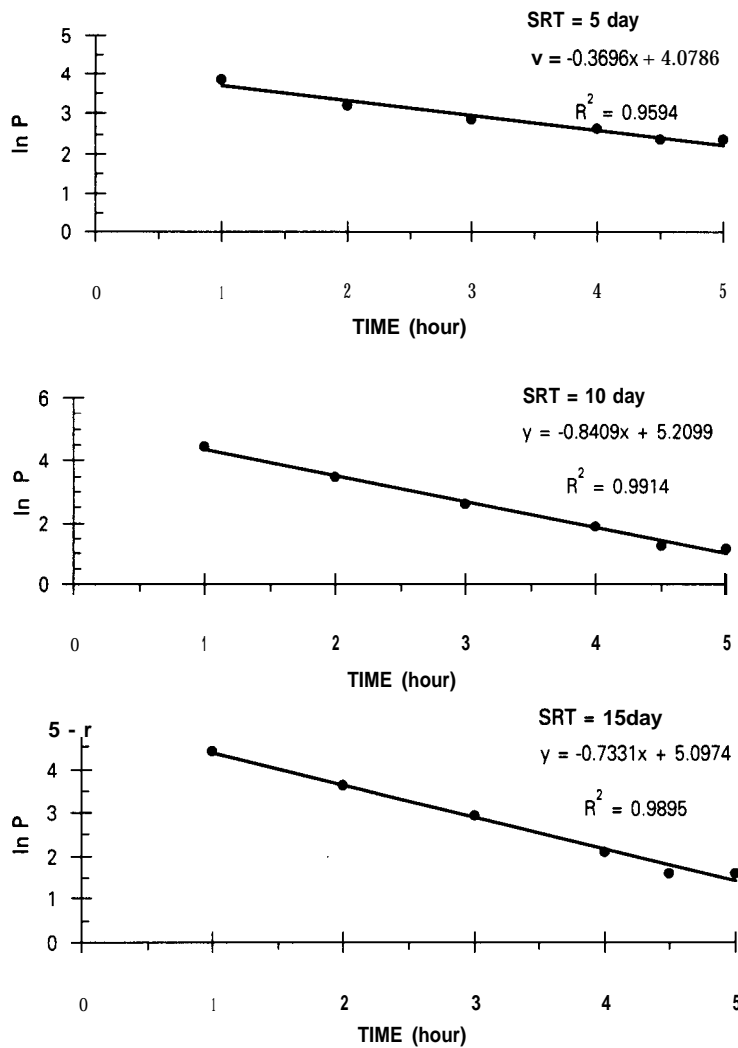


Fig. 5 Correlation between ln P and time of different SRT in Anaerobic-Aerobic SBR

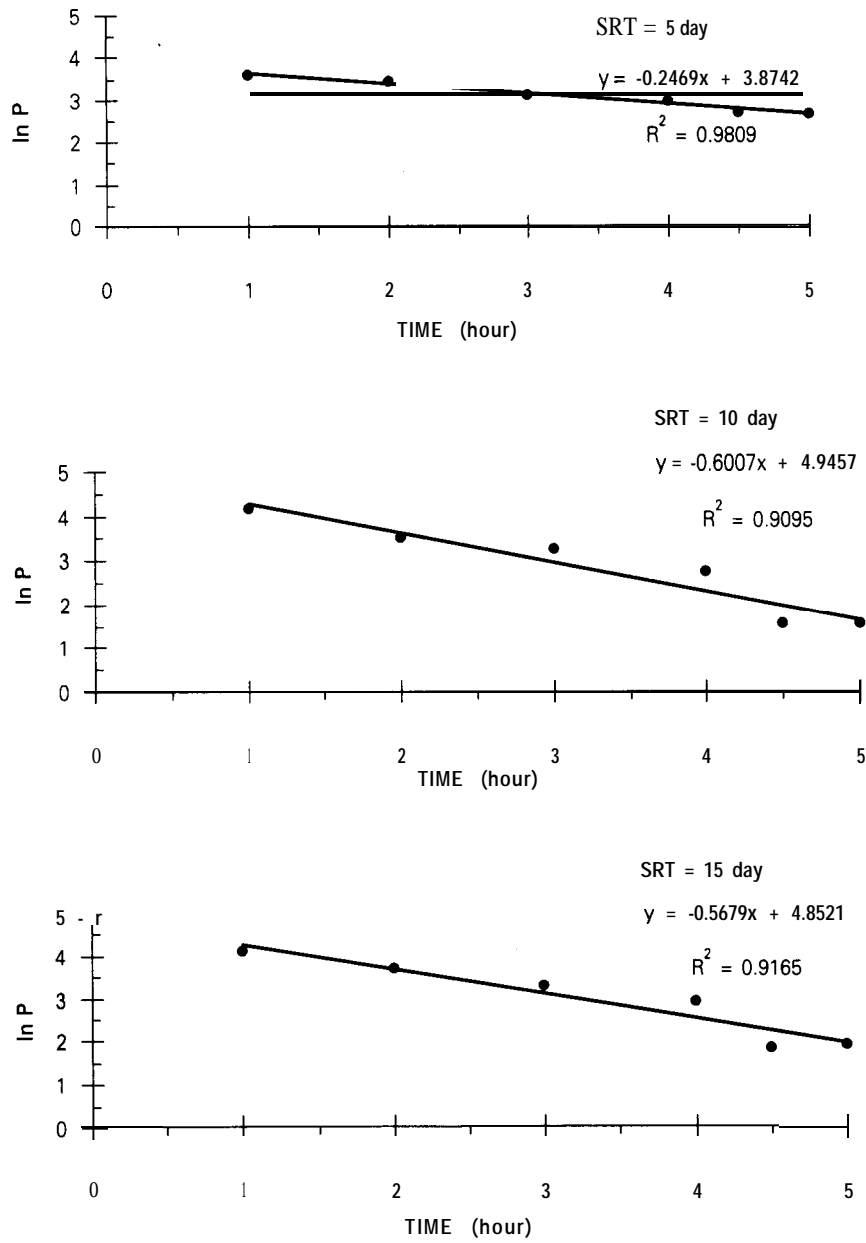


Fig. 8 Correlation between $\ln P$ and time of different SRT in Anaerobic-Anoxic SBR

Comparison of Kinetics and Treatment Effectiveness between Anaerobic, Aerobic and Anaerobic-Anoxic Processes.

Model of continuous reactor with recycle (eqs. 3 and 4) as well as first order reaction of growth rate (eq. 5) were applied and kinetics coefficients can be estimated by linearized plotting as shown in Figures 7 (7.1+7.2) and 8 (8.1+8.2). The equations of 3, 4 and 5 are as follows and the values of coefficients were summarized in Table 5.

$$\frac{\theta_c(s_o - s)}{\theta X} = \frac{k_d}{Y} \theta_c + \frac{1}{Y} \tag{3}$$

$$\mu = \frac{1}{\theta_c} + k_d \tag{4}$$

and $\mu = kS \tag{5}$

(Eq. 5 modified from Monod expression where low substrate concentration)

where θ_c = solids residence time (d), θ = hydraulic detention time (d), S_o = organic carbon concentration in feed (mg COD/l), S = effluent organic carbon concentration (mg COD/l), X = cells concentration (mg MLVSS/l), Y = growth yield (mg MLVSS/mg COD), k_d = endogenous rate constant (1/d), k = specific growth rate constant (mg COD/l/d)

Table 5 Summary of Kinetics in Anaerobic-Aerobic and Anaerobic-Anoxic SBRs

Process	Anaerobic-aerobic SBR	Anaerobic-anoxic SBR
Growth Yield, Y (mg MLVSS/mg COD)	0.412	0.313
Specific growth const., k (mg COD/l/d)	0.0128	0.0085
Endogenous const, kd (1/d)	0.027	0.021
%P removal		
SRT 5 day	47.5	28.5
SRT 10 day	84	78.8
SRT 15 day	75	07.5

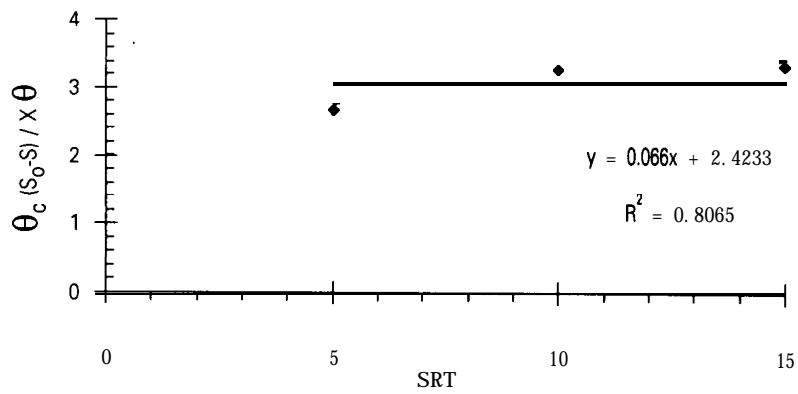


Fig. 7.1 Determination of Y and kd in Anaerobic-Aerobic SBR

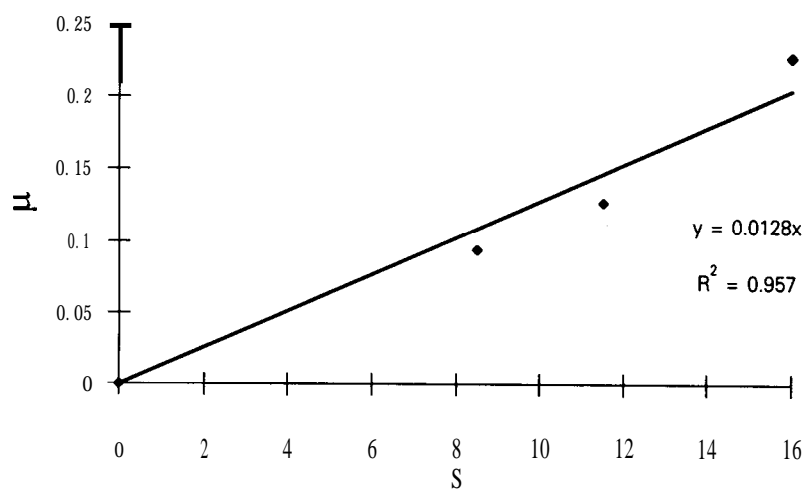


Fig. 7.2 Determination of k in Anaerobic-Aerobic SBR

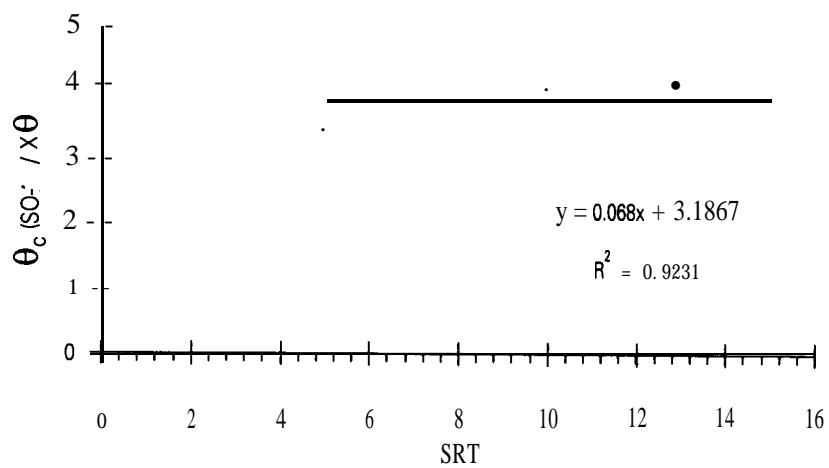


Fig. 8.1 Determination of Y and kd in Anaerobic-Anoxic SBR

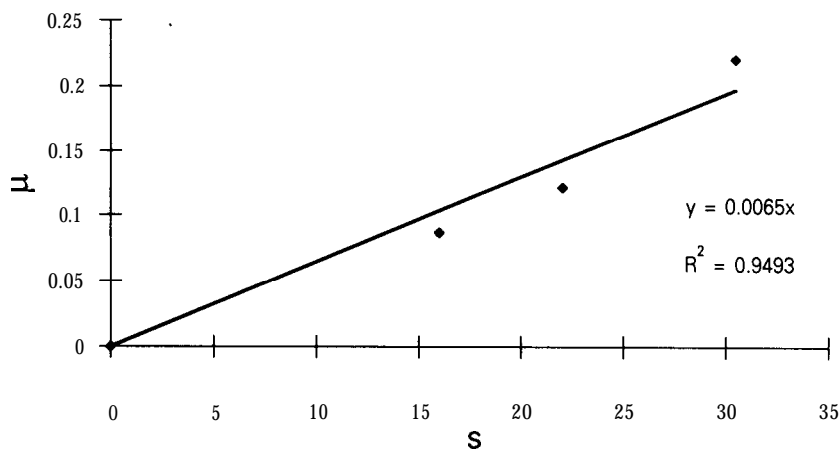


Fig. 8.2 Determination of k in Anaerobic-Anoxic SBR

The efficiencies of substrate removals were also presented in Table 5. The results implied that the ability of phosphorus removal by bacteria utilize nitrate as electron acceptor was less than that utilize oxygen. Phosphorus removal in anaerobic-anoxic SBR can be competitive to that in anaerobic-aerobic SBR when reactors were operated at longer SRT. Nitrate concentration has been monitored and there was no nitrate remaining in anaerobic phase.

Conclusions

The following conclusions have been drawn from the results of the experiments on anaerobic-aerobic SBR and anaerobic-anoxic SBR with variation of operating SRTs.

- In anaerobic aerobic SBR, phosphorus removal efficiencies were found to be 47.5%, 84% and 75% at solids residence time 5 days, 10 days and 15 days respectively.
- The effects of SRT on phosphorus removal in anaerobic anoxic process were the same as in anaerobic-aerobic process and phosphorus removal efficiencies were 28.5%, 78.8% and 87.8% under the operating SRT of 5 days, 10 days and 15 days respectively.
- The efficiencies of COD removal were in the range of 98%-97.6% for anaerobic aerobic SBR and **92.4%-96%** for anaerobic anoxic SBR.
- Kinetics coefficients calculated from this study such as specific P-uptake rate constant (k_p), specific growth rate constant (k) implied that bacteria utilize nitrate was less activity than that utilize oxygen as electron acceptor.

References

1. Somiya, I., Isuno, H., and Matsumoto, M., 1988. "Phosphorus Release Uptake Reaction and Organic Substrate Behavior in Biological Phosphorus Removal" *Wat. Res.*, Vol.22, No.1, pp 48-58.
2. Barnard, 1984, "Activated Primary Tanks for Phosphate Removal" *Wat. SA*, Vol.10, No.3 pp 131-136.
3. Lin. L., 1988, "Nitrogen and phosphorus Removal in Intermittent Activated Sludge Process", Master *of Engineering* Thesis, Environmental Engineering Program, Asian Institute of Technology, pp 14-54.
4. Viekke, G.J.F.M., Comeau, Y. and Oldham, W.K.. 1988, "Biological Phosphate Removal from Wastewater with Oxygen or Nitrate in Sequencing Batch Reactors" *Envi. Tech. Let.* Vol.9, pp 791-796.
5. Wanner, J., Cech, J.S. and Kos, Mo, 1992, "New Process Design for Biological Nutrient Removal" *Wat. Sci. Tech.* Vol.25 No. 4-5, pp 445-448.
6. Kuba. T., Smolders, G., van Loosdrecht, M.C.M. and Heijnen, J.J., 1993, "Biological Phosphorus Removal from Wastewater by Anaerobic-Anoxic Sequencing Batch Reactor" *Wat. Sc. of Tech.* Vol.27 No.5-6 pp 241-252.
7. APHA, 1981, *Standard Methods for the Examination of Water and Wastewater*, 17th ed. American Public Health Association, Washington, D.C.