Kinetic Rates and Mass Balance of COD, TKN, and TP Using SBR Treating Domestic and Industrial Wastewater

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Objective: To assess the performance of SBR to treat three different types of wastewater from domestic, hospital, slaughterhouse and investigate the kinetic rates of active biomass. Mass balance calculation of COD, TKN and TP was further performed to explain the mechanisms of the biological nutrient removals processed in the SBR system. The measured kinetic rates were in turn used to evaluate the process performances under different types of wastewater.

Material and Method: Experimental research involving 3 similar SBR lab-scales were installed and operated at the Sanitary Engineering Laboratory. The reactors were seeded with sludge biomass obtained from the Sri-Phraya Domestic Wastewater Treatment Plant in Bangkok. The slaughterhouse, hospital and domestic wastewaters were treated by SBR system for biological organic carbon (COD), nitrogen (TKN) and phosphorus removals. Biological methods for kinetic rates evaluation were conducted in five replicated batch tests.

Results: The removal efficiencies of COD and TKN were greater than 90% for all three types of wastewater while the biological phosphorus removal for domestic and hospital wastewaters were less than 60% and phosphorus removal for slaughterhouse exceeded 95%. The kinetic rates of nitrification and denitrification of hospital wastewater was lower than those the domestic and slaughterhouse wastewaters. Phosphorus release and uptake rates of slaughterhouse wastewater were high but domestic and hospital wastewaters were very low.

Conclusion: The result of system removal efficiency and batch test for kinetic rates confirmed that the domestic and hospital wastewaters were in deficiency of organic carbon with respect to its ability to support successful biological phosphorus removal.

Keywords: Domestic wastewater, Industrial wastewater, Sequencing batch reactors, Kinetic rate, Biological nutrient removal

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Discharges of wastewater with organic carbon and nutrient (nitrogen, and phosphorus) can lead to adverse effects in water bodies. Nitrogen and phosphorus are the essential nutrients for the growth of algae and cyanobacteria. Where both nitrogen (N) and phosphorus (P) are plentiful, algal blooms can occur extensively which may produce a variety of nuisance condition. This could be harmful to the aquatic life and related public health problems⁽¹⁾. Contamination of nitrate nitrogen in public water supplies as an example often causes methemoglobinemia (Blue baby syndrome) in infants and cancer in $man^{(2,3)}$.

Simultaneous removal of organic carbon and nutrients can be achieved through a biological nutrient removal (BNR) scheme. The primary characteristics of BNR system is the alternate conditions of anaerobic, anoxic, and aerobic environments to stimulate the growth of autotrophs, heterotrophs, and phosphorus accumulating organisms (PAOs)⁽⁴⁻⁶⁾. However, full-scale BNR facilities are normally characterized by significant land requirements and operational complexity. Sequencing batch reactor (SBR) technology can serve

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as an attractive alternative solution, particularly when land availability as well as flexibility and simplicity of operation are of concern⁽⁷⁻⁹⁾. Domestic, hospital, and slaughterhouse have also produced high quantities of wastewater with their major pollutants are organic carbon substances, nitrogen, and phosphorus^(10,11). All three different types of wastewater were treated by SBR^(12,13) system for biological COD, TKN and phosphorus removals. The main objectives of this research were to (i) assess the performance of SBR system; (ii) investigate the effect of wastewater type on the kinetic rates of active biomass, and (iii) explain the fate of COD, TKN, and TP in the system. The result of kinetic studies and fate of COD, TKN, TP can be used to justify the feasibility and effectiveness of SBR as an alternative for the BNR system.

Material and Method

Experimental procedure

Biological treatment was accomplished using three identical SBR systems. Cylindrical reactors were made of plastic (acrylic) material with 14.3-cm diameter and 38-cm height. Each reactor had an actual volume of 5 l, equipped with cover plate, rubber stopper, air diffuser, and stirrer. Other accessories included feeding pumps, influent and effluent containers, valves, air compressors, and microprocessor time controllers. The systems were sealed to prevent any air entrapment during the non-aerated periods. The operation patterns of SBR performed under anaerobic static fill and reacts mode, consisting of anoxic/oxic/anoxic/oxic condition (AnA²/O² SBR).

The reactors were seeded with biomass obtained from the Sri-Phraya Domestic Wastewater Treatment Plant in Bangkok. The slaughterhouse wastewater was collected from the Pork Traders Cooperative of Bangkok Limited while hospital and domestic wastewaters were taken from Rajavithi Hospital Wastewater Treatment Plant and Huay Kwang Wastewater Treatment Plant in Bangkok, respectively. A summary of important influent characteristics was presented in Table 1.

Prior to start the continuous operation of sequencing batch reactor, the reactors were seeded with sludge biomass to achieve an initial mixes liquor suspended solids (MLSS) concentration of approximately 6,000 mg/l for each reactor. To allow the biomass to get acclimatized with the wastewater, a step-by-step feeding approach was followed during acclimatization period, starting with an active volume of 2.5 l. Each system was allowed to achieve at least 80% COD removal under a reasonably stable operation (*i.e.* no more than 10% fluctuation in the removal values) prior to any further increase in flow rate of about 20%. This incremental addition was (without any liquid wastage) made until the targeted operating volume of 5l was accomplished.

Batch test for kinetic rate evaluation

After the system reached the steady-state (of about 4 months) as mentioned earlier, batch test of nitrification rate (NR), denitrification rate (DNR), phosphorus release rate (PRR), and phosphorus uptake rate (PUR) of the sludge were determined under different characteristics of sludge biomass at steady state condition of SBR. Kinetic rates were characterized by bacterial functional group and determined by a specific process rates. Reactor batch experiments of 1 L were set up to monitor the NR, DNR, PRR, and PUR separately for all three types of wastewater. Numerous batch tests were conducted on different dates. Each batch experiment was performed in five replicated tests. In the NR and DNR tests, the linear profile of nitrate concentration in batch experiment was determined. In the PRR and PUR test, the linear profile of phosphorus concentration in batch experiment was determined. To evaluate the specific nitrification rate (SNR), specific denitrification rate (SDNR), specific phosphorus

Parameters	Slaughterhouse		Hospital		Domestic	
	Mean	Range	Mean	Range	Mean	Range
pH COD (mg/l) TKN (mg-N/l) TP (mg-P/l)	$\begin{array}{c} 7.4 \pm 0.1 \\ 1468.0 \pm 234.0 \\ 186.0 \pm 23.5 \\ 19.0 \pm 3.6 \end{array}$	6.7-7.8 1108-1980 140-235 15.4-37	$7.3 \pm 0.14 \\ 300.0 \pm 44.3 \\ 45.8 \pm 3.9 \\ 5.6 \pm 0.7$	7.0-7.4 240-453 26.6-46.2 3.2-6.8	$7.2 \pm 0.1 \\ 290.0 \pm 30.0 \\ 52.1 \pm 7.5 \\ 6.9 \pm 0.9 \\$	6.9-7.5 263-369 39.2-64.4 5.2-9.3

Table 1. Wastewater characteristics of different types of wastewater



Fig. 1 Typical kinetic rates determination of slaughterhouse wastewater; a) denitrification rate, b) nitrification rate, c) phosphorus release rate, d) phosphorus uptake rate

release rate (SPRR), and specific phosphorus uptake rate (SPUR), the rates were calculated by the slope of the graph (linear) divided by the mixed liquor volatile suspended solids (MLVSS) in the batch reactor as illustrated in Fig. 1.

Analytical methods and sampling schedule

Monitoring studies conducted in SBR system involve the sampling for Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (TKN), and Total phosphorus (TP) analyses. The Dissolved Oxygen (DO) concentration was measured with a DO electrode (YSI 550DO), measurements of COD, nitrate (NO₃N), mixes liquor suspended solids (MLSS), and mixed liquor volatile suspended solids (MLVSS) were conducted according to those procedures in Standard Methods for the Examination of Water and Wastewater⁽¹⁴⁾. Throughout the study, influent and effluent sampling were collected from each SBR three times a week and analyzed for COD, TKN, and TP while the reactor MLVSS, MLSS, DO, and pH were measured on a daily basis.

Results

System Performance

Designated conditions of the experiment were carried out after the seeding and acclimatization processes till reaching the pseudo-steady state condition. The overall system performances were presented in terms of COD, TKN, and TP removal efficiencies as shown in Table 2. High removal efficiencies of COD and TKN were exhibited in all systems. But removal efficiency of phosphorus taken from the domestic and hospital wastewater were 44.7%, and 65.1%, respectively while that of the slaughterhouse wastewater was in good performance. These indicated that the characteristics of different types of wastewater have an effect on the biological phosphorus removal process (BPR).

Kinetic rates evaluation

The specific nitrification rates (SNR) and specific denitrification rates (SDNR) of three types of wastewater are presented in Table 3, according to the results of nitrification test from five replicated tests. The average nitrification rate of domestic, hospital, and slaughterhouse wastewater were found to be $1.99 \pm 0.42, 0.93 \pm 0.18, 2.66 \pm 0.37 \text{ mg NO}_2-N/g-VSS/h,$ respectively. The SDNR trends of three type of wastewater were similar to those of the SNR and the average denitrification rate of hospital wastewater was lower than those of domestic and slaughterhouse wastewaters. The specific phosphorus release rates (SPRR) and specific phosphorus uptake rate (SPUR) were shown in Table 3. The results of SPRR and SPUR from domestic and hospital wastewater are very low, but those of the slaughterhouse wastewater are very high.

Wastewater	COD		TKN		ТР	
	Effluent (mg/l)	Removal efficiency (%)	Effluent (mg/l)	Removal efficiency (%)	Effluent (mg/l)	Removal efficiency (%)
Domestic Hospital Slaughterhouse	$\begin{array}{c} 28.0 \pm 7.8 \\ 26.9 \pm 8.9 \\ 30.0 \pm 11.6 \end{array}$	91 91.6 97.9	$\begin{array}{c} 2.34 \pm 1.14 \\ 1.63 \pm 0.59 \\ 4.14 \pm 1.44 \end{array}$	95.5 95.7 97.7	$\begin{array}{c} 3.81 \pm 0.71 \\ 1.95 \pm 0.43 \\ 0.85 \pm 0.32 \end{array}$	44.7 65.1 95.5

Table 2. Effluent and removal efficiency of organic and nutrient using SBR

Table 3. Biomass kinetic rates of different types of wastewaters

Wastewater	SNR mgNO ₃ -N/g VSS/hr	SDNR mgNO ₃ -N/g VSS/hr	SPRR mg-P/g VSS/hr	SPUR mg-P/g VSS/hr
Domestic	1.99 ± 0.42	1.20 ± 0.59	0.18 ± 0.05	0.27 ± 0.19
Hospital	0.93 ± 0.18	0.67 ± 0.26	0.09 ± 0.01	0.05 ± 0.01
Slaughterhouse	2.66 ± 0.37	1.99 ± 0.82	1.99 ± 0.51	1.66 ± 0.31

Mass balance of COD, N, and P

The mass balance of organic matter, nitrogen and phosphorus will help to visualize the picture of system removal efficiency. For Stoichiometric calculation in mass balance, the Yield observes (Y_{obs}) value from domestic, hospital, and slaughterhouse wastewaters were 0.25, 0.23, and 0.3 g/d respectively. Stoichiometric coefficient of the COD-biomass was calculated as 1.42 g COD/g Biomass. This value obtained from the empirical formula represented the composition of active biomass, $C_3H_7O_2N^{(15)}$, which were in accordance with the following theoretical oxidation equation of the biomass:

$$C_5H_7O_2N + 5O_2 + H^+ \rightarrow 5CO_2 + 2H_2O + NH_4^+$$
 (1)

In addition, the nitrogen and phosphorus content of cell biomass was reported to be 12.3% and 2.6%, respectively. This the value of phosphorus content did not include the amount of the storage of poly-phosphate of PAO⁽¹⁶⁾. Based on the experimental results and the above assumptions of calculating the composition of nitrogen and phosphorus in cell biomass, the mass distribution of COD, TKN, and TP was finally calculated. The values of influent and effluent were obtained directly from the chemical analysis. The removal value was achieved from the difference between inflow (Influent), out flow (Effluent) and yield. The value of the yield was estimated through the Y_{obs} , biomass production and the stoichiometric coefficient. The yield sludge biomass of the SBR

system treating the domestic, hospital, and slaughterhouse were 0.352, 0.34, and 2.15 g-sludge biomass/d, respectively.

Table 4 shows that approximately 41.7% of the organic carbon (COD), 28.1% of the nitrogen and 59.5% of the phosphorus of the raw slaughterhouse wastewater were turned into the biomass yield. About 56.2% of the organic carbon was removed from this system in form of carbon dioxide, 63.7% of the nitrogen was removed in form of nitrogen gas, and 36.2% of the total phosphorus was removed as poly-phosphate incorporated with waste sludge. In addition, trend of COD and TN were removed from the systems treating with domestic and hospital wastewater in terms of carbon dioxide and nitrogen gas were similar to those of slaughterhouse wastewater.

Fate of COD TKN and TP in SBR treating slaughterhouse wastewater

Fate of COD, TKN, and TP could be used to illustrate and clearly visualize the removal pattern of the AnA^2/O^2 SBR process. A representative plot profile curve for slaughterhouse wastewater was presented in Fig. 2. Calculation of mass distribution of COD, TKN, and TP through the react-processes of SBR was presented in Table 5.

Fate of COD and TP

The overall COD and phosphorus removals at steady state were greater than 97% and 95%, respectively. The removal characteristic of organic

Parameters		Dome	Domestic		Hospital		Slaughterhouse	
		Load (g/d)	%	Load (g/d)	%	Load (g/d)	%	
COD	Influent	1.55	100	1.61	100	7.34	100	
	Biomass Yield	0.5	32.2	0.48	29.8	3.06	41.7	
	Remove (in CO ₂ form)	0.91	58.7	0.996	61.8	4.13	56.2	
	Effluent	0.14	9	0.13	8.32	0.15	2.1	
TKN	Influent	0.26	100	0.193	100	0.925	100	
	Biomass Yield	0.043	16.5	0.048	21.6	0.26	28.1	
	Remove (in N_2 form)	0.215	82.6	0.12	61.2	0.59	63.7	
	Effluent	0.002	0.76	0.033	17.1	0.075	8.1	
ТР	Influent	0.034	100	0.028	100	0.094	100	
	Biomass Yield	0.009	26.4	0.008	31.4	0.056	59.5	
	Remove (in poly-P form)	0.006	17.6	0.009	33.9	0.034	36.2	
	Effluent	0.019	55.8	0.009	34	0.004	4.25	

Table 4. Mass balance of organic carbon, nitrogen, and phosphorus processed in SBR

Table 5. Fate of COD, TKN, and TP in AnA²/O² SBR treating slaughterhouse wastewater

	COD		TKN		ТР	
Processes	Initial mass	Initial mass	Initial mass	Initial mass	Initial mass	Initial mass
	flow (g.cycle ⁻¹)*	* distribution (%)	flow (g.cycle ⁻¹)*	distribution (%)	flow (g.cycle ⁻¹)*	distribution (%)
Anoxic I	1.95	100	0.25	100	0.087	100
Oxic I	0.96	49.2	0.21	86	0.262	302
Anoxic II	0.48	24.6	0.045	18	0.028	32
Oxic II	0.15	7.7	0.035	14	0.006	7.1
Effluent	0.11	5.8	0.025	10	0.002	2.9
	Processes Anoxic I Oxic I Anoxic II Oxic II Effluent	CODProcessesInitial mass flow (g.cycle ⁻¹)*Anoxic I1.95Oxic I0.96Anoxic II0.48Oxic II0.15Effluent0.11	CODProcessesInitial mass flow (g.cycle ⁻¹)* distribution (%)Anoxic I1.95100Oxic I0.9649.2Anoxic II0.4824.6Oxic II0.157.7Effluent0.115.8	COD TKN Processes Initial mass flow (g.cycle ⁻¹)* distribution (%) Initial mass flow (g.cycle ⁻¹)* Anoxic I 1.95 100 0.25 Oxic I 0.96 49.2 0.21 Anoxic II 0.48 24.6 0.045 Oxic II 0.15 7.7 0.035 Effluent 0.11 5.8 0.025	COD TKN Processes Initial mass flow (g.cycle ⁻¹)* distribution (%) Initial mass flow (g.cycle ⁻¹)* distribution (%) Anoxic I 1.95 100 0.25 100 Oxic I 0.96 49.2 0.21 86 Anoxic II 0.48 24.6 0.045 18 Oxic II 0.15 7.7 0.035 14 Effluent 0.11 5.8 0.025 10	COD TKN TP Processes Initial mass

* Measured in form of soluble



Fig. 2 Profile concentration of COD, TKN, and TP using SBR to treat slaughterhouse wastewater

carbon in terms of COD was shown in Table 5. The reduction of COD occurred within the first anoxic and continues to the end of the process operation (Fig. 2). The removal efficiency of COD was 50.8% in the first anoxic, 24.6% in the first Oxic, 16.9% in the second anoxic and 1.9% in the second oxic. However, the

phosphorus distribution in the reactor was increased up to 302% at the end of the first anoxic. This mass distribution decreased from the first oxic to the second anoxic, and finally to the second oxic at 32%, and 7.1%, respectively.

Fate of TKN

The initial mass distribution of TKN from the first anoxic to the first oxic, the second anoxic, and finally to the second oxic at 86%, 18%, and 14%, respectively (Table 5). These data show that TKN reduction under anaerobic and aerobic conditions were 14%, and 72%, respectively.

Discussion

System performance

Hospital and domestic raw wastewaters used in this study were poorly characterized for biological phosphorus removal process. Considering on the ratio of COD:TKN from the presented data (Table 1), it reveals that domestic and hospital wastewater was lower than the slaughterhouse wastewater. The result reminds that the wastewater lacks of sufficient and suitable COD to support phosphorus removal^(10,17).

Kinetic rates evaluation

The results reveal that the hospital wastewaters have SNR and SDNR lower than those of the domestic and slaughterhouse wastewaters. The lowrate of nitrification occurred in hospital wastewater reminded that the nitrifying bacteria quite low function when treated wastewater from hospital. Comparing the result of denitrification rates between wastewater sources, it was found that the slaughterhouse wastewater has a high quality source serving as a substrate for denitrification. Several researchers have reported that the high-rate of denitrification was referring to a high quality of organic carbon source serving as a main substrate for microorganism growth under anoxic processes^(18,19). SPRR and SPUR tests, the result indicated that the process rates are clear with the result of phosphorus removal efficiency. From this result, it suggests that slaughterhouse wastewater has sufficient and suitable COD used as carbon source for Phosphorus Accumulating Organisms (PAOs) under the process of anaerobic phosphorus release. The SPUR related to the aerobic phosphorus release process. Considering on the COD:TKN ratio, it can be calculated from wastewater characteristic (Table 1) as 8, 6, and 5 for slaughterhouse, hospital, and domestic wastewaters respectively. These results indicated that the PAOs were not able to function well under low COD:TKN ratio, this observation was agreed with those studied by Fongsatitkul⁽¹⁷⁾ as increasing the COD:N feeding ratio could significantly stimulate the growth of PAO.

Mass balance of COD, TKN, and TP

The result of calculated mass balance indicated that the main mechanism of COD and TKN removals in SBR were a cell-biomass growth (synthesis) and biochemical oxidation processes. In addition, phosphorus removal mechanism was classified as; (1) phosphorus served as a nutrient for biomass growth and a new cell synthesis, and (2) phosphorus was kept in form of intra-cellular storage product as a poly-phosphate.

Fate of COD, TKN, and TP

Fate of substrate could be used to illustrate and clearly visualize the removal pattern of the SBR

process. The results suggest that the main process for COD and phosphorus removal occur within two first phase of SBR (first anoxic and first oxic). In first anoxic, the main reactions were poly-phosphate cleavage and COD consumed for phosphorus accumulating organisms (PAOs). For the first oxic phase, the main reaction was phosphorus uptake and oxidation of organic matter during the growth of PAOs. In these behaviors, it reminded that the composition of COD in slaughterhouse wastewater was in a good quality for being consumed or adsorbed by PAOs in the anoxic/ anaerobic conditions. In TKN removal pattern, the result suggests that TKN reduction under anaerobic condition was assimilation for biosynthesis of bacterial cell while under aerobic condition it was a dissimilation through nitrification process. These results indicated that the main reaction of TKN removal was a nitrification process in the first oxic.

In conclusion, the SBR system employed in this research has successfully treated the three different types of wastewater, namely as domestic, hospital and slaughterhouse wastewaters. Characteristics of active biomass were investigated using a calculated mass balance and kinetic rates approaches. The COD and TKN removal efficiencies were in excess of 90% for all types of wastewater, while TP removal ranged from 44-95%. Biological phosphorus removal (BPR) process was occurred in the SBR when slaughterhouse wastewater was treated. Phosphorus removal efficiency of slaughterhouse wastewater exceeded 95%. In addition, the result of system removal efficiency and batch experiment confirmed that the domestic and hospital wastewaters were in deficiency of organic carbon with respect to its ability to support successful biological phosphorus removal.

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อัตราทางจลนศาสตร์และสมดุลมวลของ ซีโอดี, ทีเคเอ็น, และฟอสฟอรัส โดยการใช้ SBR สำหรับ การบำบัดน้ำเสียชุมชนและน้ำเสียอุตสาหกรรม

ชวลิต วโรดมรังสิมันตุ์, ประยูร ฟองสถิตย์กุล

วัตถุประสงค์: เพื่อหาประสิทธิภาพของระบบ SBR ในการบำบัดน้ำเสียสามประเภทด้วยกันคือ น้ำเสียจากซุมซน, โรงพยาบาล, และโรงงานฆ่าสัตว์ พร้อมกับการศึกษาอัตราทางจลนศาสตร์ของมวลชีวภาพ นอกจากนี้การคำนวณ สมดุลมวลของ COD, TKN, และ TP ได้ถูกใช้เพื่ออธิบายกลไกของขบวนการกำจัดสารอาหารทางชีวภาพในระบบ SBR ซึ่งอัตราที่วัดได้นี้จะถูกนำมาใช้ในการประเมินประสิทธิภาพและใช้ในการคำนวณปรับเปลี่ยนรูปแบบของขบวนการ ในการรับน้ำเสียที่ต่างประเภทกัน

วัสดุและวิธีการ: เป็นการทดลองในระดับห้องปฏิบัติการด้วยชุดทดลอง SBR ที่มีลักษณะเหมือนกัน 3 ชุดติดตั้ง และเดินระบบที่ห้องปฏิบัติการวิศวกรรมสุขาภิบาล ถังปฏิกรณ์ใช้สลัดจ์ชีวภาพจากโรงบำบัดน้ำเสียชุมชนสี่พระยา ระบบ SBR บำบัดน้ำเสียจากชุมชน, โรงพยาบาล, และโรงงานฆ่าสัตว์เพื่อการกำจัดสารอินทรีย์คาร์บอน, ไนโตรเจน, และ ฟอสฟอรัส วิธีการทางชีววิทยาสำหรับการหาอัตราทางจลนศาสตร์ของมวลชีวภาพทำโดยชุดทดลอง แบบแบตซ์ (Batch Test)

้ผลการศึกษา: ประสิทธิภาพการกำจัด ซีโอดีและทีเคเอ็น มีค่ามากกว่าร้อยละ 90 ในน้ำเสียทั้งสามประเภท ในขณะที่ ประสิทธิภาพการกำจัดฟอสฟอรัสทางชีวภาพเกิดขึ้นน้อยกว่าร้อยละ 60 ในน้ำเสียซุมซนและน้ำเสียโรงพยาบาล และ มากกว่าร้อยละ 95 ในน้ำเสียโรงงานฆ่าสัตว์ สำหรับอัตราทางจลนศาสตร์ของไนตริฟิเคชันและดีไนตริฟิเคชันของ น้ำเสียโรงพยาบาลมีค่าต่ำกว่าน้ำเสียซุมชน ในส่วนของอัตราการปลดปล่อยและนำเข้าฟอสฟอรัสของน้ำเสีย โรงฆ่าสัตว์ มีค่าสูงแต่น้ำเสียซุมชนและน้ำเสียโรงพยาบาลมีค่าต่ำกว่ามาก

สรุป: จากประสิทธิภาพของระบบและผลของการทดลองแบบแบตซ์ในการหาค่าอัตราทางจลนศาสตร์ยืนยันว่า น้ำเสียจากชุมชนและโรงพยาบาลมีปริมาณสารอินทรีย์คาร์บอนไม่เพียงพอต่อความต้องการของขบวนการกำจัด ฟอสฟอรัสทางชีวภาพ