



EFFECTS OF COD/TN RATIO AND LOADING RATES ON PERFORMANCE OF MODIFIED SBRs IN SIMULTANEOUS REMOVAL OF ORGANIC MATTER AND NITROGEN FROM RUBBER LATEX PROCESSING WASTEWATER

Duong Van Nam^{1,2}, Nguyen Hoai Chau^{2,3}, Hamasaki Tatsuhide⁴,
Dinh Van Vien^{2,3}, Phan Do Hung^{2,3,*}

¹*Institute of Materials Science, VAST, 18 Hoang Quoc Viet, Cau Giay, Hanoi*

²*Graduate University of Science and Technology, VAST, 18 Hoang Quoc Viet, Cau Giay, Hanoi*

³*Institute of Environmental Technology, VAST, 18 Hoang Quoc Viet, Cau Giay, Hanoi*

⁴*Faculty of Design Technology, Osaka Sangyo University, 3-1-1 Nakagaito, Daito City, Osaka, Japan*

*Email: phdhung2000@yahoo.com

Received: 17 October 2017; Accepted for publication: 9 March 2018

Abstract. Two modified sequencing batch reactors (SBRs), specially configured to consist of both oxic and anoxic zones, and be operated with only a single simultaneous oxic/anoxic phase in each treatment batch, were tested to evaluate their applicability in the treatment of rubber latex processing (RLP) wastewater. Reactor R1 was operated with a constant aeration, by contrast, reactor R2 was operated with an air flow varied from a lower rate in the early period of the reaction phase to a higher rate in the later period. The effects of the chemical oxygen demand (COD) to total nitrogen (TN) ratio and their loading rates on the performance of the modified SBRs in the simultaneous removal of organic matter and nitrogen from RLP wastewater were investigated. It was observed that the performance of the two reactors in removal of COD and ammonium nitrogen (ammonium-N) was similar, and did not remarkably change when varying the COD/TN ratio, as well as COD and TN loading rates in the ranges of 3.4 – 6.0 gCOD/gN, 0.8 – 1.7 kgCOD·m⁻³·d⁻¹ and 0.15 – 0.34 kgN·m⁻³·d⁻¹, respectively. The average COD removal efficiencies were over 95 %. Ammonium-N was almost completely eliminated in both reactors (influent concentrations were 160 – 500 mg/L). The average ammonium-N removal efficiencies were over 99 % with effluent concentrations of less than 1.0 mg/L. Nevertheless, the TN removal efficiencies of both reactors were significantly increased by increasing the COD/TN ratio from 3.4 to 6.0, and slightly decreased when increasing the TN loading rate from 0.15 to 0.34 kgN·m⁻³·d⁻¹. The most effective COD/TN ratios were in the range of 5 – 6, at which the maximal TN removal efficiencies of R1 and R2 were 92 % and 97 %, respectively.

Keywords: modified SBR, simultaneous removal of organic matter and nitrogen, rubber latex processing wastewater, COD/TN ratio, COD and TN loading rates.

Classification numbers: 3.3.3, 3.4.2, 3.7.2

1. INTRODUCTION

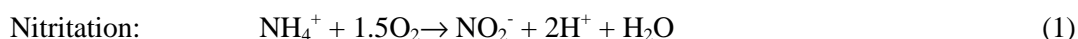
Viet Nam is one of the three leading countries in the world for natural rubber exploitation and export, after Thailand and Indonesia. Rubber latex processing (RLP) wastewater has extremely high concentrations of biological oxygen demand (BOD), chemical oxygen demand (COD), total nitrogen (TN) and total suspended solids (TSS), with their values up to 7,590 – 13,820 mg/L, 11,935 – 26,914 mg/L, 450 – 1,306 mg/L and 468 – 2,220 mg/L, respectively [1, 2].

Currently, several processes such as latex decantation, flotation, anaerobic digestion, activated sludge, oxidation ditches, biofilters, and pond systems have been applied in combination for treating RLP wastewater in Viet Nam [1, 3]. However, according to a survey conducted by Nguyen Nhu Hien and Luong Thanh Thao (2012) [1], several limitations exist in many rubber processing factories in the Southeastern region. These include: a low efficiency of the wastewater treatment systems; a routine overload for treatment units, causing poor removal of pollutants; a lack of effective units for nitrogen removal; and a high treatment cost.

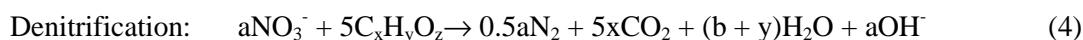
The main methods currently applied in RLP factories in Viet Nam for the removal of nitrogen from wastewater are oxidation ditches and biological ponds. However, the treatment efficiency of these processes is insufficient to meet the required discharge regulation. Furthermore, these processes require a long hydraulic retention time (HRT) and a large construction area [1 – 3]. The required HRT for a lagoon system is as long as over 30 days [1], and that for an algal pond system is around 21 days [3]. Therefore, effective nitrogen removal processes for RLP wastewater are of paramount concern.

For the purposes of improving the performance of conventional sequencing batch reactors (SBRs) in the simultaneous removal of organic matter and nitrogen as well as simplifying the reactors' operating modes, we have been developing modified SBRs consisting of both an oxic zone with aeration and an anoxic zone without aeration in a single-stage reactor [4]. In these reactors, mixed liquor is able to continuously circulate from one zone to the other one during an aeration phase. Thus, nitrification and denitrification could occur simultaneously in the two zones of these reactors through the following reactions.

Nitrification



Denitrification



where, $\text{C}_x\text{H}_y\text{O}_z$ denotes organic substrate, $a = (4x + y - 2z)$ and $b = (y + z - 2x)$.

It is therefore unnecessary to perform separate anoxic phases in the modified SBRs. Our previous study [4] showed that the modified SBRs were highly effective in removing both COD and nitrogen from RLP wastewater. In this study, the effects of COD/TN ratios, and the organic and nitrogen loading rates on the performance of the modified SBRs in treatment of RLP wastewater were investigated.

2. MATERIALS AND METHODS

2.1. Wastewater

The wastewater used in this study was anaerobically digested wastewater from Ha Tinh Rubber Factory. The COD, ammonium-N and TN in the wastewater were 1,520 – 2,240 mg/L, 160 – 280 mg/L and 270 – 410 mg/L, respectively.

2.2. Experimental reactor systems

Two modified SBRs, R1 and R2, made of transparent acrylic plastic as illustrated in Fig. 1 were used for the study. The two reactors had the same configure, but were operated under different modes. Reactor R1 was operated under a conventional mode with a constant aeration, by contrast, reactor R2 was operated under the specific mode with a varied aeration (Table 1). The effective volume and height of the reactors were 15 L and 1.34 m, respectively. The reactors were equipped with wastewater feeding pumps, air blowers and automatic control valves for drawing treated water. The reactors' operating modes were automatically controlled by timer controllers.

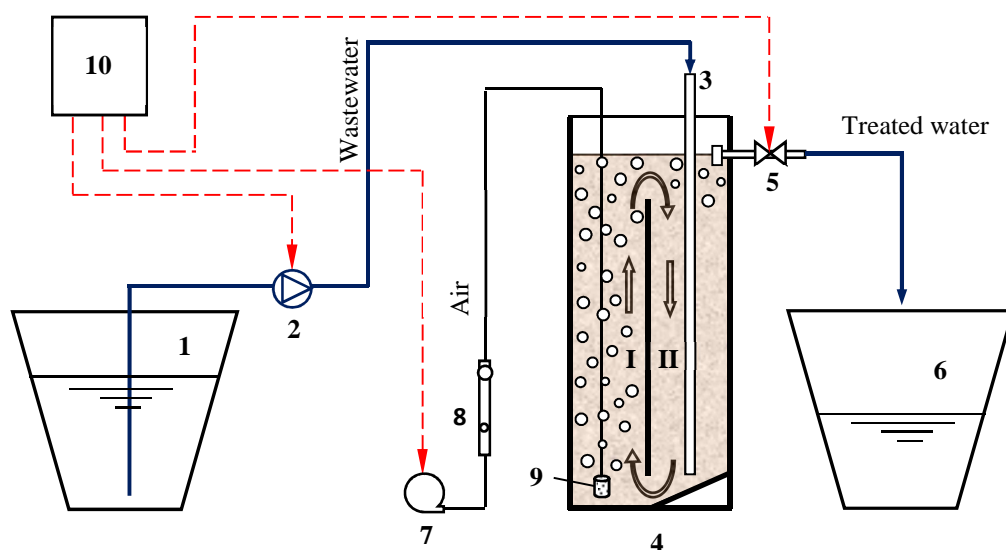


Figure 1. Experimental diagram with a modified SBR:

- | | | |
|--------------------|----------------------------|-----------------------|
| 1. Wastewater tank | 2. Feeding pump | 3. Feeding pipe |
| 4. Modified SBR | 5. Automatic control valve | 6. Treated water tank |
| 7. Blower | 8. Air flow-meter | 9. Air diffuser |
| 10. Controller | I. Oxic zone | II. Anoxic zone. |

The modified SBRs developed in this study were divided into two zones by a partition, but they communicated with each other at both the top and the bottom of the reactors. Aeration in the reaction phase of each batch was carried out only in one zone. During the aeration phase, due to the difference in densities of the mixed liquor in the two zones, the mixed liquor was circulated from one zone to the other, creating a closed loop between the two zones (Fig. 1). With this configuration, both oxic and anoxic zones existed in these reactors, and the mixed liquor was circulated from the former to the latter without any additional external energy.

The operating strategy for the reactors was also modified to combine the drawing stage of the treated water from the previous batch and the filling stage for the new batch into the same phase, i.e., simultaneous filling and drawing (Fig. 2).

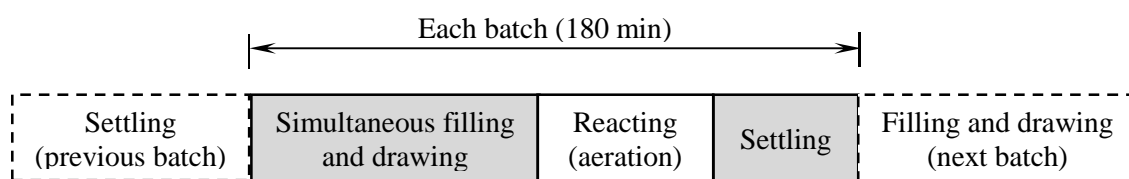


Figure 2. Experimental systems' operation cycle.

2.3. Experimental procedure and conditions

2.3.1. Experimental procedure

As shown in Fig. 2, each operating cycle for the modified SBRs includes three sequential phases: simultaneous filling and drawing, reacting with aeration, and settling.

The operating modes for the experimental reactors are as in Table 1. The total time for each treatment batch was 180 min, in which the simultaneous filling and drawing, reaction and settling phases were performed for 10 min, 145 min and 25 min, respectively.

Table 1. Operation modes for reactors R1 and R2.

Reactor	Time for simultaneous filling and drawing, min	Time of reaction phase, min		Settling time, min
		Air flow 0,4 L/min	Air flow 2,0 L/min	
R1	10	0	145	25
R2		55	90	

For reactor R1, aeration was conducted at a constant air flow-rate of 2.0 L/min in the reaction phase.

In reactor R2, during the reaction phase, aeration was performed in two stages with different air flow-rates. During the initial 55 min, the air flow-rate was maintained at a low level of 0.4 L/min to keep low DO (dissolved oxygen) in the reactor (< 0.5 mg/L) for simultaneous nitrification and denitrification in both compartments. During the next 90 min, the air flow-rate was raised to 2.0 L/min to increase DO in the reactor for complete oxidation of the remaining organic matter and ammonium.

2.3.2. Experimental conditions

The modified SBR reactors were started up with seeding sludge collected from a nitrification – denitrification submerged biofilter treating domestic wastewater with an initial MLSS concentration of around 5,000 mg/L. The start-up was carried out by gradually increasing the wastewater flow-rate for 36 days. In this period, the COD and TN loading rates were gradually increased from 0.5 kgCOD·m⁻³·day⁻¹ and 0.07 kgN·m⁻³·day⁻¹ at the beginning to 0.9 kgCOD·m⁻³·day⁻¹ and 0.16 kgN·m⁻³·day⁻¹ at the end, respectively.

Experiments were carried out at room temperature in the range of 27 – 33°C. The pH of the influent was in the range of 6.0 – 7.0, and that in the reactors in ranged of 7.6 – 8.6. The MLSS

concentration in both reactors was maintained at the same level in the range of 6,000 – 6,500 mg/L.

The COD/TN ratios of the original wastewater were in the range of 4.9 – 6.0. In the study on the effects of COD/TN ratios, the experiments with COD/TN ratios of less than 4.9 were performed through the addition of ammonium chloride solution to the original wastewater to obtain the desired COD/TN ratios.

The effects of COD/TN ratio and loading rates on the performance of the modified SBRs were studied in the COD loading rate range of 0.8 – 1.7 kgCOD·m⁻³·day⁻¹, and the TN loading rate range of 0.15 – 0.34 kgN·m⁻³·day⁻¹ (Table 2).

Table 2. Investigated ranges of COD/TN ratio and loading rates.

Experimental conditions	Study of effects of COD/TN ratio (Wastewaters with COD/TN below 4.9 were added with ammonium chloride)	Study of effects of loading rates (Real wastewater)
Influent COD, mg/L	1,540 – 2,240	1,540 – 2,110
Influent TN, mg/L	270 – 590	270 – 410
COD/TN (g/g)	3.4– 6.0	4.9 – 6.0
COD loading rate, kgCOD·m ⁻³ ·day ⁻¹	0.8 – 1.7	0.8 – 1.7
TN loading rate, kgN·m ⁻³ ·day ⁻¹	0.15 – 0.34	0.15 – 0.34

2.4. Analytical methods

COD was measured according to Viet Nam Standard, TCVN 6491: 1999 (ISO 6060: 1989): Water quality - Determination of the chemical oxygen demand.

Ammonium-N was determined according to Viet Nam Standard, TCVN 6179: 1996 (ISO 7150-1: 1984): Water quality - Determination of ammonium, part 1: Manual spectrometric method.

Nitrate was determined according to Viet Nam Standard, TCVN 6180: 1996 (ISO 7890-3: 1988): Water quality - Determination of nitrate, spectrometric method using sulfosalicylic acid.

Nitrite was determined according to Viet Nam Standard, TCVN 4561: 1988, waste water, method for determination of nitrite content.

Total Nitrogen was determined according to Viet Nam Standard, TCVN 6638: 2000 (ISO 10048: 1991): Water quality - Determination of nitrogen - Catalytic digestion after reduction with Devarda's alloy

Suspended Solids was determined according to Viet Nam Standard, TCVN 6625: 2000 (ISO 11923: 1997): Water quality - Determination suspended solids by filtration through glass-fiber filters.

3. RESULTS AND DISCUSSION

3.1. Effects of COD/TN ratio

Figure 3 shows the relations between the COD removal efficiencies of the two reactors and COD/TN ratio in the range of 3.4 - 6.0. It can be observed that no significant differences in the COD removal efficiencies versus COD/TN ratio were observed. The COD removal efficiencies of both reactors were similar, with an average of over 95 %.

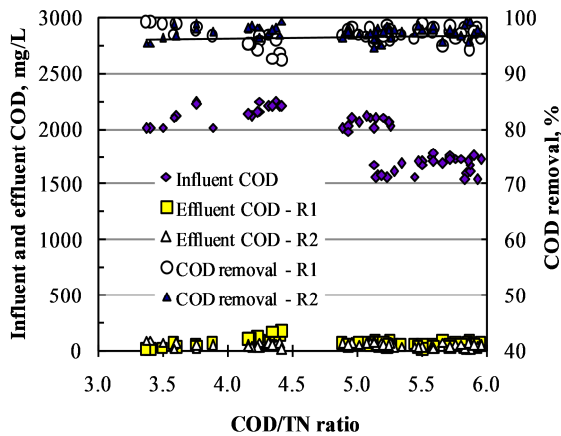


Figure 3. Effects of COD/TN ratio on COD removal.

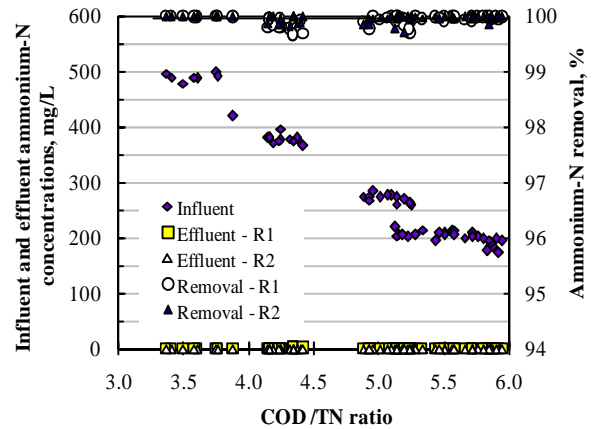


Figure 4. Effects of COD/TN ratio on ammonium-N removal.

Ammonium-N removal efficiencies were not significantly influenced by a COD/TN ratio in the investigated range for both reactors (Fig. 4). There were no significant differences in the ammonium-N removal efficiencies of the two reactors. For both reactors, the elimination of ammonium-N was almost complete, with removal efficiencies of over 99.5 % and effluent ammonium-N concentrations of less than 1.0 mg/L.

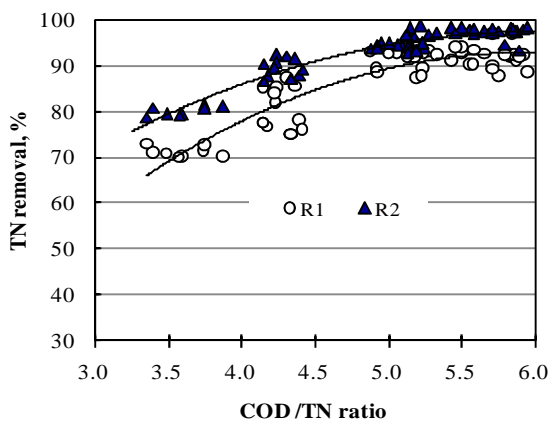


Figure 5. TN removal efficiencies vs. COD/TN.

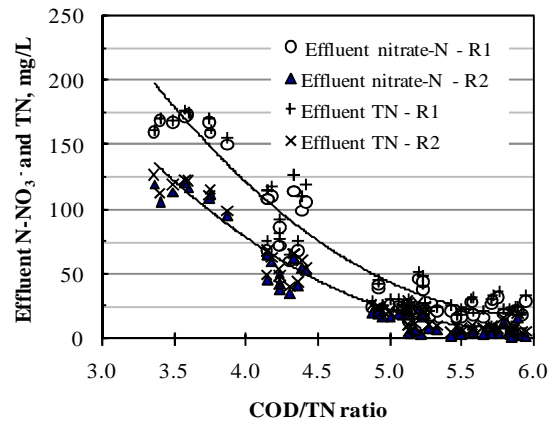


Figure 6. Effluent NO_3^- -N and TN vs. COD/TN.

The effects of the COD/TN ratio on TN removal efficiencies are shown in Fig. 5. Contrary to the trends of COD and ammonium, the TN removal efficiencies of both reactors tended to increase when increasing in the COD/TN ratio. These results are consistent with the expectations, since a low COD/TN ratio leads to a shortage of organic substrates for denitrification, resulting in low TN removal [5 – 7].

The mean TN removal efficiency for reactor R1 increased from 70 % to 92 % when raising the COD/TN ratio from 3.4 to 6.0; meanwhile, that of reactor R2 increased from 80 % to 97 %.

Many studies have reported a wide range of COD/TN ratios required for satisfactory or complete denitrification processes between 4 and 15 gCOD/gN [5 – 7]. In this study, it was observed that for the modified SBRs, the most effective COD/TN ratio for TN removal from RLP wastewater was in the range of 5 – 6.

It was also observed that TN removal efficiency of reactor R2 was remarkably higher than that of reactor R1 at all COD/TN ratios investigated. This result can be explained as follows.

Both oxic and anoxic zones existed in the modified SBRs. Therefore, both nitrification and denitrification occurred simultaneously through the reactions (1) – (4).

In reactor R1, under the strong aeration (DO in the reactor greater than 3 mg/L for most of the reaction phase time), ammonium was oxidized not only to nitrite according to Equation (1) but also to nitrate by reaction (2). Nitrate required much more organic substrate than nitrite to be denitrified to free nitrogen (Equations (4) and (3)). However, under this condition, organic matter was also rapidly oxidized to carbon dioxide and water. Therefore, the remaining organic substrate available for denitrification was deficient and denitrification occurred incompletely in reactor R1.

In the case of reactor R2, because of low DO (less than 0.5 mg/L in early 55 min of the reaction phase) during the reaction phase, ammonium was oxidized mostly to nitrite (Equation 1), which needs less organic substrate for denitrification (Equation (3)). In addition, due to low DO concentration, the amount of organic matter consumed by organic compounds oxidizing bacteria was less than that in reactor R1, resulting in much available organic substrate for denitrification remaining. Consequently, denitrification was more complete in reactor R2, resulting in an enhancement of nitrogen removal.

The above results indicate that aeration mode and appropriate air flow-rate are important for improving TN removal in the modified SBRs.

Figure 6 shows effluent nitrate-N and TN concentrations versus COD/TN ratios. It was observed that nitrogen in treated water was mostly nitrate-N and effluent TN was very close to nitrate-N. This means that all nitrogen compounds were nearly oxidized to nitrate. When decreasing the COD/TN ratio, effluent nitrate-N and TN concentrations increased. This is due to that organic substrate was insufficient for denitrification at low COD/TN ratios. For the real wastewater with COD/TN ratio of 4.9 – 6.0, effluent TN concentrations of the two reactors R1 and R2 were below 60 mg/L and 30 mg/L, respectively.

3.2. Effects of loading rates

The effects of COD, ammonium-N and TN loading rates on their removal rates and efficiencies were investigated using real wastewater with COD/TN ratio ranges of 4.9 – 6.0, in which there was virtually no influence on TN removal efficiencies. Removal rates were calculated as removed amounts in a time unit for an effective volume unit of the reactors.

The COD removal rates and efficiencies at different COD loading rates are shown in Fig. 7. In the range of COD loading rates of 0.8 – 1.7 kg COD·m⁻³·day⁻¹, the two reactors' COD removal rates at each COD loading rate were almost the same and increased proportionally to COD loading rate. The two reactors' COD removal efficiencies were not significantly different and nearly unvaried when changing the COD loading rate. Both reactors could achieve high COD removal efficiencies, averagely 95%. Effluent COD was usually less than 100 mg/L with an average of around 50 mg/L for both reactors.

Figure 8 represents the relationships between ammonium-N removal rates and efficiencies and the ammonium-N loading rate. The ammonium-N removal rates of both reactors, similarly to the case of COD, were proportional to the ammonium-N loading rate. Ammonium was almost completely removed for both reactors with removal efficiencies of more than 99.5 %.

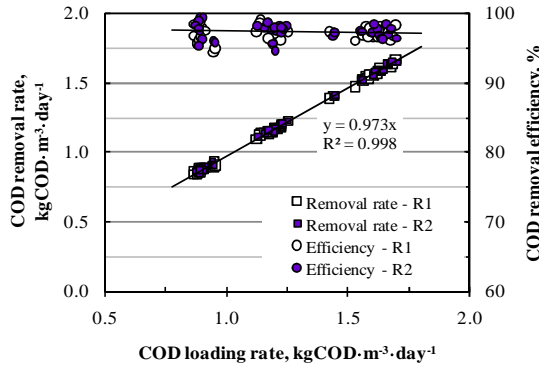


Figure 7. Effects of COD loading rate on COD removal rates and efficiencies.

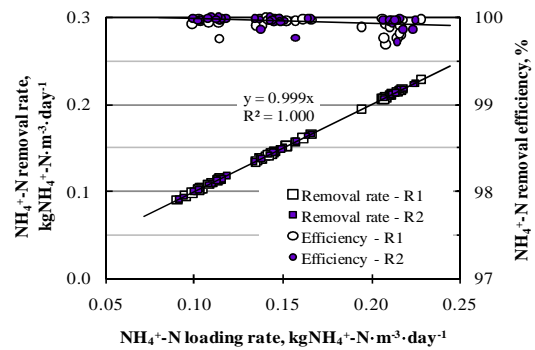


Figure 8. Effects of NH_4^+ -N loading rate on NH_4^+ -N removal rates and efficiencies.

The effects of the TN loading rate on TN removal rates and efficiencies are expressed in Fig. 9. The removal rates of both reactors increased linearly with an increase in the TN loading rate. However, that of reactor R2 was always higher than that of reactor R1 at all COD/TN ratios. As a result, TN removal efficiency of the reactor R2 was higher than that of the reactor R1. When increasing the TN loading rate, the removal efficiencies slightly decreased. The mean TN removal efficiency of reactor R1 ranged from 88 % to 92 %, and that of reactor R2 was in the range of 94 – 97 %.

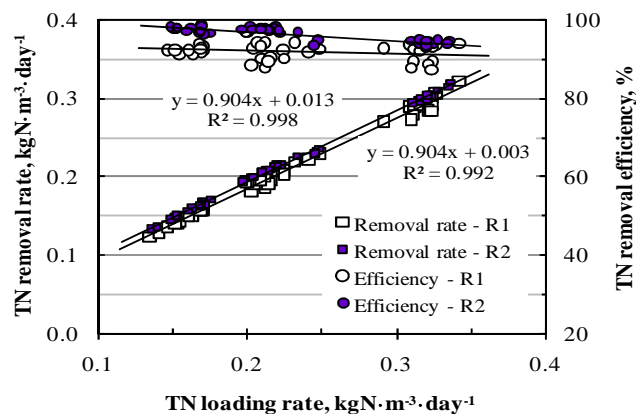


Figure 9. Effects of TN loading rate on TN removal rates and efficiencies.

For conventional SBRs, the aeration mode has significant effects on the TN removal efficiency [5, 7]. In this study, the two reactors were operated under very different aeration flow-rates, but the TN treatment efficiencies of both reactors were also high. This result indicates that the modified SBRs are less affected by the aeration flow-rate, and therefore have high stability.

Further, in order to improve the nitrogen removal efficiency of conventional SBRs, complicated operation modes with multiple anoxic – oxic phases associated with step feeding may be required [5, 8 – 11]. In this study, the modified reactors could achieve high performance in the simultaneous removal of organic matter and nitrogen with just very simple operating

modes consisting of only a single simultaneous oxic – anoxic phase. This is also an advanced feature of the modified SBRs.

4. CONCLUSION

The modified SBRs consisting of both oxic and anoxic zones showed high performance in the simultaneous removal of organic matter and nitrogen from rubber latex processing wastewater even under very simple operation modes without any separate anoxic phases and without any additional energy for recycling or mixing mixed liquor.

The COD and ammonium-N removal efficiencies of the modified SBRs did not remarkably change when varying COD/TN ratios, and COD and TN loading rates in the ranges of 3.4 – 6.0 gCOD/gN, 0.8 – 1.7 kgCOD·m⁻³·d⁻¹ and 0.15 – 0.34 kgN·m⁻³·d⁻¹, respectively. The average COD removal efficiencies were over 95 %, and ammonium-N was almost completely eliminated with effluent concentrations of less than 1.0 mg/L.

The TN removal efficiencies of the modified SBRs were significantly increased by increasing the COD/TN ratio from 3.4 to 6.0, and slightly decreased when increasing the TN loading rate from 0.15 to 0.34 kgN·m⁻³·d⁻¹. The most effective COD/TN ratio for nitrogen removal was in the range of 5 – 6, at which the maximal TN removal efficiency of the modified SBR operated under conventional aeration mode was 92 %, and that of the modified SBR operated under specific aeration mode was 97 %.

REFERENCES

1. Nguyen Nhu Hien and Luong Thanh Thao - Situation of wastewater treatment of natural rubber latex processing in The Southeastern region, Vietnam. *Journal of Vietnamese Environment* **2** (2) (2012) 58-64.
2. Tran Thi Thuy Hoa - Overview of the sustainable development requirements for rubber industry in the world and Vietnam. Training workshop on environmental and social risk mitigation for rubber enterprises in the Mekong sub-region (2017) (in Vietnamese).
3. Nguyen Ngoc Bich - The application of algal pond technology in wastewater treatment on some rubber latex processing factories belonging to the Viet Nam Rubber Industry Group. Conference on application of advanced technology in rubber processing technology and orientation of processing in the period of 2011-2015 (2011) (in Vietnamese).
4. Duong Van Nam, Phan Do Hung, Nguyen Hoai Chau and Dinh Van Vien - High performance modified SBR for simultaneous removal of organic and nitrogen matters from rubber latex processing wastewater. *Journal of Viet Nam Science and Technology B* **22** (11) (2017) 48 – 53 (in Vietnamese).
5. Pham Thi Hai Thinh, Phan Do Hung and Tran Thi Thu Lan - Simultaneous treatment of organic and nitrogen matters in swine wastewater by SBR: effect of operation regime and organic carbon/nitrogen ratio. *Journal of Science and Technology* **50** (2B) (2012) 143-152 (in Vietnamese).
6. Jafarzadeh Ghehi T, Mortezaeifar S, Gholami M, Rezaei Kalantary R and Mahvi AH - Performance evaluation of enhanced SBR in simultaneous removal of nitrogen and phosphorous. *Journal of Environmental Health Science & Engineering* **12** (1) (2014) 134-140.

7. PENG Yong-zhen, MA Yong, WANG Shu-ying - Denitrification potential enhancement by addition of external carbon sources in a pre-denitrification process. *Journal of Environmental Sciences* **19** (2007) 284–289.
8. Xiancai Song, Lejun Zhao, Dongfang Liu, and Jianqiang Zhao - Step-feeding SBR for nitrogen removal from expressway service area sewage. *AIP Conference Proceedings* (2017).
9. YANG Qing, PENG Yongzhen, YANG Anming, GUO Jianhua, LI Jianfen - Advanced nitrogen removal by pulsed sequencing batch reactors (SBR) with real-time control. *Environ. Sci. Engin. China* **1** (4) (2007) 488–492.
10. Jianhua Guo, Qing Yang, Yongzhen Peng, Anming Yang, Shuying Wang - Biological nitrogen removal with real-time control using step-feed SBR technology, *Enzyme and Microbial Technology* **40** (6) (2007) 1564-1569.
11. Mohsen Arbabi, Abbas Akbarzadeh, Abbas Khodabakhshi - Optimization of SBR system for enhanced biological phosphorus and nitrogen removal, *Int. J. Env. Health Eng.* **1** (6) (2012) 21-25.