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Effect of Cr^{+3} on the efficiency and performance of the sequencing batch reactor (SBR) system for treatment of tannery industrial wastewater

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ABSTRACT

The study focused on the treatment of tannery industrial wastewater (TIW); TIW containing 10 mg/L Cr^{3+} (TIW + 10 Cr^{3+}) and synthetic tannery industrial wastewater (STIW) containing Cr^{+3} concentrations of 0, 5, 10, 20, 30 and 40 mg/L using a sequencing batch reactor (SBR) system at hydraulic retention times (HRT) of 1.5, 3 and 5.0 d and concentrations of mixed liquor suspended solids (MLSS) of 1,000, 2,000, 3,000, 4,000 and 5,000 mg/L removal efficiency were determined. The highest Cr^{+3}, COD, BOD_5, TKN and TN removal efficiencies of 87.5 ± 0.2, 96 ± 0, 96 ± 1, 88.5 ± 0.1 and 61.0 ± 0.5%, respectively, were detected with STIW + 5 Cr^{+3} at MLSS of 5,000 mg/L and HRT of 3 d. Cr^{+3} gave a strong repression effect to the growth and activity of young bio-sludge, and the effect increased with increase in Cr^{+3}concentration or loading. However, older bio-sludge showed strong resistance to Cr^{+3} toxicity and had higher Cr^{+3} adsorption yield than younger bio-sludge. The SBR system with raw TIW showed the highest Cr^{3+}, COD, BOD_5, TKN and TN removal efficiencies of 96.9 ± 0.2, 98 ± 1, 99 ± 0, 69.2 ± 0.0 and 60.3 ± 0.1%, respectively, at HRT of 5 d and MLSS of 5,000 mg/L. Efficiency with TIW was reduced by addition of Cr^{+3}. However, the efficiency was recovered with increase in HRT. The system containing TIW + 10 Cr^{3+} showed the highest Cr^{+3}, COD, BOD_5, TKN and TN removal efficiencies of 95.6 ± 0.3, 98 ± 1, 99 ± 0, 68.6 ± 0.0 and 60.0 ± 0.1%, respectively, with SVI less than 100 mL/g at HRT of 5 d and MLSS of 5,000 m/L.

Keywords: Bio-sludge; Cr^{3+}; Sequencing batch reactor (SBR) system; Tannery industrial wastewater (TIW)

1. Introduction

The tannery industry (TW) produces large amounts of wastewater due to high water and chemical consumptions. It has been reported that tannery industrial wastewater (TIW) contained high organic matter lively of 1,000–4,200 mg BOD_5/L, 2,500–8,100 mg COD/L and 300–400 mg TN/L [1–3]. Moreover, the wastewater also contained a high Cr^{3+} concentration of 1,000–1,500 and 18–204 mg/L of wastewater from bleached clean step and sump tank of the wastewater treatment system, respectively. Several researchers reported that Cr^{3+} has shown a repression effect to the growth of microbes or bio-sludge [4,5]. However, several kinds of heavy metals (HM) such as lead,

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cadmium, copper and zinc could be adsorbed on the surface of the microbial cell or bio-sludge [6–12]. For the theoretical fact, the selection of wastewater treatment process depends on the type and concentration of the pollutant [1,13,14]. The biological treatment process is suitable for wastewater containing organic matter [13,15–17]. The chemical treatment process is suitable for wastewater containing inorganic matters, especially HM and hardly biodegradable compounds [2,18,19].

According to the above information, for TIW that contains organic and inorganic matter, especially for Cr^{3+}, the selection of wastewater treatment process should be considered carefully. Many researchers have reported that biological processes could be applied for treating wastewater containing both organic and inorganic matter due to the degradation and adsorption mechanisms of the bio-sludge [1,20–25]. It had been previously reported that the bio-sludge of the aerobic biological treatment system could be used as the adsorbent for the HM adsorption process [6–10,14,26–29]. However, the adsorption capacity of bio-sludge depends on the type and age of microbes [8–10,16].

Sequence batch reactor (SBR) system is one of the aerobic activated sludge systems that can be easily operated with various types of microbe or bio-sludge (various solid retention time (SRT) of bio-sludge) [10,16,17]. Also, it had been previously reported that HM, especially Cr^{3+}, resulted in a repression effect to the growth and activity of microbes or bio-sludge of activated sludge systems [8–10,25,30–33]. The SBR system was selected for the treatment of TIW, due to the biodegradation and bio-sorption mechanism of the bio-sludge of the system and ease of operation of the system under various SRT and oxic–anoxic conditions. In this study, the experiments were carried out using laboratory scale SBR system with TIW and synthetic tannery industrial wastewater (STIW). The effects of mixed liquor suspended solids (MLSS) and Cr^{3+} concentrations or loadings on the system efficiency and performance were observed. In addition, the effect of Cr^{3+} concentration on the bio-sludge performance and type of microbe was investigated.

2. Materials and methods

2.1. Wastewater sample

Raw TIW from the sump tanks of the wastewater treatment plant of the tannery factory (TIW) at Smutprakan Province, Thailand, was collected and kept in storage (4℃) before being used in this study to prevent any change in wastewater quality during the study. TIW was supplemented with 77.0 mg/L Cr $(NO_3)_3{\cdot}H_2O$ to be TIW containing 10 mg/L Cr^{3+} (TIW + 10 Cr^{3+}). The chemical properties of the TIW solutions are described in Table 1. The STIWs were prepared according to the chemical properties of TIW. Glucose and urea were used for the adjusted BOD_5 and TN of STIW, respectively. Then, STIW contained 1437.5 mg/L glucose, 107.3 mg/L urea, 43.8 mg/L KH_2PO_4 and 24.9 mg/L $FeSO_4{\cdot}7H_2O$ as shown in Table 1. Various amount of $Cr(NO_3)_3{\cdot}9H_2O$ of 38.5, 77.0, 154.0, 231.0 and 308.0 mg/L were added into the STIW solution to prepare STIW containing 5 mg/L Cr^{3+} (STIW + 5 Cr^{3+}), STIW containing 10 mg/L Cr^{3+} (STIW + 10 Cr^{3+}), STIW containing 20 mg/L Cr^{3+} (STIW + 20 Cr^{3+}), STIW containing 30 mg/L Cr^{3+} (STIW + 30 Cr^{3+}) and STIW containing 40 mg/L Cr^{3+} (STIW + 40 Cr^{3+}), respectively, as shown in Table 1.

2.2. Acclimatization of bio-sludge

The bio-sludge from the bio-sludge storage tank of the central sewage treatment plant of Bangkok City, Thailand (Sripaya sewage treatment plant), was used as the inoculum for the SBR system after it was acclimatized in the SBR system with STIW at an HRT of 5 d for 2 weeks.

2.3. Sequencing batch reactor

Ten 10-L reactors, made from acrylic plastics (5 mm thick) as shown in Fig. 1, were used in the experiments. Each reactor was 18 cm in diameter and 40 cm in height with a working volume of 7.5 L. Complete mixing in the reactor was adjusted by controlling the speed of the paddle-shaped impeller to 60 rpm. A low-speed gear motor, model P 630A-387, 100 V, 50/60 Hz, 1.7/1.3 A (Japan Servo Co. Ltd, Japan) was used for driving the impeller. One set of air pumps, model EK-8000, 6.0 W (President Co. Ltd., Thailand), was used for supplying air for two sets of reactors (the system had enough oxygen supply as evidenced by the dissolved oxygen in the system of about 2–3 mg/L). The excess bio-sludge was removed during the draw and idle period to control the MLSS of the system (Table 2).

2.4. Operation of SBR system

The SBR system was operated at 1 cycle/day under HRTs of 3.0, 5.0, 7.5 and 10.0 d. Exactly 1.4 L of 10 g/L acclimatized bio-sludge from Section 2.2 was inoculated in each reactor, and EPWW solutions were added (final volume of 7.5 L) within 1 h. During the reaction period, the system was continuously aerated for 19 h. Aeration was then shut down for 3 h. After

Table 1
Properties of TIW and STIW

Properties	Concentrations							
				STIW with various Cr^{3+} concentrations				
	TIW	TIW + 10 Cr^{3+}	STIW	STIW + 5 Cr^{3+}	STIW + 10 Cr^{3+}	STIW + 20 Cr^{3+}	STIW + 30 Cr^{3+}	STIW + 40 Cr^{3+}
Cr^{3+} (mg/L)	2.10 ± 0.01	11.70 ± 1.10	–	5.01 ± 0.01	10.03 ± 0.01	19.98 ± 0.02	30.00 ± 0.01	40.01 ± 0.02
COD (mg/L)	2,340 ± 356	2,340 ± 356	1,300 ± 92	1,262 ± 64	1,262 ± 64	1,262 ± 64	1,262 ± 64	1,262 ± 64
BOD_5 (mg/L)	1,015 ± 21	1,015 ± 21	1,000 ± 50	1,040 ± 37	1,040 ± 37	1,040 ± 37	1,040 ± 37	1,040 ± 37
Org-N (mg-N/L)	73.4 ± 20.1	73.4 ± 20.1	32.0 ± 1.2	32.0 ± 1.2	32.0 ± 1.2	32.0 ± 1.2	32.0 ± 1.2	32.0 ± 1.2
NH_4^+-N (mg/L)	195.7 ± 10.5	195.7 ± 10.5	35.84 ± 1.2	34.7 ± 1.1	34.7 ± 1.1	34.7 ± 1.1	34.7 ± 1.1	34.7 ± 1.1
TKN[a] (mg/L)	269.1 ± 20.1	269.1 ± 20.1	67.2 ± 2.3	67.2 ± 2.3	67.2 ± 2.3	67.2 ± 2.3	67.2 ± 2.3	67.2 ± 2.3
NO_2^--N (mg/L)	13.9 ± 19.7	13.9 ± 19.7	0.2 ± 0.0	0.2 ± 0.0	0.20 ± 0.02	0.2 ± 0.0	0.2 ± 0.0	0.2 ± 0.0
NO_3^--N (mg/L)	45.2 ± 12.4	45.2 ± 12.4	0.1 ± 0.0	0.1 ± 0.0	0.05 ± 0.01	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
TN[b] (mg/L)	328.2 ± 20.1	328.2 ± 20.1	67.5 ± 2.3	67.5 ± 2.3	67.5 ± 2.3	67.5 ± 2.3	67.5 ± 2.3	67.5 ± 2.3
pH	8.1 ± 0.7	8.1 ± 0.7	7.3 ± 0.1	7.3 ± 0.1	7.3 ± 0.1	7.3 ± 0.1	7.3 ± 0.1	7.3 ± 0.1

Notes: TIW: Tannery industrial wastewater collected from sump tank of wastewater treatment plant of tannery industrial factory in Samutprakan Province. TIW + 10 Cr^{3+}: TIW supplemented with 77.0 mg/L Cr $(NO_3)_3{\cdot}9H_2O$. STIW: Synthetic tannery industrial wastewater containing 1437.5 mg/L glucose, 107.3 mg/L urea, 43.8 mg/L KH_2PO_4 and 24.9 mg/L $FeSO_4{\cdot}7H_2O$. STIW + 5 Cr^{3+}: STIW supplemented with 38.5 mg/L $Cr(NO_3)_3{\cdot}9H_2O$. STIW + 10 Cr^{3+}: STIW supplemented with 77.0 mg/L $Cr(NO_3)_3{\cdot}9H_2O$. STIW + 20 Cr^{3+}: STIW supplemented with 154.0 mg/L $Cr(NO_3)_3{\cdot}9H_2O$. STIW + 30 Cr^{3+}: STIW supplemented with 231.0 mg/L $Cr(NO_3)_3{\cdot}9H_2O$. STIW + 40 Cr^{3+}: STIW supplemented with 308.0 mg/L $Cr(NO_3)_3{\cdot}9H_2O$.

[a]TKN: Organic-N + NH_4^+-N.

[b]TN: Total nitrogen: TKN + $NO_2^- - N + NO_3^-$-N.

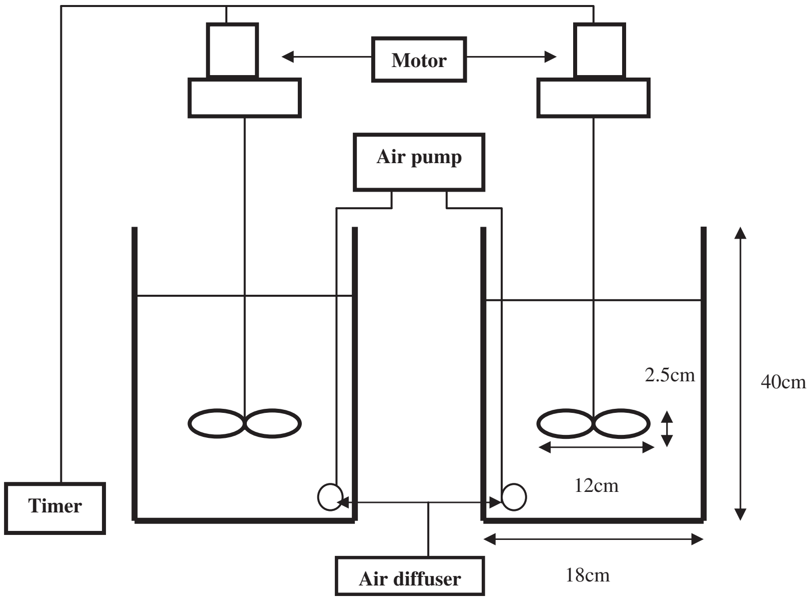

Fig. 1. Flow diagram of the SBR systems.
Notes: The physical operation controls had 60 rpm of impellar speed, full aeration with an air-pump system (one air pump system supplied air to two sets of reactors) and a working volume of the reactor of 75% of the total volume (7.5 L).

Table 2
The operating parameters of the SBR system with STIW

Parameters	STIW and STIW + 5 Cr^{3+}					STIW with various Cr^{3+} concentrations			
						STIW + 10 Cr^{3+}	STIW + 20 Cr^{3+}	STIW + 30 Cr^{3+}	STIW + 40 Cr^{3+}
MLSS (mg/L)	1,000	2,000	3,000	4,000	5,000	5,000	5,000	5,000	5,000
HRT (d)	3	3	3	3	3	3	3	3	3
Flow rate (mL/d)	2,500	2,500	2,500	2,500	2,500	2,500	2,500	2,500	2,500
F/M ratio	0.34	0.17	0.11	0.085	0.068	0.0687	0.068	0.068	0.068
Hydraulic loading	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
BOD_5 loading (g/d)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Volumetric BOD_5 loading (kg BOD_5/m^3 d)	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Cr^{3+} loading (g/d)	0.013	0.013	0.013	0.013	0.013	0.026	0.052	0.078	0.104
Volumetric Cr^{3+} loading (g Cr^{3+} loading)	0.001	0.001	0.001	0.001	0.001	0.002	0.004	0.006	0.008

Notes: STIW: Synthetic tannery industrial wastewater containing 1,437.5 mg/L glucose, 107.3 mg/L urea, 43.8 mg/L KH_2PO_4 and FeSO4·$7H_2O$. STIW + 5 Cr^{3+}: STIW supplemented with 38.46 mg/L $Cr(NO_3)_3 \cdot 9H_2O$. STIW + 10 Cr^{3+}: STIW supplemented with 76. 92 mg/L $Cr(NO_3)_3 \cdot 9H_2O$. STIW + 20 Cr^{3+}: STIW supplemented with 153.84 mg/L $Cr(NO_3)_3 \cdot 9H_2O$. STIW + 30 Cr^{3+}: STIW supplemented with 230.76 mg/L $Cr(NO_3)_3 \cdot 9H_2O$. STIW + 40 Cr^{3+}: STIW supplemented with 307.68 mg/L $Cr(NO_3)_3 \cdot 9H_2O$.

the sludge was fully settled, the supernatant was drawn out within 0.5 h and the system was kept under anoxic conditions for 0.5 h. After that, the reactor was filled with fresh STIWs or TIWs solutions to the final volume of 7.5 L and the above operation was repeated. The operation parameters of the SBR system with STIWs and TIWs solutions are described in Table 2 and Table 3.

2.5. Chemical analysis

Chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), TKN, organic-N, NH_4^+-N, NO_3^--N, NO_2^--N, total nitrogen (TN), Cr^{3+}, suspended solids (SS) and MLSS, as well as the pH of the influent, effluent and sludge volume index (SVI) of the SBR system were determined according to the standard methods for the examination of water and wastewater [34]. The bio-sludge age was determined as the ratio of total biomass (MLSS) of the system to the amount of excess sludge wasted per day.

2.6. Statistical analysis method

Each experiment was repeated at least three times. All data were subjected to two-way analysis of variance using the statistical analysis system [35,36]. Statistical significance was tested using the least significant difference at the $p < 0.05$ level. The results shown are the mean ± the standard deviation.

3. Results

3.1. Effect of MLSS on the efficiency and performance of the SBR system

The SBR system evaluated with STIW + 5 Cr^{3+} at various MLSS of 1,000, 2,000, 3,000, 4,000 and 5,000 mg/L and HRT of 3.0 d as shown in Table 2. For the control, the system was operated with STIW without Cr^{+5} at MLSS of 3,000 mg/L and HRT of 3 d as shown in Table 2. The system efficiency and performance were observed as follows.

3.1.1. COD and BOD_5

COD and BOD_5 removal efficiencies with STIW + 5 Cr^{3+} increased with the increase in MLSS, and the highest COD and BOD_5 removal efficiencies of 96 ± 0 and 96 ± 1%, respectively, were detected at MLSS of 5,000 mg/L and HRT of 3.0 d (F/M of 0.07, BOD_5 loading of 0.34 kg/m^3 d and Cr^{3+} loading of 0.001 g/L d) as shown in Table 4. The system with STIW at MLSS of 3,000 mg/L and HRT of 3 d (F/M of 0.11 and BOD_5 loading of 0.34 kg/m^3 d) showed COD and BOD_5 removal efficiencies of 98 ± 1 and 97 ± 1%, respectively.

3.1.2. Nitrogenous compounds

TN and TKN removal efficiencies of the system with STIW + 5 Cr^{3+} increased with increase in MLSS, and the highest TKN and TN removal efficiencies of 61.0 ± 0.5 and 88.5 ± 0.1%, respectively, were detected at MLSS of 5,000 mg/L and HRT of 3 d (F/M of 0.07 and BOD_5 and Cr^{3+} loadings of 0.34 kg/m^3 d and 0.001 g /L d, respectively) as shown in Table 4. However, the system with STIW at MLSS of 3,000 mg/L and HRT of 3 d (F/M of 0.11 and BOD_5 loading of 0.34 kg/m^3 d) showed TN and TKN removal efficiencies of 58.6 ± 0.6 and 91.8 ± 0.1%. The effluents nitrogenous compounds (organic-N, NH_4^+-N, NO_2^--N, NO_3^--N) were decreased with the increase of MLSS. Effluent nitrogenous compounds of the system with STIW were lower than that with STIW + 5 Cr^{3+} as shown in Table 4. Moreover, the effluent nitrogenous compounds profile of the system with STIW and STIW + 5 Cr^{3+} became stable after 7–10 d operation in all experiments tested as shown in Fig. 2.

3.1.3. Cr^{3+}

Cr^{3+} removal efficiency of the system with STIW + 5 Cr^{3+} increased with increase in MLSS, and the highest Cr^{3+} removal efficiency of 87.5 ± 0.2% was detected at the MLSS of 5,000 mg/L and HRT of 3 d (F/M ratio of 0.07) as shown in Table 4. Moreover, Cr^{+3} of the wastewaters was rapidly decreased at the first day of operation in all experiments tested as shown in Fig. 3. After that, the effluent Cr^{3+} increased and became stable within 10–11 d of operation as shown in Fig. 3. The lowest effluent Cr^{+3} of about 0.6 mg/L was detected at MLSS of 5,000 mg/L as shown in Fig. 3.

3.1.4. pH

The pH of the system with STIW and STIW + 5 Cr^{3+} was at the level of 6.70–7.09 at MLSS of 1,000–5,000 mg/L and HRT of 3 d. However, the pH of the system with STIW at MLSS of 3,000 mg/L and HRT of 3 d was highest of 7.21 ± 0.09 as shown in Table 4.

3.1.5. Bio-sludge properties

Effluent SS of the system with STIW + 5 Cr^{3+} decreased with increase in MLSS, and the lowest effluent SS of 36 ± 1 was detected at the highest MLSS operation of 5,000 mg/L as shown in Table 5. However, the system with STIW showed lowest effluent SS, and the system with STIW at F/M of 0.11, MLSS of 3,000 mg/L gave the effluent SS of 12 ± 1 mg/L as shown in Table 5. The bio-sludge quality: SVI was less than 80 mL/g in all experiments tested. The bio-sludge age, called SRT, was increased with the increase in MLSS. The SRT of 15 ± 5 d was detected with STIW + 5 Cr^{3+} at MLSS of 5,000 mg/L. The SRT of the system with STIW and STIW + 5 Cr^{3+}at MLSS of 3,000 mg/L and HRT of 3 d (F/M of 0.11) was 8 ± 2 and 9 ± 1 d, respectively, as shown in Table 5.

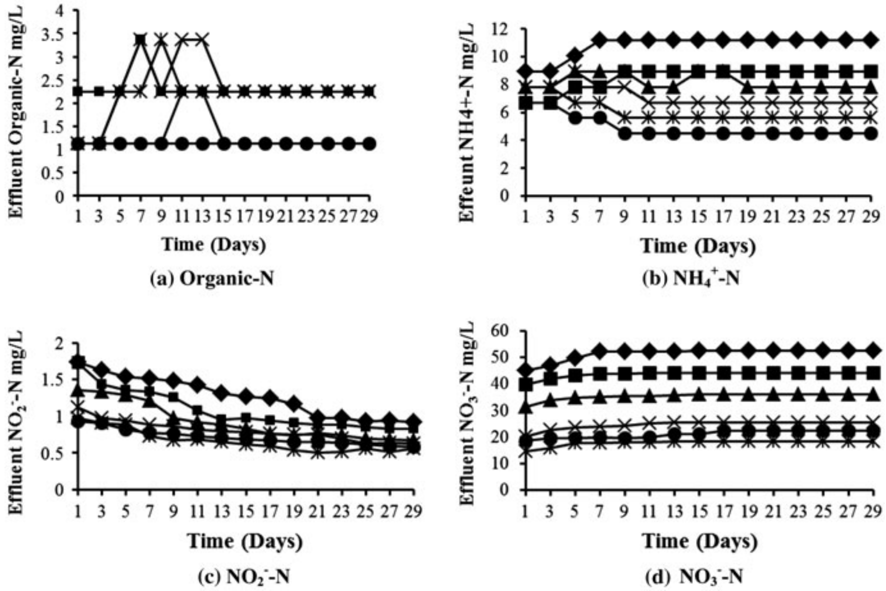

Fig. 2. Effluent nitrogen compound profiles of the SBR system with STIWW containing 5 mg/L Cr^{3+} under various MLSS of (♦) 1,000 mg/L; (■) 2,000 mg/L; (▲) 3,000 mg/L; (×) 4.000 mg/L and (✱) 5,000 mg/L; (●) with STIWW without Cr^{3+} at MLSS of 3,000 mg/L.

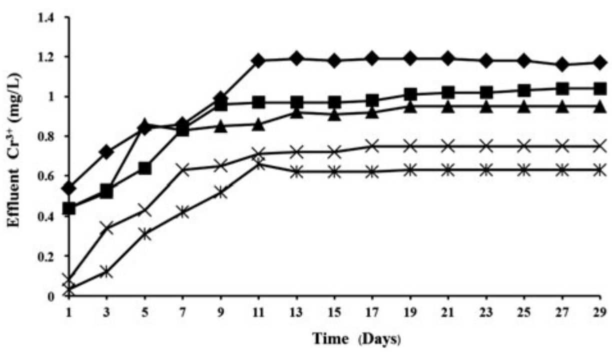

Fig. 3. Effluent Cr^{3+} profiles of the SBR system with STIWW containing 5 mg/L Cr^{3+} under various MLSS of (♦) 1,000 mg/L; (■) 2,000 mg/L; (▲) 3,000 mg/L; (×) 4.000 mg/L; and (✱) 5,000 mg/L.

3.2. *Effect of Cr^{+3} concentration on the efficiency and performance of the SBR system*

The SBR system was operated with STIW containing various concentration of Cr^{+3} (5, 10, 20, 30 and 40 mg/L) at MLSS of 5,000 mg/L and HRT of 3.0 d. For the control, the system was operated with STIW without Cr^{+3} as shown in Table 1. The system efficiency and performance were observed as follows.

3.2.1. *COD and BOD_5*

COD and BOD_5 removal efficiencies of the system with STIW + Cr^{3+} decreased with increase in Cr^{3+} concentration or loading, and the highest COD and BOD_5 removal efficiencies of 96–95 ± 0% and 96–95 ± 0%, respectively, were detected at Cr^{3+} concentration or loading of less than 30 mg/L and 0.006 g/L d. However, they were 99 ± 0% and 99 ± 0% with STIW without Cr^{3+}, respectively, as shown in Table 6.

3.2.2. *Nitrogenous compounds*

TN and TKN removal efficiencies decreased with increase in Cr^{3+} concentration or loading as shown in Table 6. The highest TKN and TN removal efficiencies

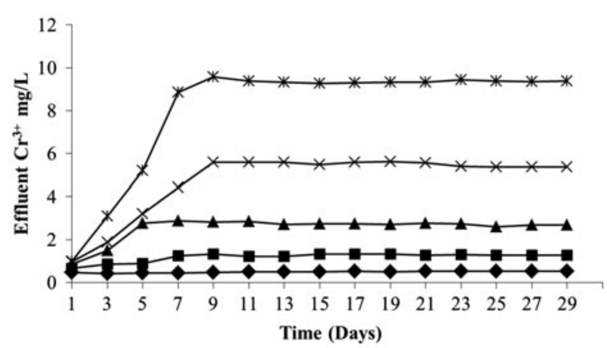

Fig. 4. Effluent Cr^{3+} profiles of the SBR system with STIWW containing various Cr^{3+} concentrations of (♦) 5 mg/L; (■) 10 mg/L; (▲) 20 mg/L; (×) 30 mg/L; and (✱) 40 mg/L at MLSS of 3,000 mg/L and HRT of 3.0 d.

of 69.8 ± 2.5 and 88.4 ± 0.6%, respectively, of the system with STIW + 5 Cr^{3+} were detected at MLSS of 5,000 mg/L and HRT of 3 d (BOD_5 and Cr^{3+} loadings of 0.34 kg/m^3 d and 0.001 g/L d, respectively). The TN and TKN removal efficiencies of 60.7 ± 3.2 and 79.3 ± 2.4%, respectively, were detected with STIW without Cr^{3+}. The effluents organic-N, NH_4^+-N, NO_2^--N and NO_3^--N, with STIW + 5 Cr^{3+} were 2.2 ± 0.4, 5.5 ± 0.0, 0.1 ± 0.1 and 12.4 ± 1.9 mg/L, respectively, when they were 1.7 ± 0.6, 12.1 ± 0.7, 0.1 ± 0.0 and 12.4 ± 0.9 mg/L, respectively, with STIW as shown in Table 6.

3.2.3. Cr^{3+}

Cr^{3+} removal efficiency decreased with increase in Cr^{3+} concentration or loading, and the highest Cr^{3+} removal efficiency of 89.7 ± 0.1% was detected with STIW + 5 Cr^{3+} (loading of 0.001 g/L d) as shown in Table 6. Moreover, Cr^{3+} of the wastewater was rapidly decreased at the first day of operation in all experiments tested as shown in Fig. 4. After that, the effluents Cr^{3+} were rapidly increased and became almost stable after 10 d of operation as shown in Fig. 4.

3.2.4. pH

The pH of the system with STIW + Cr^{3+} was at the level of 6.71–7.14 at the Cr^{3+} concentration or loading of 5–40 mg/L or 0.001–0.008 g/L d, respectively. A pH of the system with STIW was 7.21 ± 0.06 as shown in Table 6.

3.2.5. Bio-sludge property

Effluent SS of the system with STIW + Cr^{3+} increased with increase in Cr^{3+} concentration or loading, and the lowest effluent SS of 28 ± 1 mg/L was detected at the lowest Cr^{3+} concentration of 5 mg/L or loading of 0.001 g/L d, but the effluent SS of 12 ± 1 mg/L system was detected with STIW as shown in Table 5. The sludge quality, or the SVI, of 72 ± 16 mL/g and sludge age, or SRT, of 15 ± 1 d were detected with STIW + 5 Cr^{3+} at MLSS of 5,000 mg/L. The SVI and SRT of the system with STIW were 77 ± 3 and 15 ± 5 d, respectively, as shown in Table 5.

3.3. The SBR system efficiency on the treatment of TW W and TWW+ 10 Cr^{3+}

The SBR system was operated with TIW and TIW+10Cr^{+3} at MLSS of 5,000 mg/L and HRT of 1.5, 3.0 and 5.0 d as shown in Table 3. The system efficiency and performance were observed as follows.

3.3.1. COD and BOD_5

COD and BOD_5 removal efficiencies of the system with raw TIW increased with decrease in BOD_5 and Cr^{3+} loadings (increase in HRT) as shown in Table 7. The highest COD and BOD_5 removal efficiencies of 96.9 ± 0.2 and 99 ± 0%, respectively, were detected with TIW at BOD_5 and Cr^{3+} loadings of 0.68 kg/m^3d and 0.0010 g/L d, respectively (HRT of 1.5 and F/M of 0.16). However, the COD and BOD_5 removal efficiencies with TWW + 10 Cr^{3+} were lower than that with TIW at the same HRT and F/M operations as shown in Table 7. However, the system with TIW and TIW + 10 Cr^{+3} did not show any significant difference on COD and BOD_5 removal efficiencies for the same HRT operation as shown in Table 7.

Table 3
The operating parameters of the SBR system with TIW

Parameters	Type of TIW					
	TIW			TIW + 10 Cr^{3+}		
HRT (d)	1.5	3	5	1.5	3	5
MLSS (mg/L)	5,000	5,000	5,000	5,000	5,000	5,000
Flow rate (mL/d)	5,000	2,500	1,500	5,000	2,500	1,500
F/M ratio	0.16	0.08	0.05	0.16	0.08	0.05
Hydraulic loading	0.6	0.3	0.2	0.6	0.3	0.2
BOD_5 loading (g/d)	5.0	2.5	1.5	5.0	2.5	1.5
Volumetric BOD_5 loading (kg BOD_5/m^3 d)	0.68	0.34	0.20	0.68	0.34	0.20
Cr^{3+} loading (g/d)	0.0104	0.0052	0.0031	0.0520	0.0260	0.0160
Volumetric Cr^{3+} loading (g Cr^{3+}/L d)	0.0010	0.0005	0.0003	0.0040	0.0020	0.0010

Notes: TIW: Tannery industrial wastewater collected from sump tank of wastewater treatment plant of tannery industrial factory in Samuthprakarn Province. TIW + 10 Cr^{3+}: TIW was supplemented with 76.92 mg/L $Cr(NO_3)_3 \cdot 9H_2O$.

3.3.2. Nitrogen compounds

TN and TKN removal efficiencies of the system with TIW and TWW + 10 Cr^{3+} decreased with increase in Cr^{3+} concentration or loading as shown in Table 7. The system with TIW and TWW + 10 Cr^{3+} for the same HRT and F/M operations did not show any significant difference on TKN and TN removal efficiencies for the same HRT operation as shown in Table 7.

3.3.3. Cr^{3+}

Cr^{3+} removal efficiency increased with increase in HRT or decrease of F/M ratio as shown in Table 7. The highest Cr^{3+} removal efficiency of 96.9 ± 0.2 and 95.6 ± 0.3% was detected with TIW and TWW +10 Cr^{3+}, respectively, at HRT of 5.0 d or F/M of 0.05, as shown in Table 7. However, the system with TIW and TWW +10 Cr^{3+} at HRT of higher than 3 d did not show any significant difference on the Cr^{3+} removal yield as shown in Table 7. For the effluent nitrogen compounds profiles of the system with TIW and TWW +10Cr^{3}, the systems showed the different patterns as shown in Fig. 5. The effluent Cr^{3+} of the system with TIW rapidly decreased within 10 d, after that they were stable at the HRT of higher than 3.0 d. For TWW +10 Cr^{3+}, the effluent Cr^{3+} was increased after operation at the low HRT operation of lower than 30 d as shown in Fig. 5.

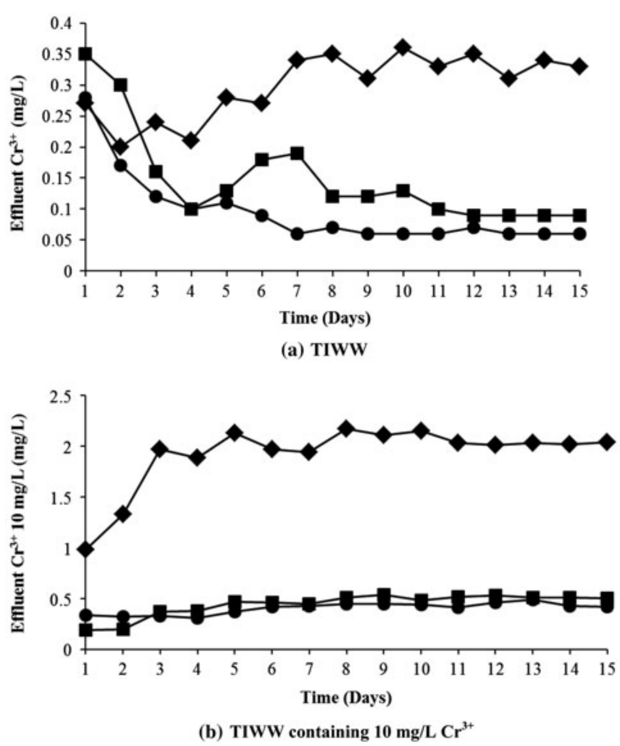

Fig. 5. Effluent Cr^{3+} profiles of the SBR system with tannery industrial wastewater: TIWW (a) and TIWW containing 10 mg/L Cr^{3+} (b) TIW + 10 Cr^{3+} at MLSS of 5,000 mg/L and various HRTs of (♦) 1.5 d; (■) 3.0 d; (●) 5.0 d.

3.3.4. pH

The pH of the system with both TIW and TIW +10 Cr^{3+} was almost stable in the range of 6.8–7.2 as shown in Table 7.

3.3.5. Bio-sludge properties

Effluents SS and SVI of the system with both TIW and TIW +10 Cr^{3+} increased with increase in HRT, and the lowest effluent SS of 15 ± 3 and 16 ± 4 mg/L was detected with TIW and TIW +10 Cr^{3+}, respectively, at HRT of 5 d as shown in Table 5. The sludge quality, or the SVI, of less than 100 mL/g was detected with TIW and TIW +10 Cr^{3+} at HRT of 5 d as shown in Table 5. Sludge age, or the SRT, was increased with the increase in HRT, and the increase in Cr^{3+} concentration or loading resulted in the increase in SRT as shown in Table 5.

4. Discussion

A SBR system is a suitable biological treatment process to treat the wastewater that contained high nitrogenous compounds due to the easily oxic-anoxic controlling condition [13,15–17]. The TIW contained not only high nitrogenous compound such as CN^-, but also HM and especially Cr^{3+} [3,25,37,38]. Moreover, TIW contained a COD: BOD_5 ratio of about 2:1 as shown in Table 1. Also, it was reported that HM might be toxic to the growth and activity of microorganisms [4,37,39,40]. Many researchers reported that HM could be adsorbed onto microbial cell or bio-sludge [31,33,37,41,42]. Experiments were carried out on the SBR system with both STIW and TIW containing various Cr^{3+} concentrations or loadings at various HRT and F/M ratios to observe the optimal condition for highest removal efficiency. First, the effect of various MLSS of SBR system with STIW + 5 Cr^{+3} and STIW on the removal efficiency was investigated. It was found that Cr^{3+} showed a repression effect on COD and BOD_5 removal yields. Moreover, the removal efficiencies decreased with increase in Cr^{3+} loading. This was previously reported on effects of type and concentration of HM on the growth and activity of microbes or bio-sludge [9,10,27,31,43]. It could be concluded that the growth and activity of heterotrophic bacteria group were repressed by the toxicity of HM.

Table 4
Removal efficiencies and effluent nitrogen compounds of SBR system with STIW containing 5 mg/L Cr^{3+} (STIW + Cr^{3+}) at various MLSS of 1,000, 2,000, 3,000, 4,000 and 5,000 mg/L and HRT of 3 d

MLSS (mg/L)	F/M	BOD_5 Loading (kg/m^3 d)	Cr^{3+} Loading (g/L d)	Removal efficiency (%)					Effluent nitrogen compounds (mg/L)				Effluent pH
				Cr^{3+}	COD	BOD_5	TN	TKN[a]	Org-N	NH_4^+-N	NO_2^--N	NO_3^--N	
1,000	0.34	0.34	0.001	76.4 ± 0.2	81 ± 1	90 ± 1	3.7 ± 1.1	81.9 ± 0.2	1.1 ± 0.0	11.2 ± 0.0	1.1 ± 0.2	52.4 ± 0.1	6.70 ± 0.20
2,000	0.17	0.34	0.001	79.9 ± 0.6	85 ± 0	92 ± 1	17.8 ± 0.9	83.5 ± 0.2	2.2 ± 0.0	9.0 ± 0.0	0.9 ± 0.1	44.1 ± 0.0	6.73 ± 0.30
3,000	0.11	0.34	0.001	81.3 ± 0.3	93 ± 0	93 ± 1	32.5 ± 1.3	86.3 ± 0.9	1.2 ± 0.6	8.1 ± 0.5	0.7 ± 0.1	36.0 ± 0.1	6.81 ± 0.15
4,000	0.09	0.34	0.001	85.2 ± 0.2	95 ± 0	95 ± 1	48.4 ± 1.0	86.7 ± 0.6	2.4 ± 0.4	6.7 ± 0.0	0.7 ± 0.1	25.5 ± 0.0	6.91 ± 0.19
5,000	0.07	0.34	0.001	87.5 ± 0.2	96 ± 0	96 ± 1	61.0 ± 0.5	88.5 ± 0.1	2.2 ± 0.0	5.6 ± 0.0	0.6 ± 0.1	18.2 ± 0.0	7.09 ± 0.19
Control[b]	0.11	0.34	–	–	98 ± 1	97 ± 1	58.6 ± 0.6	91.8 ± 0.1	1.1 ± 0.0	4.5 ± 0.0	0.6 ± 0.1	22.0 ± 0.6	7.21 ± 0.09

Notes: [a]TKN: Organic-N+NH_4^+-N.
[b]Control: SBR system operated with STIW without Cr^{3+} at MLSS of 3,000 mg/L.

Furthermore, it had been reported that older bio-sludge (long SRT bio-sludge) showed more resistance to HM than the younger bio-sludge (short SRT bio-sludge) [9,10]. This study confirmed that the long SRT bio-sludge showed higher Cr^{3+} adsorption yield than young bio-sludge. This could be related to the cell membrane characteristic or property of long SRT bio-sludge [39,41,44,45]. However, the bio-sludge of SBR contained not only heterotrophic bacteria group but also nitrogenous removal bacteria group (both nitrifying and denitrifying bacteria), and nitrogenous compounds were removed by both assimilation and oxidation–reduction mechanisms. [13,16,17]. But, the main nitrogenous compound removal mechanism was oxidation–reduction mechanism by nitrifying and denitrifying bacteria. This was confirmed by the results shown in Table 4 that show the TN removal efficiency of the system with STIW + Cr^{+5} at MLSS of 5,000 mg/L which was higher than that with STIW at MLSS of 3,000 mg/L. This suggests that the system was operated at higher MLSS of 5,000 mg/L gave the high SRT bio-sludge resulted to consist of high population of nitrogen removal bacteria [13,16]. Then, the SBR system was a mostly suitable process to treat wastewater containing HM and nitrogenous compounds due to easy operation on the oxic-anoxic condition. This evidence was also strongly reconfirmed by the results shown in Table 5, which shows that the long SRT bio-sludge showed higher TN and TKN removal yields than that with short SRT bio-sludge [13]. This also suggests that the nitrogenous compound removal bacteria group showed higher HM adsorption ability than the heterotrophic bacteria group [9].

Moreover, Cr^{3+} showed more repression effect to the denitrifying mechanism than the nitrification mechanism due to the higher effluent nitrate value with STIW + Cr^{3+} compared with STIW. According to the results and discussions above, the SBR system was controlled at low F/M ratio, resulting in the generation of large populations of nitrifying and denitrifying bacteria. The growth and activity of nitrifying and denitrifying bacteria were not repressed by a Cr^{3+} concentration or loading of 5 mg/L and 0.001 g/L d, respectively. The main HM removal mechanism might be given by the nitrogenous removal bacteria group. This could be confirmed by the high TN and TKN removal efficiency and low effluent NH_4^+-N and NO_3^--N of the system with high MLSS operation as shown in Table 4 [9,10,13,16,40].

The other advantages of this SBR system are the good bio-sludge quality and low effluent SS at high MLSS (low F/M) operation. This may be because the system was controlled at high MLSS or low F/M, resulting in producing low excess bio-sludge (long

Table 5
Bio-sludge properties of the SBR system with various types of TIWs and various types of STIWs under various operation conditions (various MLSS, Cr^{3+} and HRT operations)

Operation under various MLSS[a]				Operation under various Cr^{3+} concentration[c]				Operation under various HRT[e]				
MLSS (mg/L)	Effluent SS (mg/L)	SVI (mL/mg)	SRT (d)	Cr^{3+} (mg/L)	SS (mg/L)	SVI (mL/mg)	SRT (d)	Types	HRT (d)	SS (mg/L)	SVI (mL/mg)	SRT (d)
1,000	95 ± 3	20 ± 3	1 ± 0	5	28 ± 1	72 ± 16	15 ± 1	TWW	1.5	123 ± 19	174 ± 7	15 ± 2
2,000	82 ± 2	52 ± 3	4 ± 0	10	31 ± 2	94 ± 17	16 ± 1		3.0	19 ± 4	92 ± 3	15 ± 2
3,000	70 ± 3	62 ± 5	9 ± 1	20	55 ± 4	113 ± 16	21 ± 4		5.0	15 ± 3	79 ± 3	17 ± 2
4,000	40 ± 1	71 ± 3	12 ± 1	30	66 ± 1	135 ± 19	30 ± 3					
5,000	36 ± 1	77 ± 3	15 ± 5	40	82 ± 0	146 ± 17	44 ± 10	TWW + 10 Cr^{3+}	1.5	186 ± 50	171 ± 3	10 ± 1
Control[b]	12 ± 1	64 ± 3	8 ± 2	Control[d]	19 ± 1	61 ± 16	10 ± 1		3.0	22 ± 10	95 ± 2	13 ± 2
									5.0	16 ± 4	93 ± 1	28 ± 8

Notes: [a]The experiment was carried out in SBR system with STIW containing 5 mg/L Cr^{3+} (STIW + 5 Cr^{3+}) at various MLSS of 1,000, 2,000, 3,000, 4,000 and 5,000 mg/L and HRT of 3 d.

[b]Control: SBR system was operated with STIW (without Cr^{3+}) at MLSS of 3,000 mg/L.

[c]The experiment was carried out with STIW containing various Cr^{3+} concentrations of 0, 5, 10, 20, 30 and 40 mg/L at MLSS of 5,000 mg/L and HRT of 3 d.

[d]The experiment was carried out in SBR system with TIW and TIW + 10 mg/L Cr^{3+} at MLSS of 5,000 mg/L and various HRT of 1.5, 3.0 and 5.0 d.

[e]Control: SBR system was operated with STIW without Cr^{3+} at MLSS of 5,000 mg/L.

Table 6
Removal efficiencies and effluent nitrogen compounds of SBR system with STIW containing various Cr^{3+} concentrations of 0, 5, 10, 20, 30 and 40 mg/L at MLSS of 5,000 mg/L and HRT of 3 d

Cr^{3+} (mg/L)	F/M	BOD Loading (kg/m^3 d)	Cr^{3+} Loading (g/L d)	Removal efficiency (%)					Effluent nitrogen compounds (mg/L)				Effluent pH
				Cr^{3+}	COD	BOD_5	TN	TKN[a]	Org-N	NH_4^+-N	NO_2^--N	NO_3^--N	
5	0.067	0.34	0.001	89.7 ± 0.1	96 ± 0	96 ± 0	69.8 ± 2.5	88.4 ± 0.6	2.2 ± 0.4	5.5 ± 0.0	0.1 ± 0.1	12.4 ± 1.9	7.14 ± 0.10
10	0.067	0.34	0.002	87.1 ± 0.4	96 ± 0	95 ± 0	67.8 ± 2.7	85.4 ± 1.2	0.7 ± 0.8	9.0 ± 0.0	0.2 ± 0.0	11.7 ± 2.3	7.06 ± 0.12
20	0.067	0.34	0.004	86.4 ± 0.3	96 ± 0	95 ± 0	51.8 ± 2.1	77.6 ± 1.2	6.8 ± 0.8	8.1 ± 0.5	0.2 ± 0.0	17.1 ± 0.9	7.07 ± 0.07
30	0.067	0.34	0.006	81.7 ± 0.4	95±0	95 ± 0	29.6 ± 3.0	65.5 ± 1.0	10.0 ± 0.6	13.0 ± 0.5	0.5 ± 0.0	23.6 ± 2.4	7.01 ± 0.08
40	0.067	0.34	0.008	76.6 ± 0.1	94 ± 0	93 ± 0	10.8 ± 7.4	62.2 ± 3.9	10.0 ± 2.6	15.2 ± 0.0	0.7 ± 0.1	33.8 ± 3.2	6.71 ± 0.12
0(Control)[a]	0.067	0.34	–	–	99 ± 0	99 ± 0	60.7 ± 3.2	79.3 ± 2.4	1.7 ± 0.6	12.1 ± 0.7	0.1 ± 0.0	12.4 ± 0.9	7.21 ± 0.06

Notes: [a]TKN: Organic-N+NH_4^+-N.

[b]Control: SBR system operated with STIW without Cr^{3+} at MLSS of 5,000 mg/L.

Table 7
Removal efficiencies and effluent nitrogen compounds of SBR system with TIW and TIW + 10 mg/L Cr^{3+} at MLSS of 5,000 mg/L and various HRT of 1.5, 3.0 and 5.0 d

Types	HRT (d)	F/M ratio	BOD Loading (kg/m^3 d)	Cr^{3+} Loading (g/L d)	Removal efficiency (%)					Effluent nitrogen compounds (mg/L)				pH
					Cr^{3+}	COD	BOD_5	TN	TKN[a]	Org-N	NH_4^+-N	NO_2^--N	NO_3^--N	
TIW [b]	1.5	0.16	0.68	0.0010	83.3 ± 0.8	92 ± 1	97 ± 1	51.6 ± 0.2	64.3 ± 0.3	13.3 ± 0.9	110.3 ± 0.6	0.1 ± 0.0	63.9 ± 0.6	6.8 ± 0.1
	3.0	0.08	0.34	0.0005	95.1 ± 0.8	98 ± 1	99 ± 0	56.9 ± 0.2	67.5 ± 0.1	10.5 ± 0.5	101.7 ± 0.8	0.0 ± 0.0	54.9 ± 0.6	7.0 ± 0.0
	5.0	0.05	0.20	0.0003	96.9 ± 0.2	98 ± 1	99 ± 0	60.3 ± 0.1	69.2 ± 0.0	3.7 ± 0.0	102.7 ± 0.6	0.0 ± 0.0	47.5 ± 0.2	7.1 ± 0.0
TIW + 10 Cr^{3+} [c]	1.5	0.16	0.68	0.0040	79.6 ± 0.5	91 ± 1	96 ± 0	51.9 ± 0.4	63.3 ± 0.3	16.6 ± 1.2	110.3 ± 0.6	0.1 ± 0.0	59.7 ± 0.6	6.8 ± 0.1
	3.0	0.08	0.34	0.0020	94.9 ± 0.2	96 ± 1	97 ± 0	56.7 ± 0.2	67.2 ± 0.1	3.9 ± 0.5	109.4 ± 1.7	0.0 ± 0.0	54.5 ± 0.4	7.2 ± 0.0
	5.0	0.05	0.20	0.0010	95.6 ± 0.3	98 ± 1	99 ± 0	60.0 ± 0.1	68.6 ± 0.0	6.7 ± 0.0	101.9 ± 0.0	0.0 ± 0.0	46.4 ± 0.2	7.1 ± 0.0

Notes: [a]TKN: Organic-N + $NH_4^+ - N$.
[b]TIW: Tannery industrial wastewater, TIW was collected from a sump tank of the tannery factory wastewater treatment plant in Samutprakan Province. The wastewater contained 2.1 mg/L Cr^{3+}.
[c]TIW + 10 Cr^{3+}: Tannery industrial wastewater contained 10 mg/L Cr^{+3}, TIW was supplemented with 76. 92 mg/L $Cr(NO_3)_3{\cdot}9H_2O$.

SRT bio-sludge). Also, the long SRT bio-sludge was more easily flocculated than the short SRT bio-sludge [13,16]. This could also be confirmed by the result and the decrease of effluent SS with the increase in MLSS or decrease of F/M ratio as shown in Table 4. From the above results, it could conclude that the SBR system with STIW +5 Cr^{3+} at MLSS of 5,000 mg/L (F/M ratio of 0.07) showed the highest removal efficiency and good bio-sludge quality. In addition, the effect of the various Cr^{3+} concentrations or loadings on the system efficiency at high MLSS of 5,000 mg/L operation was observed. The results showed that the system with STIW containing Cr^{3+} of 5–40 mg/L at MLSS of 5,000 mg/Land HRT of 3 d did not show any significant difference on the COD and BOD_5 removal efficiencies. This suggests that the Cr^{3+} concentration of 5–30 mg/L (Cr^{3+} loading of 0.001–0.006 g/L d) did not give any significant repression effect on the growth and activity of heterotrophic bacteria group. But, the increase in Cr^{3+} concentration or loading affected the growth and activity of the nitrogenous compound removing bacteria group (nitrifying and denitrifying bacteria).

The results shown in Table 6 confirmed that the TN and TKN removal efficiencies were decreased with the increase in Cr^{3+} concentration or loading. This may also be confirmed by the increase in effluent NH_4^+-N and NO_3^--N concentrations with the increase in Cr^{3+} concentration or loading. According to the increase in NO_3^--N concentration during operation as mentioned above, the system pH was decreased to the acidic level [13,16]. For the bio-sludge quality observation, SRT of the system was increased with the increase in SRT resulting by the repression of both nitrifying and denitrifying bacteria [13,16]. Moreover, the increase in Cr^{3+} concentration or loading resulted in increase in effluents SS and SVI. The effect of the Cr^{3+} may be toxic the bio-sludge (both heterotrophic and nitrogenous compound removal bacteria).

It was determined that TIW (containing 2.1 mg/L Cr^{3+}) was suitable for treatment by the SBR system. Moreover, the increase in HRT (or to decrease F/M ratio) resulted in the increase in the Cr^{3+} adsorption yield. This is because of the increases in HRT resulting from the increase in bio-sludge age (SRT), and the high SRT bio-sludge gave higher Cr^{3+} adsorption yield than the short SRT bio-sludge [9,10,40]. The other advantage was that the system could be controlled at a high HRT of 5.0 d and provided a high SRT. This was a result of a low SVI below 80 mL/g and low effluent SS of 15 mg/L. The system could also be used to treat TIW + 10 Cr^{3+} with high removal efficiencies and good bio-sludge quality, but it must operate at high HRT of

5 d (F/M of 0.05). According to the above results, the system could be used to treat TIW with a Cr^{3+} concentration of higher than 10 mg/L (Cr^{3+} loading of higher than 0.001 g/L d) by adding organic matter (to increase the BOD loading) [9,10,40].

5. Conclusion

The SBR system was evaluated in the treatment of TIW containing high HM, organic matter and nitrogenous compounds. The experiments were carried out using a laboratory scale of the SBR system with TIW and STIW to observe the optimal conditions for highest removal efficiency. It was found that the system with STIW + 5 Cr^{3+} had to be operated at a high SRT of 15 ± 5 d (high MLSS of 5,000 mg/L and F/M of 0.07) to show the highest COD, BOD5, TKN, TN and Cr^{3+} removal efficiencies of 96 ± 0, 96 ± 1, 88.5 ± 0.1, 61.0 ± 0.5 and 87.5 ± 0.2%, respectively. The bio-sludge quality had an SVI of 77 ± 3. Moreover, the system operating at the highest MLSS of 5,000 mg/L showed high COD and BOD_5 removal efficiencies of about 95–96%; even the Cr^{3+} concentration or loading of up to 40 mg/L and 0.008 g/L d, respectively, without any significant effect to the heterotrophic bacteria. The Cr^{3+} concentration or loading of higher than 20 mg/L or 0.004 g/L d had a repression effect to both nitrifying and denitrifying bacteria. The application, the SBR, system would be most suitable in treating a raw TIW with high removal efficiency because Cr^{3+} concentration of the collected TIW sample was quite low at only 2.10 ± 0.01 mg/L.

The SBR system evaluated with TIW + 10 Cr^{3+} to observe the efficiency and performance of the system. It was found that the system with TIW + 10 Cr^{3+} at HRT of 5 d showed high removal efficiency and good bio-sludge quality. This is because the system operating at high HRT generated by old age bio-sludge resulted in resistant to toxic substances, especially Cr^{3+}. Moreover, the high HRT operation was one of the solutions to reduce or dilute the toxic effect of Cr^{3+} and the other toxic substances in TIW. However, the operation conditions above diluted the toxic substances that caused diluting or reducing the BOD_5 loading of the system as well. This might be a disadvantage that will decrease the growth of bio-sludge.

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Nomenclature

BOD_5	—	biochemical oxygen demand
CN^-	—	cyanide
COD	—	chemical oxygen demand
Cr^{3+}	—	chromium
DO	—	dissolved oxygen
EPWW	—	electroplating wastewater
HM	—	heavy metals
HRT	—	hydraulic retention time
MLSS	—	mixed liquor suspended solids
NH_4^+-N	—	ammonium–nitrogen
NO_3^--N	—	nitrate–nitrogen
NO_2^--N	—	nitrite–nitrogen
SBR	—	sequencing batch reactor
SRT	—	solids retention time
SVI	—	sludge volume index
SS	—	suspended solids
STIW	—	synthetic tannery industrial wastewater
STIW + Cr^{3+}	—	synthetic tannery industrial wastewater containing chromium
TIW	—	tannery industrial wastewater
TKN	—	total Kjeldahl nitrogen
TN	—	total nitrogen

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