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Full Length Research Paper

Effects of Cr^{3+} and Ni^{2+} on the efficiency and performance of sequencing batch reactor (SBR) system

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Sequencing batch reactor (SBR) system at hydraulic retention time (HRT) of 1.5 days could be used for the treatment of Ladkrabang industrial estate wastewater (LIWW) with high Cr^{3+} and Ni^{2+} removal efficiencies of 80.7 ± 17.9 and 53.5 ± 25.1%, respectively. Bio-sludge of SBR system with synthetic industrial estate wastewater (SIWW) showed the highest Cr^{3+} and Ni^{2+} adsorption yields of 36.00 ± 9.80 and 31.59 ± 9.67 mg/g, respectively but they were reduced to 25.20 ± 8.38 and 20.49 ± 7.20 mg/g, respectively with LIWW. Cr^{3+} and Ni^{2+} strongly suppressed the growth and activity of heterotrophic bacteria. Ni^{2+} at 3.0 mg/L did not impact either nitrifying or denitrifying bacteria, while the growth and activity of denitrifying bacteria was suppressed at 3.0 mg/L Cr^{3+}. The other advantage of SBR system was that the bio-sludge could adsorb inorganic matters from LIWWs, which contains high inorganic content about 33%.

Key words: Adsorption, chromium, heavy metals, nickel, sequencing batch reactor (SBR) system.

INTRODUCTION

An industrial estate is the area planned for industry where space is available for large buildings expansion and unlimited resources such as water and electricity supplies. Industrial estates often have good internal road layouts and occupy accessible sites near main road junctions but away from the central business district (Metcalf and Eddy, 2004; Sirianuntapiboon and Boonchupleing, 2009). Usually, each industrial estate consists of the same type of industry such as petro-chemical, food processing, electronic industrial estates. However, some industrial estates consist of several types of industry such as food processing, electroplating, metal-processing, paint and battery industries (Metcalf and Eddy, 2004; Sirianuntapiboon and Boonchupleing, 2009; Sirianuntapiboon and Chaiyasing, 2000), so the waste-water from the industrial estates contains both organic and inorganic matter, especially heavy metals. The selection of wastewater treatment process depends on the type of pollutants in the wastewater. The biological treatment process is suitable for wastewater containing organic matter (Metcalf and Eddy, 2004; Arora et al., 1985; Kagi and Uygur, 2002). The chemical treatment process is suitable for wastewater containing inorganic matters or heavy metals (Metcalf and Eddy, 2004; Bansode et al., 2003; Carl et al., 1982; Fahim et al., 2006). As mentioned above, most industrial wastewaters contain both organic and inorganic matters, thus the type of wastewater treatment process should be carefully considered.

Many researchers reported that the biological process could be applied for treating the wastewater containing both organic and inorganic matters (Al-Asheh and Duvnjak, 1995; Aricana et al., 2002; Chen et al., 2000; Chen and Gu, 2005; David and Bohumil, 1998; Mattuschka and Straube, 1993; Wang et al., 2006). Several kinds of heavy metals such as lead, cadmium, copper and zinc could be adsorbed on the surface of the microbial cell (Sirianuntapiboon and Boonchupleing,

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Abbreviations: **SBR**, Sequencing batch reactor; **HRT**, hydraulic retention time; **LIWW**, Ladkrabang industrial estate wastewater; **SIWW**, synthetic industrial estate wastewater.

2009; Arican and Yetis, 2003; Kapoor and Viraraghavan, 1997; Sirianuntapiboon and Hongsrisuwan, 2007; Sirianuntapiboon and Ungkaprasatcha, 2007).

Sequencing batch reactor (SBR) and granular activated sludge-SBR (GAC-SBR) systems could be used to treat the wastewater containing heavy metals due to their high mixed liquor suspended solids (MLSS) operation and resistance to the shock load and toxic substance (Metcalf and Eddy, 2004; Sirianuntapiboon and Chaiyasing, 2000; Sirianuntapiboon and Ungkaprasatcha, 2007; Ong et al., 2005). However, the application of GAC-SBR system for the treatment of wastewater containing heavy metals might be unsuitable due to excess bio-sludge harvesting district (Metcalf and Eddy, 2004; Arora et al., 1985; Sirianuntapiboon and Hongsrisuwan, 2007; Sirianuntapiboon and Ungkaprasatcha, 2007; Cheng et al., 1975; Gulnaz et al., 2005). Also, the heavy metals, especially, Cr^{3+} and Ni^{2+} might be toxic to the bio-sludge of the wastewater treatment system (Sirianuntapiboon and Hongsrisuwan, 2007; Sirianuntapiboon and Ungkaprasatcha, 2007; Ong et al., 2005; Gikas and Romanos, 2006; Lee et al., 1997). The standard permission of effluent Cr^{3+} and Ni^{2+} were 0.75 and 1.0 mg/L by the Department of Industrial Works, Thailand (Department of Industrial Works, 1992).

The objectives of this study were; a) to investigate the hydraulic retention times (HRTs) of SBR system with wastewater containing Cr^{3+} and Ni^{2+} for the highest removal efficiencies, b) to test the effects of Cr^{3+} and Ni^{2+} on bio-sludge performance and removal efficiencies, c) to monitor the effects of Cr^{3+} and Ni^{2+} on the types of microorganism in the bio-sludge, and d) to use the SBR system for treatment raw industrial estate wastewater containing high heavy metals.

MATERIALS AND METHODS

Wastewater samples

Two kinds of wastewater samples were used in this study: (1) Ladkrabang industrial estate wastewater (LIWW) and (2) synthetic industrial estate wastewater (SIWW). LIWW was collected from the influent sump tank of a central wastewater treatment plant of Ladkrabang industrial estate, Bangkok, Thailand. The chemical characteristics of LIWWs are described in Table 1. Two other types of wastewater were prepared namely: LIWW supplemented with 38.46 mg/L $Cr(NO_3)_3.9H_2O$ (LIWW+ 3.0 mg/L Cr^{3+}) and LIWW supplemented with 20.0 mg/L $NiCl_2$ (LIWW+ 3.0 mg/L Ni^{2+}). The chemical composition and properties of LIWWs were shown in Table 1. SIWWs were prepared according to the LIWW characteristic. The chemical compositions and properties of each type of SIWWs were described in Table 1.

Acclimatization of bio-sludge

The bio-sludge from bio-sludge storage tank of the central sewage treatment plant of Bangkok city, Thailand (Sripaya sewage treatment plant) was used as the inoculums for the SBR system after acclimatized in SBR system with SIWW without heavy metals at hydraulic retention time (HRT) of 2 days for a week.

Sequencing batch reactor (SBR)

Ten 10-L reactors made from acrylic plastics (5 mm thick) as shown in Figure 1 were used in the experiments. Each reactor was 18 cm-diameter and 40 cm-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, 100V, 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 as evidenced by the dissolved oxygen in the system of about 2 to 3 mg/L). The excess sludge was removed during the draw and idle period to control mixed liquor suspended solids (MLSS) of the system (Table 2).

Operation of SBR system

SBR system was operated at 1 cycle/day under an HRT of 1.0, 1.5 and 2.0 days. Exactly 1.4 L of 10 g/L of acclimatized bio-sludge as earlier described was inoculated in each reactor, and LIWWs or SIWWs were added (to a final volume of 7.5 L) within 1 h. During reaction period, the system was continuously aerated for 19 h. Aeration was then shut down for 3 h. After 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. Afterwards the reactor was filled with fresh wastewater to the final volume of 7.5 L and the above operation was repeated. The operation parameters of the SBR system with IEWWs and SIEWWs are described in Table 2.

Chemical analysis

Chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), organic-N, NH_4^+-N, NO_3^--N, NO_2^--N, total nitrogen (TN), Cr^{3+}, Ni^{2+}, suspended solids (SS), total dissolved solids (TDS), mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), organic matters and inorganic matters as well as the pH of influent and effluent and sludge volume index (SVI) of the SBR system, were determined according to the standard methods for the examination of water and wastewater (APHA, AWWA, WPCF, 1995). The bio-sludge age was determined as the ratio of total biomass (mixed liquor suspended solids: MLSS) of the system to the amount of excess sludge wasted per day.

Statistical analysis method

Each experiment was repeated at least three times. All the data were subjected to two-way analysis of variance (ANOVA) using SAS Windows Version 6.12 (SAS Institute, 1996). Statistical significance was tested using least significant difference (LSD) at the $p<0.05$ level. The results shown are mean ± standard deviation.

RESULTS

Effect of HRT on the removal efficiencies of SBR system with LIWW

The experiments were carried out in SBR system with LIWW at various HRTs operation of 1.0, 1.5 and 2.0 days. The results on the effects of HRTs on the removal

Table 1. Chemical compositions and properties of LIWWs and SIWWs.

Parameter	LIWW			SIWW			SIWW	
	Chemical property			Chemical property			Chemical composition	
	LIWW[a]	LIWW+Ni^{+2} [b]	LIWW+Cr^{+3} [c]	SIWW [d]	SIWW+ Ni^{+2}[e]	SIWW+ Cr^{+3}[f]	Parameter	Concentration (mg/L)
COD (mg/L)	369 ± 76	369 ± 17	366 ± 51	480 ± 7	480 ± 6	480 ± 5	Glucose	282
BOD_5 (mg/L)	222 ± 12	219 ± 19	220 ± 15	230 ± 3	230 ± 4	228 ± 4	$Cr(NO_3)_3.9H_2O$ [g]	38.46
Organic-N (mg/L)	8.3 ± 0.6	8.3 ± 0.6	8.3 ± 0.6	7.8 ± 0.6	7.8 ± 0.6	7.8 ± 0.6	$NiCl_2$ [h]	20.0
NH_4^+-N (mg/L)	8.3 ± 0.5	8.3 ± 0.5	8.3 ± 0.5	8.6 ± 0.2	8.6 ± 0.2	8.6 ± 0.2	Urea	21.4
NO_2^--N (mg/L)	6.7 ± 0.2	6.7 ± 0.2	6.7 ± 0.2	3.5 ± 0.2	3.5 ± 0.2	3.5 ± 0.2	KH_2PO_4	8.72
NO_3^--N(mg/L)	5.8 ± 0.7	5.8 ± 0.7	5.8 ± 0.7	4.4 ± 0.6	4.4 ± 0.6	4.4 ± 0.6	$FeSO_4.7H_2O$	4.978
Total Nitrogen (mg/L)	29.2 ± 0.9	29.2 ± 0.9	29.2 ± 0.9	24.3 ± 0.6	24.3 ± 0.6	24.3 ± 0.6		
Ni^{2+} (mg/L)	0.30 ± 0.03	3.30 ± 0.27	0.30 ± 0.03	0.00 ± 0.00	3.03 ± 0.10	0.00 ± 0.00		
Cr^{3+} (mg/L)	0.13 ± 0.02	0.13 ± 0.02	3.14 ± 0.16	0.00 ± 0.00	0.00 ± 0.00	3.01 ± 0.07		
Other heavy metals (mg/L)[i]	6.29 ± 0.05	6.29 ± 0.05	6.29 ± 0.05	-	-	-		
SS (mg/L)	21 ± 3	157 ± 44	158 ± 35	11 ± 4	21 ± 3	21 ± 3		
Organic/ SS	0.3 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.6 ± 0.2	0.5 ± 0.1	0.6 ± 0.1		
Inorganic/SS	0.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	0.4 ± 0.1	0.5 ± 0.1	0.4 ± 0.1		
TDS (mg/L)	383 ± 43	678 ± 70	691 ± 46	341 ± 20	354 ± 4	383 ± 43		
Organic/ TDS	0.3 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	0.5 ± 0.1		
Inorganic/TDS	0.7 ± 0.1	0.8 ± 0.1	0.7 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	0.5 ± 0.1		

[a] LIWW: Raw Ladkrabang industrial estate wastewater; [b]LIWW+Ni^{2+}: LIWW containing 20.0 mg/L $NiCl_2$; [c]LIWW+Cr^{3+}: LIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$; [d] SIWW: synthetic industrial estate wastewater; [e] SIWW+Ni^{2+}: SIWW containing 20.0 mg/L $NiCl_2$; [f] SIWW+Cr^{3+}: SIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$; [g]For SIWW+Cr^{3+}; [d]For SWW+Ni^{2+}; [i]Other heavy metals contained Zn^{2+}, Mn^{2+}, Fe^{2+}, Pb^{2+}, Cu^{2+}, etc.

efficiencies and bio-sludge performances of SBR system with LIWW were described as follows.

BOD_5 and COD

The SBR system at the optimal HRT of 1.5 days showed the highest BOD_5 and COD removal efficiencies of 48 ± 6 and 59 ± 8%, respectively as shown in Table 3. However, the effluent BOD_5 and COD were still high at 116 ± 14 and 150 ± 19 mg/L, respectively.

Nitrogen compounds

The SBR system with LIWW did not show any significant difference on TN removal efficiency at the HRT of 1.0 to 2.0 days (Table 4). The system at the lowest HRT of 1.0 days showed that more stable TN removal efficiency than that at HRT of 1.5 and 2.0 days resulted by the lowest standard deviation of only ±2.6. The effluent NO_3^--N was about 2 times of influent NO_3^--N in all experiments. However, the system showed quite high organic-N and NH_4^+-N removal efficiencies of about 50%. The accumulated NO_2^-N in the

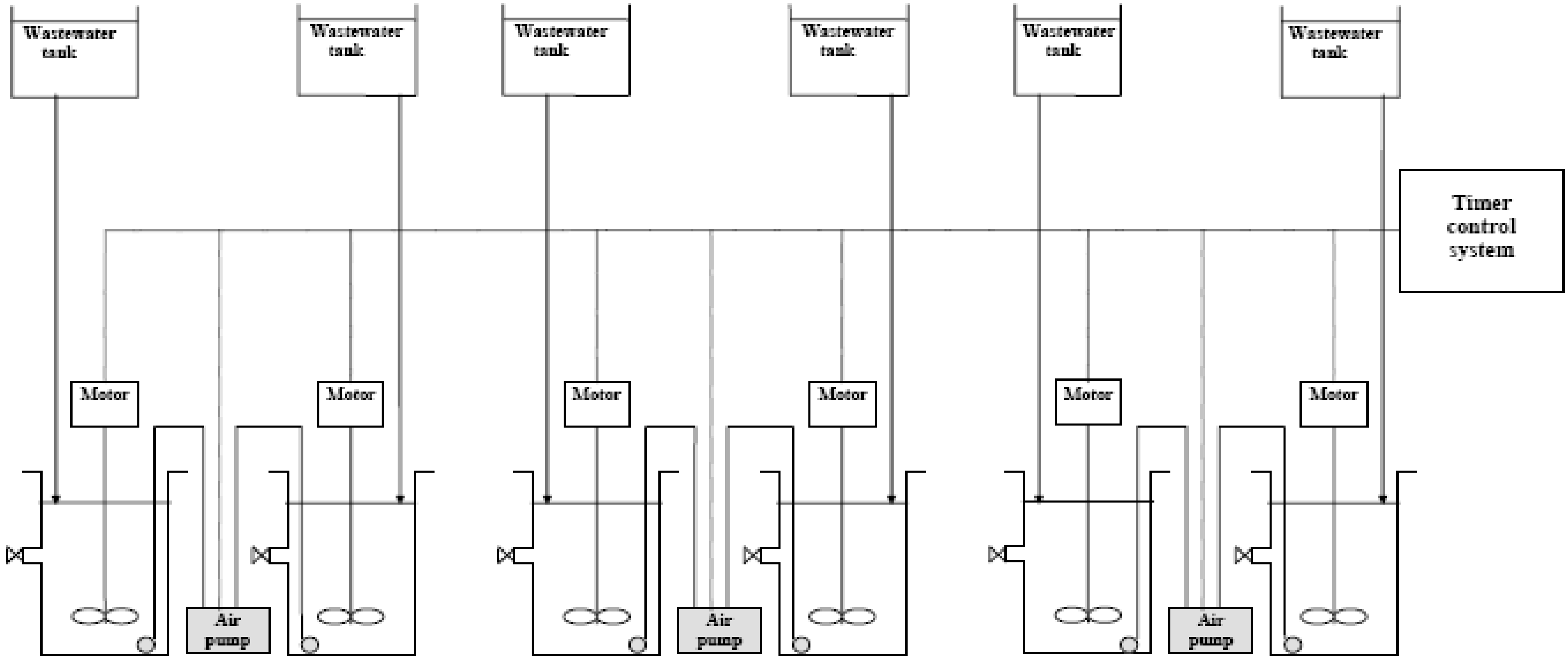

Figure 1. Flow diagram of SBR treatment system. The physical operation control were 60 rpm of impeller speed, fully aeration with air-pump system model EK-8000, 6.0 W (one set of air pump supplied for 2 sets of reactor the working volume of the reactor was 75% of total volume (7.5 L). The chemical and biological operations controls were described in the text according to each experiment.

system was quite low of only 1.1-1.2 mg/L in all experiments.

Heavy metals (Cr^{3+} and Ni^{2+})

The SBR system with LIWW at the HRT of 1.0 to 2.0 days showed higher Cr^{3+} removal efficiency than Ni^{2+} removal efficiency (Table 5). The system at HRT of 1.5 days showed the highest Cr^{3+} and Ni^{2+} removal efficiencies of 80.7 ± 17.9 and 53.5 ± 25.1%, respectively. Both $Cr^{3+}$and Ni^{2+} could be adsorbed onto the bio-sludge. The maximum Cr^{3+} and Ni^{2+}adsorption yields of the bio-sludge in SBR system with LIWW at HRT of 1.5 days were 0.94 ± 0.06 and 0.48 ± 0.12 mg/g of bio-sludge, respectively. However, the heavy metals adsorption capacities of the bio-sludge were decreased with the increase of HRT, BOD_5 loading or heavy metals loading (Tables 2 and 5).

SS and TDS

The system with LIWW at HRT of 1.0 to 2.0 days contained very high effluents SS and TDS of over 75 and 650 mg/L, respectively (Table 3). HRT did

Table 2. The operating parameters of the SBR system.

Parameter	LIWW[a]			SIWW [d]	SIWW+Ni [2+ e]	SIWW+Cr[3+f]	LIWW+Ni[2+b]	LIWW+Cr[3+c]
HRT, days	1.0	1.5	2.0	1.5	1.5	1.5	1.5	1.5
MLSS, mg/L	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000
Flow rate, L/d	7.50	5.00	3.75	5.00	5.00	5.00	5.00	5.00
F/M ratio (1/d)	0.11	0.08	0.06	0.08	0.08	0.08	0.08	0.08
BOD_5 loading (g/d)	1.65	1.15	0.83	1.15	1.15	1.15	1.15	1.15
Volumetric BOD_5 loading (kg BOD_5/m^3.d)	0.22	0.15	0.11	0.15	0.15	0.15	0.15	0.15
Ni^{2+} loading (g Ni^{2+}/d)	0.0023	0.0015	0.0011	0.0000	0.0142	0.0000	0.0148	0.0015
Volumetric Ni^{2+}loading (kg Ni^{2+}/m^3.d)	0.0003	0.0002	0.0001	0.0000	0.0020	0.0000	0.0020	0.0003
Cr^{3+}loading (g Cr^{3+}/d)	0.0010	0.0007	0.0005	0.0000	0.0000	0.0108	0.0007	0.0112
Volumetric Cr^{3+}loading (kg Cr^{3+}/ m^3.d)	0.0001	0.0001	0.0001	0.0000	0.0000	0.0014	0.0001	0.0015

[a]LIWW: Raw Ladkrabang industrial estate wastewater; [b] LIWW+Ni^{2+} : LIWW containing 20.0 mg/L $NiCl_2$; [c] LIWW+Cr^{3+} : LIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$; [d] SIWW: synthetic industrial estate wastewater; [e] SIWW+ Ni^{2+}: SIWW containing 20.0 mg/L $NiCl_2$; [f] SIWW+Cr^{3+} : SIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$.

Table 3. Removal efficiency and effluent properties of SBR system operated with LIWWs and SIWWs.

Type of wastewater	HRT (day)	Organic loading (kg BOD_5/ m^3.d)	Ni^{2+} loading (kg Ni^{2+}/ m^3.d)	Cr^{3+} loading (kg Cr^{3+}/ m^3.d)	BOD_5		COD		Effluent quality			
					Effluent (mg/L)	Removal (%)	Effluent (mg/L)	Removal (%)	SS (mg/L)	Org/ SS	TDS (mg/L)	Org/ TDS
LIWW [a]	1.0	0.22	0.0003	0.0001	126 ± 16	43 ± 7	162 ± 34	56 ± 9	79 ± 27	0.3 ± 0.1	656 ± 134	0.3 ± 0.1
LIWW [a]	1.5	0.15	0.0002	0.0001	116 ± 14	48 ± 6	150 ± 19	59 ± 8	74 ± 16	0.3 ± 0.1	647 ± 88	0.3 ± 0.1
LIWW [a]	2.0	0.11	0.0001	0.0001	125 ± 19	44 ± 10	163 ± 30	55 ± 12	78 ± 19	0.3 ± 0.1	671 ± 64	0.3 ± 0.1
SIWW[d]	1.5	0.15	0.0000	0.0000	45 ± 9	81 ± 4	84 ± 15	82 ± 3	12 ± 5	0.6 ± 0.2	153 ± 56	0.5 ± 0.1
SIWW+Ni^{2+}[e]	1.5	0.15	0.0020	0.0000	74 ± 17	68 ± 8	124 ± 32	74 ± 7	42 ± 16	0.5 ± 0.1	142 ± 8	0.6 ± 0.1
SIWW+Cr^{3+}[f]	1.5	0.15	0.0000	0.0014	72 ± 14	69 ± 6	129 ± 30	73 ± 6	24 ± 14	0.6 ± 0.1	147 ± 20	0.5 ± 0.1
LIWW[a]	1.5	0.15	0.0002	0.0001	116 ± 14	48 ± 6	150 ± 19	59 ± 8	74 ± 16	0.3 ± 0.1	647 ± 88	0.3 ± 0.1
LIWW+Ni^{2+}[b]	1.5	0.15	0.0020	0.0001	134 ± 23	38 ± 11	158 ± 42	57 ± 12	93 ± 25	0.3 ± 0.1	612 ± 103	0.2 ± 0.1
LIWW+Cr^{3+}[c]	1.5	0.15	0.0003	0.0015	135 ± 23	39 ± 10	173 ± 40	52 ± 12	86 ± 27	0.3 ± 0.1	654 ± 134	0.3 ± 0.1

[a]LIWW: Raw Ladkrabang industrial estate wastewater; [b]LIWW+Ni^{2+} : LIWW containing 20.0 mg/L $NiCl_2$; [c] LIWW+Cr^{3+}: LIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$; [d]SIWW: synthetic industrial estate wastewater; [e] SIWW+Ni^{2+}: SIWW containing 20.0 mg/L $NiCl_2$; [f]SIWW+Cr^{3+}: SIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$.

not give any significant effect to the SS and TDSremoval efficiencies. Moreover, no significant difference on the effluents SS and TDS were observed even when the HRT of the system was varied. HRT did not show any effect on the organic content of effluents SS and TDS. The

Table 4. Nitrogenous compounds removal efficiency and effluent properties of SBR system operated with LIWWs and SIWWs.

Type of Wastewater	HRT (day)	Organic loading ($kgBOD_5/m^3.d$)	Ni^{2+} loading (kg $Ni^{2+}/m^3.d$)	Cr^{3+} loading (kg $Cr^{3+}/m^3.d$)	Organic-N (mg/L)		NH_4^+-N (mg/L)		NO_2^--N (mg/L)		NO_3^--N (mg/L)		Total-nitrogen (TN)	
					Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Effluent (mg/L)	Removal (%)
LIWW [a]	1.0	0.22	0.0003	0.0001	8.3 ± 0.3	4.1 ± 0.8	8.3 ± 0.5	5.1 ± 1.0	6.7 ± 0.2	1.2 ± 0.4	5.8 ± 0.7	9.3 ± 2.1	19.7 ± 3.3	32.4 ± 2.6
LIWW [a]	1.5	0.15	0.0002	0.0001	8.3 ± 0.3	3.7 ± 1.6	8.3 ± 0.5	5.4 ± 1.0	6.7 ± 0.2	1.2 ± 0.4	5.8 ± 0.7	9.7 ± 3.3	19.9 ± 5.1	31.9 ± 7.6
LIWW [a]	2.0	0.11	0.0001	0.0001	8.3 ± 0.3	3.8 ± 1.3	8.3 ± 0.5	5.3 ± 1.1	6.7 ± 0.2	1.1 ± 0.3	5.8 ± 0.7	9.6 ± 2.9	19.9 ± 4.8	31.9 ± 6.5
SIWW [d]	1.5	0.15	0.0000	0.0000	7.8 ± 0.6	3.8 ± 0.8	8.6 ± 0.2	4.4 ± 0.8	3.5 ± 0.2	1.5 ± 0.2	4.4 ± 0.6	8.1 ± 1.2	17.8 ± 1.6	26.7 ± 7.0
SIWW+Ni^{2+} [e]	1.5	0.15	0.0020	0.0000	7.8 ± 0.6	3.9 ± 1.6	8.6 ± 0.2	5.3 ± 1.4	3.5 ± 0.2	1.4 ± 0.3	4.4 ± 0.6	7.3 ± 2.1	17.9 ± 2.2	26.2 ± 9.3
SIWW+Cr^{3+} [f]	1.5	0.15	0.0000	0.0014	7.8 ± 0.6	3.0 ± 1.1	8.6 ± 0.2	5.2 ± 1.5	3.5 ± 0.2	1.6 ± 0.3	4.4 ± 0.6	9.4 ± 1.2	19.2 ± 2.0	20.8 ± 8.3
LIWW [a]	1.5	0.15	0.0002	0.0001	8.3 ± 0.6	3.7 ± 1.6	8.3 ± 0.5	5.4 ± 1.0	6.7 ± 0.2	1.2 ± 0.4	5.8 ± 0.7	9.7 ± 3.3	19.9 ± 5.1	31.9 ± 7.6
LIWW+Ni^{2+} [b]	1.5	0.15	0.0020	0.0001	8.3 ± 0.6	4.3 ± 0.6	8.3 ± 0.5	5.4 ± 1.1	6.7 ± 0.2	1.2 ± 0.4	5.8 ± 0.7	9.5 ± 1.5	20.4 ± 2.0	30.1 ± 5.1
LIWW+Cr^{3+} [c]	1.5	0.15	0.0003	0.0015	8.3 ± 0.6	4.3 ± 1.0	8.3 ± 0.5	5.3 ± 1.0	6.7 ± 0.2	1.2 ± 0.4	5.8 ± 0.7	10.0 ± 1.6	20.9 ± 2.5	28.9 ± 4.3

[a]LIWW: Raw Ladkrabang industrial estate wastewater; [b]LIWW+Ni^{2+}: LIWW containing 20.0 mg/L $NiCl_2$; [c]LIWW+Cr^{3+}: LIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$; [d]SIWW: synthetic industrial estate wastewater; [e] SIWW+ Ni^{2+}: SIWW containing 20.0 mg/L $NiCl_2$; [f]SIWW+Cr^{3+}: SIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$.

organic content of effluents SS and TDS at HRT of 1.0 to 2.0 days were about 30%.

Bio-sludge performance

HRT strongly affected the bio-sludge age of the SBR system. The bio-sludge age increased with the increase of HRT. The bio-sludge age of the system with LIWW at HRT of 2.0 days was 10 ± 3 days, while it was only 6 ± 2 days at HRT of 1.0 days. In addition, HRT did not impact the organic content of MLSS. The ratio of MLVSS: MLSS of the bio-sludge was about 0.65 to 0.67 in all experiments. HRT did not affect the sludge volume index (SVI) of the system; the SVI of the system with LIWW was 135 ml/g at HRT of 1.0 to 2.0 (Table 6).

Effect of heavy metals on the removal efficiencies and performances of SBR with LIWWs and SIWWs

BOD_5 and COD

SBR system with SIWW at HRT of 1.5 days showed the high BOD_5 and COD removal efficiencies of 81 ± 4 and 82 ± 3. The removal efficiencies were reduced by adding heavy metals (3.0 mg/L Cr^{3+} and 3.0 mg/L Ni^{2+}). The BOD_5 removal efficiencies were reduced to 68 ± 8 and 69 ± 6%, respectively by adding 3.0 mg/L Cr^{3+} and 3.0 mg/L Ni^{2+}, respectively. Also, the COD removal efficiency of the system was reduced to 74 ± 7 and 73 ± 6% by adding 3.0 mg/L Cr^{3+} or 3.0 mg/L Ni^{2+}. For application, the SBR was carried out with LIWWs; the BOD_5 and COD removal efficiencies also decreased by adding 3.0 mg/L Cr^{3+}or 3.0 mg/L Ni^{2+}. The removal efficiencies of the system were fluctuated during the operation due to the high standard deviation (±SD) of over 30%. The BOD_5 removal efficiencies of the SBR system with LIWW at HRT of 1.5 days was reduced from 48 ± 6 to 38 ± 11% and 39 ± 10% by 3.0 mg/L Ni^{2+} and 3.0 mg/L Cr^{3+}, respectively.

Nitrogen compounds

The SBR system with SIWWs at HRT of 1.5 days showed the interesting results on the nitrogen compounds removal efficiencies (Table 4). TN removal efficiency at HRT of 1.5 days was not effect by 3.08 ± 0.10 mg/L Ni^{2+} (Ni^{2+} loading of

Table 5. Heavy metals and bio-sludge properties of SBR system operated with LIWWs and SIWWs.

Type of Wastewater	HRT (day)	Organic loading (kg BOD_5/ m^3.d)	Ni^{2+} loading (kg Ni^{2+}/ m^3.d)	Cr^{3+} loading (kg Cr^{3+}/m^3.d)	Nickel (Ni^{2+})			Chromium (Cr^{3+})		
					Effluent (mg/L)	Removal (%)	Max. Ni^{2+} In bio-sludge (mg/g)	Effluent (mg/L)	Removal (%)	Max.Cr^{3+} In bio-sludge (mg/g)
LIWW [a]	1.0	0.22	0.0003	0.0001	0.13 ± 0.07	44.5 ± 24.8	0.26 ± 0.08	0.03 ± 0.03	80.7 ± 20.1	0.94 ± 0.20
LIWW [a]	1.5	0.15	0.0002	0.0001	0.14 ± 0.06	53.5 ± 25.1	0.48 ± 0.12	0.03 ± 0.02	80.7 ± 17.9	0.94 ± 0.06
LIWW [a]	2.0	0.11	0.0001	0.0001	0.18 ± 0.05	46.6 ± 17.8	0.39 ± 0.11	0.04 ± 0.03	70.0. ± 24.0	0.74 ± 0.16
SIWW [d]	1.5	0.15	0.0000	0.0000	-	-	0.58 ± 0.14	-	-	0.09 ± 0.02
SIWW+Ni^{2+} [e]	1.5	0.15	0.0020	0.0000	0.58 ± 0.36	90.5 ± 10.6	31.59 ± 9.67	-	-	0.09 ± 0.03
SIWW+Cr^{3+} [f]	1.5	0.15	0.0000	0.0014	-	-	0.75 ± 0.21	0.19 ± 0.10	91.2 ± 4.9	36.00 ± 9.80
LIWW [a]	1.5	0.15	0.0002	0.0001	0.14 ± 0.06	53.5 ± 25.1	0.48 ± 0.12	0.03 ± 0.02	80.7 ± 17.9	0.94 ± 0.22
LIWW+Ni^{2+} [b]	1.5	0.15	0.0020	0.0001	1.10 ± 0.40	55.4 ± 16.3	20.49 ± 7.20	0.02 ± 0.02	85.7 ± 12.5	0.25 ± 0.05
LIWW+Cr^{3+} [c]	1.5	0.15	0.0003	0.0015	0.15 ± 0.06	56.1 ± 19.1	0.34 ± 0.10	0.25 ± 0.14	79.5 ± 8.2	25.20 ± 8.38

[a] LIWW: Raw Ladkrabang industrial estate wastewater; [b] LIWW+Ni^{2+}: LIWW containing 20.0 mg/L $NiCl_2$; [c]LIWW+Cr^{3+} : LIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$; [d] SIWW: synthetic industrial estate wastewater; [e] SIWW+ Ni^{2+}: SIWW containing 20.0 mg/L $NiCl_2$; [f] SIWW+Cr^{3+}: SIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$. Remark: Influent Ni^{2+} of LIWW was 0.30 ± 0.04 mg/L, influent $Cr^{3+}$of LIWW was 0.13 ± 0.02 mg/L, influent Ni^{2+} of LIWW+ Ni^{2+} was 2.95 ± 0.67 mg/L, influent Cr^{3+} of LIWW+ Cr^{3+} was 2.24 ± 0.16 mg/L

Table 6. Bio-sludge properties of SBR system operated with LIWWs and SIWWs.

Type of Wastewater	HRT (day)	Organic loading (kg BOD_5/m^3.d)	Ni^{2+}loading (kg Ni^{2+}/m^3.d)	Cr^{3+}loading (kg Cr^{3+}/m^3.d)	Bio-sludge properties			
					F/M Ratio (1/d)	MLVSS/MLSS	Bio-sludge age (days)	SVI (ml/g)
LIWW [a]	1.0	0.22	0.0003	0.0001	0.11	0.67 ± 0.04	6 ± 2	134 ± 14
LIWW [a]	1.5	0.15	0.0002	0.0001	0.08	0.66 ± 0.04	8 ± 2	135 ± 19
LIWW [a]	2.0	0.11	0.0001	0.0001	0.06	0.65 ± 0.03	10 ± 3	137 ± 17
SIWW [d]	1.5	0.15	0.0000	0.0000	0.08	0.80 ± 0.07	7 ± 2	82 ± 12
SIWW+Ni^{2+} [e]	1.5	0.15	0.0020	0.0000	0.08	0.82 ± 0.06	14 ± 3	121 ± 19
SIWW+Cr^{3+} [f]	1.5	0.15	0.0000	0.0014	0.08	0.80 ± 0.04	12 ± 3	141 ± 22
LIWW [a]	1.5	0.15	0.0002	0.0001	0.08	0.66 ± 0.04	8 ± 2	135 ± 19
LIWW+Ni^{2+} [b]	1.5	0.15	0.0020	0.0001	0.08	0.67 ± 0.04	15 ± 4	142 ± 12
LIWW+Cr^{3+} [c]	1.5	0.15	0.0003	0.0015	0.08	0.66 ± 0.03	13 ± 3	153 ± 19

[a]LIWW: Raw Ladkrabang industrial estate wastewater; [b] LIWW+Ni^{2+} : LIWW containing 20.0 mg/L $NiCl_2$; [c] LIWW+Cr^{3+}: LIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$; [d]SIWW: synthetic industrial estate wastewater; [f]SIWW+Cr^{3+}: SIWW containing 38.46 mg/L $Cr(NO_3)_3.9H_2O$; [e]SIWW+ Ni^{2+}: SIWW containing 20.0 mg/L $NiCl_2$.

0.0020 kg Ni^{2+}/m^3.d). TN removal efficiency of26.7 ± 7.0 and 26.2 ± 9.3% were observed with SIWW and SIWW+Ni^{2+}, respectively but Cr^{3+} had greater effect than Ni^{2+} to reduce TN removal efficiency. TN removal efficiency with SIWW+ Cr^{3+} (Cr^{3+} loading of 0.0014 Kg Cr^{3+}/m^3.d) was about 30% lower than that with SIWW. Moreover, the system with SIWW+Cr^{3+} showed low effluent organic-N of 3.01±0.07 mg/L and high effluent NO_3^--N of 9.4±1.2 mg/L. For the treatment of LIWWs by SBR system at HRT of 1.5 days, the system showed quite similar TN removal efficiency pattern to that with SIWWs, but TN removal efficiency of the system with LIWW was about 24% higher than that with SIWW as shown in Table 4. The system with LIWW+Ni^{2+} at HRT of 1.5 days showed high TN removal efficiency of 30.1 ± 5.1%. However, NO_3^--N of both LIWWs and SIWWs were increased after being treated by SBR system, although their organic-N, NH_4^+-N and NO_2^--N were reduced. The effluents NO_3^--N of the system with SIWW+Cr^{3+} and LIWW+Cr^{3+} were 9.4 ± 1.2 and 10.0 ± 1.6 mg/L, respectively. The effluents organic-N and NH_4^+-N of the system with LIWWs and SIWWs were in the range of 3.0 to 4.4 and 4.4 to 5.4 mg/L, respectively.

Heavy metals (Cr^{3+} and Ni^{2+})

SBR system with SIWW+Ni^{2+} and SIWW+Cr^{3+} at 1.5 days showed similar heavy metal removal efficiency of over 90% (Table 5). The bio-sludge showed higher Cr^{3+} adsorption yield (36.00 ± 9.80 mg/g) than Ni^{2+} adsorption yield (31.59 ± 9.67 mg/g). Cr^{3+} and Ni^{2+} removal efficiencies with LIWW were 53.5 ± 25.1 and 80.7±17.9%, respectively. The 3.0 mg/L supplemented-Ni^{2+} and 3.0 mg/L supplemented-Cr^{3+} in LIWWs did not show any significant effect on Ni^{2+} and Cr^{3+} removal efficiencies of the bio-sludge. The Ni^{2+} and Cr^{3+} adsorption yields with LIWW+Ni^{2+} and LIWW+Cr^{3+} were 20.49 ± 7.20 mg/g and 25.20 ± 8.38 mg/g, respectively.

SS and TDS

The effluents SS of SBR system with SIWW and LIWW were increased by adding heavy metals (Cr^{3+} and Ni^{2+}) as shown in Table 3. The organic contents of effluents SS and TDS with SIWWs were about 50 to 60%, while they were only about 30% with LIWWs. The effluents SS and TDS with LIWWs were quite over 70 and 600 mg/L, respectively, while they were about 12 to 42 and 142 to 153 mg/L, respectively with SIWWs.

Bio-sludge performances

Cr^{3+} and Ni^{2+} could increase bio-sludge age of SBR system. The bio-sludge age of the system with SIWW increased from 7 ± 2 days to 14 ± 3 and 12 ± 3 days by adding 3.0 mg/L Ni^{2+} and 3.0 mg/L Cr^{3+}, respectively (Table 6). Moreover, SVI of the system with SIWW was increased by adding $Ni^{2+}$and Cr^{3+}. SVI of the system with SIWW was 82 ± 12 ml/g and increased to 121 ± 19 ml/g and 141 ± 22 ml/g after adding $Ni^{2+}$and Cr^{3+}, respectively. MLVSS/MLSS of the system with SIWWs were quite stable of 0.8. For treatment of LIWWs, a bio-sludge age with LIWW was 8 ± 2 days and increased to 15 ± 4 and 13 ± 3 days with added Ni^{2+} and Cr^{3+}, respectively. Also, SVI of the system with LIWWs at HRT of 1.5 days were 135 ± 19 ml/g, but increased to 142 ± 12 and 153 ± 19 ml/g with adding Ni^{2+} and Cr^3, respectively. In addition, the organic content of the bio-sludge with SIWWs was about 80 to 82%, while it was only about 65 to 67% with LIWWs.

DISCUSSION

LIWW showed high inorganic matter content in both SS and TDS of about 70% resulting from the high heavy metal contents of over 6.0 mg/L (Table 1). LIWW contained not only Ni^{2+} and Cr^{3+}, but also other heavy metals such as Pb^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, etc, of 6.29 ± 0.05 mg/L (Table 1). The biological treatment process as SBR system was applied for treatment LIWW, because it contained both inorganic and organic matters of 222 ± 12 mg/L BOD_5. The results show that SBR system could be used to treat LIWWs, but the operation condition must be considered, especially the HRT. At the HRTs of 1.0 to 2.0 days, the system showed quite low BOD_5 and COD removal efficiencies of only 43 to 48 and 55 to 59% because LIWWs might contain some toxic substances (Acikel and Alpa, 2009; David and Bohumil, 1998) and heavy metals that could suppress the growth and activity of bio-sludge (Chen and Gu, 2005; Arican and Yetis, 2003; Sirianuntapiboon and Ungkaprasatcha, 2007; Ong et al., 2005; Gikas and Romanos, 2006; Lee et al., 1997).

To confirm the above suggestion, another experiment on the treatment of LIWW at various HRT of 1.0, 1.5 and 2.0 days was conducted. The results show the highest BOD_5 and COD removal efficiencies of 48 ± 6 and 59 ± 8%, respectively, at HRT of 1.5 days. Moreover, HRT did not strongly affect TN removal efficiency. This confirmed that the SBR system at the optimal HRT of 1.5 days could be applied for the treatment of LIWW, and the toxic substances in LIWW, especially, Cr^{3+} or Ni^{2+} could suppress the growth and activity of heterotrophic bacteria, but they did not affect either nitrifying or denitrifying bacteria similar to the suggestion by previous reports (Sirianuntapiboon and Boonchupleing, 2009; Ong et al., 2005; Gikas and Romanos, 2006; Malik, 2004; Stasinakis et al., 2003; Awasthi and Rai, 2005; Wang and Chen, 2006). The system also showed the highest Ni^{2+} and Cr^{3+} removal efficiencies of 53.5 ± 25.1 and 80.7 ± 17.9% at HRT of 1.5 days (Table 5). This could explain that the heavy metal adsorption abilities of bio-sludge were dependent on the bio-sludge age (Metcalf and Eddy, 2004; Sirianuntapiboon and Boonchupleing, 2009; Sirianuntapiboon and Ungkaprasatcha, 2007; Al-Qodah, 2006). Moreover, the system showed higher Cr^{3+} removal efficiency than Ni^{2+} removal efficiency. This suggests that Cr^{3+} (molecular weight of 51.9962, atomic number of 24) has a smaller molecular size than Ni^{2+} (molecular weight of 58.6934, atomic number of 28) (Scerri, 2007), which makes Cr^{3+} easier to adsorb into the bio-sludge than Ni^{2+}. This could also confirm why Cr^{3+} adsorption ability of the bio-sludge with SIWW+Cr^{3+} (36.00±9.80 mg/g) was higher than SIWW+Ni^{2+} (31.59±9.67 mg/g).

However, Cr^{3+} and Ni^{2+} concentrations of LIWW were very low (0.13 ± 0.02 and 0.30 ± 0.03 mg/L). To verify this statement, the experiments on the treatment of LIWWs and SIWWs containing high Cr^{3+} and Ni^{2+} were conducted. The results show that 3 mg/L of Cr^{3+} and Ni^{2+} reduced BOD_5 and COD removal efficiencies. BOD_5 and COD removal efficiencies of the system with SIWWs were higher than that with LIWWs because LIWWs contained not only Cr^{3+} and Ni^{2+} but also other heavy metals, such as Zn^{2+}, Mn^{2+}, Fe^{2+}, Pb^{2+}, Cu^{2+}, etc suggested by previous reports (Chen and Gu, 2005; Arican and Yetis, 2003; Sirianuntapiboon and Hongsrisuwan, 2007; Ong et al., 2005; Gikas and Romanos, 2006; Lee et al., 1997; Al-Qodah, 2006; Acikel and Alpa, 2009). Moreover, 3 mg/L Ni^{2+} did not suppress TN removal efficiency, while TN removal efficiency of the system was reduced by 25% with 3 mg/L Cr^{3+} (Table 4). This might imply that Cr^{3+} and Ni^{2+} suppressed the growth and activity of heterotrophic bacteria (Sirianuntapiboon and Boonchupleing, 2009; Stasinakis et al., 2003; Al-Qodah, 2006; Ozer and Ozer, 2003). Ni^{2+} at 3.0 mg/L did not suppress the growths and activities of nitrifying and denitrifying bacteria. In contrast, Cr^{3+} at low concentration of 0.13±0.02 mg/L did not affect to the growths and activities of nitrifying and denitrifying bacteria. However, at 3.0 mg/L, Cr^{3+} suppressed the growth and activity of denitrifying bacteria, but it did not affect the growth and activity of nitrifying bacteria. This condition was similar to other previous works on the effect of Pb^{2+} and Ni^{2+} on the efficiency of SBR system. Pb^{2+} and Ni^{2+} concentrations of 5 mg/L could suppress the growths and activities of nitrifying and denitrifying bacteria (Sirianuntapiboon and Boonchupleing, 2009; Awasthi and Rai, 2005; Ferraz et al., 2004).

Furthermore, to observe the toxicities of the other toxic substances and heavy metals (Zn^{2+}, Mn^{2+}, Fe^{2+}, Pb^{2+}, Cu^{2+}, etc), LIWW containing 3 mg/L of heavy metals (Cr^{3+} or Ni^{2+}) were tested. The results showed that the maximum Cr^{3+} or Ni^{2+} adsorption yields of bio-sludge with SIWWs were higher than that with LIWWs. This could explain why some adsorption sides on the bio-sludge were filled up with others heavy metals and inorganic matters instead of Cr^{3+} and Ni^{2+} (Metcalf and Eddy, 2004; Sirianuntapiboon and Boonchupleing, 2009; Bansode et al., 2003; Sirianuntapiboon and Hongsrisuwan, 2007; Amini et al., 2009; Ansari and Malik, 2007). In addition, the inorganic contents of bio-sludge from the systems with LIWWs were higher than that with SIWWs. This might be the advantage of the system with LIWWs that bio-sludge could adsorb inorganic substances from the wastewater as suggested by previous paper (Bansode et al., 2003; Carl et al., 1982; Fahim et al., 2006; Chen et al., 2000; Chen and Gu, 2005; David and Bohumil, 1998; Arican and Yetis, 2003; Cheng et al., 1975; Ayten, 2007; Gabra et al., 2008). Many reports suggested that the heavy metals and inorganic matters adsorption abilities depended on the bio-sludge age (Metcalf and Eddy, 2004; Sirianuntapiboon and Boonchupleing, 2009; Sirianuntapiboon and Hongsrisuwan, 2007; Sirianuntapiboon and Ungkaprasatcha, 2007). The optimal bio-sludge age should be over 10 days. According to the long bio-sludge age, both nitrifying and denitrifying bacteria were dominated (Metcalf and Eddy, 2004; Sirianuntapiboon and Boonchupleing, 2009; Chen and Gu, 2005; David and Bohumil, 1998; Sirianuntapiboon and Hongsrisuwan, 2007; Sirianuntapiboon and Ungkaprasatcha, 2007; Cheng et al., 1975). This confirms that TN and heavy metals removal efficiencies increased with the increase of bio-sludge age. It also summarizes that nitrifying and denitrifying bacteria were the major groups that showed heavy metals adsorption abilities (Metcalf and Eddy, 2004; Sirianuntapiboon and Boonchupleing, 2009; Chen and Gu, 2005; David and Bohumil, 1998; Sirianuntapiboon and Hongsrisuwan, 2007; Cheng et al., 1975; Amini et al., 2009).

For application, SBR system at HRT of 1.5 days could be used for the treatment of LIWW containing Cr^{3+}or $Ni^{2+}$of up to 3.0 mg/L with high removal efficiencies even the growth and activity of heterotrophic bacteria was suppressed. However, the disadvantage of the system is the high effluents SS and TDS of about 80 and 650 mg/L, respectively and the inorganic content of effluents SS and TDS was high at about 70 to 80% (Table 3). Hence, the tertiary treatment process should be applied to reduce both effluents SS and TDS (Metcalf and Eddy, 2004).

Conclusion

The SBR system at HRT of 1.5 days could be applied for the treatment of LIWW with high BOD_5, COD and TN removal efficiencies of 48 ± 6, 59 ± 8 and 31.9 ± 7.6%, respectively. Both Cr^{3+} and Ni^{2+} in LIWW could suppress the growth and activity of heterotrophic bacteria, while they did not affect both the nitrifying and denitrifying bacteria. Moreover, the growths and activities of both nitrifying and denitrifying bacteria would not be repressed even when the concentration of Ni^{2+} was 3.0 mg/L, but the denitrifying bacteria was affected by 3.0 mg/L of Cr^{3+}. Bio-sludge of the system with SIWWs showed high Cr^{3+}

and Ni^{2+} adsorption abilities of 36.00 ± 9.80 and 31.59 ± 9.67 mg/g, respectively. However, the Cr^{3+} and Ni^{2+} adsorption abilities in LIWWs were reduced to 25.20 ± 8.38 and 20.49 ± 7.20 mg/g, respectively. Since the LIWWs contained not only Cr^{3+} and Ni^{2+} but also others heavy metals and inorganic matters, some adsorption sides on the bio-sludge might be filled up with the others heavy metals and inorganic matters. The advantage of the SBR system is that the bio-sludge could adsorb both heavy metals and inorganic substances, which will result in a reduction of SS and TDS of the wastewater.

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Nomenclature

BOD_5: Biochemical oxygen demand
COD: Chemical oxygen demand
Cr^{3+}: Chromium ion
F/M: Food (BOD_5 loading)/ Microbe (total Bio-sludge)
HRT: Hydraulic retention time
LIWW: Ladkrabang industrial estate wastewater
MLSS: Mixed liquor suspended solids
MLVSS: Mixed liquor volatile suspended solids
NH_4^+-N: Ammonium nitrogen
Ni^{2+}: Nickel ion
NO_2^- -N: Nitrite nitrogen
NO_3^- -N: Nitrate nitrogen
Organic-N: Organic nitrogen
SBR: Sequencing batch reactor
SS: Suspended solids
SIWW: Synthetic industrial estate wastewater
SVI: Sludge volume index
TDS: Total dissolved solids
TN: Total nitrogen

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