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Treatability studies with granular activated carbon (GAC) and sequencing batch reactor (SBR) system for textile wastewater containing direct dyes

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ABSTRACT

The GAC-SBR efficiency was decreased with the increase of dyestuff concentration or the decrease of bio-sludge concentration. The system showed the highest removal efficiency with synthetic textile wastewater (STWW) containing 40 mg/L direct red 23 or direct blue 201 under MLSS of 3000 mg/L and hydraulic retention time (HRT) of 7.5 days. But, the effluent NO_3^- was higher than that of the influent. Direct red 23 was more effective than direct blue 201 to repress the GAC-SBR system efficiency. The dyes removal efficiency of the system with STWW containing direct red 23 was reduced by 30% with the increase of direct red 23 from 40 mg/L to 160 mg/L. The system with raw textile wastewater (TWW) showed quite low BOD_5 TKN and dye removal efficiencies of only 64.7 ± 4.9% and 50.2 ± 6.9%, respectively. But its' efficiencies could be increased by adding carbon sources (BOD_5). The dye removal efficiency with TWW was increased by 30% and 20% by adding glucose (TWW + glucose) or Thai rice noodle wastewater (TWW + TRNWW), respectively. SRT of the systems were 28 ± 1 days and 31 ± 2 days with TWW + glucose and TWW + TRNWW, respectively.

1. Introduction

Textile wastewater contains mainly coloring substances, which are toxic to the environment [1–3] and need to be removed. Chemical treatment processes such as adsorption, precipitation, coagulation and chemical oxidation are commonly used to remove dyestuffs from the textile wastewater [3–7]. Although these chemical treatment processes might be effective for color removal but they consume high energy and chemical agents. Chemical waste is also generated from these processes. However, color substances (dyestuffs) in the textile wastewater are a kind of refractory organic matter, and it can be biodegraded or utilized as carbon and energy sources of the microorganisms [8–11]. Many researchers were [12–16] interested in biological treatment processes due to low cost and absence of chemical waste production. They usually focused on the biological treatment of textile wastewater containing disperse dye because it is commonly used in the textile factory especially, cotton and silk [17–21]. Our previous work found that not only disperse dye but also vat and direct dyes could be degraded and adsorbed by bio-sludge of the wastewater treatment system [22–24]. However, direct dye is commonly used in the printing process of the textile industry. And most of the printing process-textile factories belong to the small factory group (home-made textile products) [25–29]. But, little research work on the application of biological process, especially SBR or GAC-SBR system for treatment of textile wastewater containing direct dyes has been reported. It was found that bio-sludge of the aerobic treatment plant could be used as the adsorbent for direct dyestuff [23]. And, the GAC-SBR system could be applied to treat textile wastewater containing direct dyestuff, but the efficiency quite low [23].

In this study, the GAC-SBR system is applied to treat both synthetic and raw textile wastewater containing direct dyes (direct blue 201 and direct red 23) under various concentrations of bio-sludge and dyestuffs to observe the highest removal efficiency. The use of Thai rice noodle wastewater (TRNWW) as carbon source for raw textile wastewater was tested.

2. Materials and methods

2.1. Dyes

Two types of direct dyes were selected for use in this study, viz., Direct Red 23 and Direct Blue 201 [30]. The properties of the direct dyes are described in Table 1.

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Nomenclature

BOD_5	biochemical oxygen demand
COD	chemical oxygen demand
F/M	food (BOD_5 loading)/microbe (total bio-sludge)
GAC	granular activated carbon
GAC-SBR	granular activated carbon-sequencing batch reactor
HRT	hydraulic retention time
MLSS	mixed liquor suspended solids
SBR	sequencing batch reactor
SRT	solid retention time
SS	suspended solids
STWW	synthetic textile wastewater
SVI	sludge volume index
TRNWW	Khanom-chin wastewater (Thai-rice noodle wastewater)
TWW	textile wastewater
TKN	total kjeldahl nitrogen

2.2. *Granular activated carbon (GAC)*

The GAC type CGC-11 from coconut charcoal (C. Gigan Co. Ltd., Thailand) with a mesh size of 8 mm × 10 mm, total surface area of 1050–1150 m^2/g and apparent density of 0.46–0.48 g/mL was used in the experiment.

2.3. *Wastewater samples*

Two types of wastewater as textile wastewater and khanum-chin (Thai rice noodle) wastewater were used in this study as followed:

2.3.1. *Khanom-chin wastewater (Thai-rice noodle wastewater: TRWW)*

TRWW was collected from the Khanom-chin (Thai-rice noodle) factory in Rajchaburi province, Thailand. The chemical property and composition of TRNWW was shown in Table 2.

2.3.2. *Textile wastewater*

Two types of textile wastewater were used in this study: (1) textile wastewater (TWW) from the textile factory and (2) synthetic textile wastewater (STWW). TWW was collected from the influent sump tank of the central wastewater treatment plant of a textile factory in Samutprakarn province, Thailand. The TWW sample was taken only once and stored in the refrigerator for using in this experiment. The chemical property of TWW is described in Table 2. TWW supplemented with 1.1 g/L glucose (final biochemical oxygen demand (BOD_5) concentration of 1500 ± 30 mg/L), was used as TWW + glucose according to our previously work [23]. TWW was added with TRNWW at the ratio of 10 mL/L (final BOD_5 concentration of 1500 ± 27 mg/L) was used as TWW + TRNWW. STWW was prepared based on the characteristics to TWW. The BOD_5 concentration of STWW was about 1000 ± 25 mg/L and the dyes concentrations (Direct Red 23 and Direct Blue 201) were 40 mg/L as shown in Table 2. The chemical compositions of STWW were shown in Table 2.

Table 2
Characteristics of STWW, TWW, TRNWW, TWW containing glucose and TWW containing TRNWW

STWW			
Compositions	mg/L	Characteristic	
		Parameter	Level
Glucose	1900	COD, mg/L	2000 ± 50
Urea	115	BOD_5, mg/L	1000 ± 25
$FeCl_2$	3.5	TKN, mg/L	40.0 ± 5.0
$NaHCO_3$	675	NH_4^+, mg/L	8.1 ± 0.5
KH_2PO_4	55	NO_2^-, mg/L	1.2 ± 0.2
$MgSO_4·7H_2O$	42.5	NO_3^-, mg/L	1.4 ± 0.1
Direct dye[e]	40	pH	7.9 ± 0.2

Characteristic	Types of wastewater			
	TWW[a]	TRNWW[b]	TWW + glucose[c]	TWW + TRNWW[d]
COD, mg/L	2.045 ± 75	11.000 ± 540	3.450 ± 80	4200 ± 100
BOD_5, mg/L	645 ± 25	7.850 ± 75	1.500 ± 30	1.500 ± 27
TKN, mg/L	26 ± 1	–	29 ± 2	28 ± 2
NH_4^+, mg/L	13.0 ± 0.5	–	18 ± 1	18 ± 1
NO_2^-, mg/L	–	0.13 ± 0.01	–	–
NO_3^-, mg/L	33.0 ± 1.2	–	41 ± 2	74 ± 3
pH	8.2 ± 0.3	6.0 ± 0.4	8.2 ± 0.4	8.0 ± 0.5

±S.D. of three replicates.

[a] Wastewater from textile factory in Samuthpakarn province, Thailand. The wastewater was contaminated with both direct red 23 and direct blue 201.

[b] Wastewater from Khanum-chin (Thai rice noodle) factory in Ratchaburi province, Thailand.

[c] TWW + glucose: TWW supplemented with 1.1 g/L of glucose.

[d] TWW + TRNWW: TWW supplemented with 10 mL/L of TRNWW.

[e] Two kinds of disperse dye (direct red 23 and direct blue 201) as shown in Table 1 were used in this experiment.

2.4. *Acclimatization of bio-sludge for GAC-SBR system*

Bio-sludge from the bio-sludge storage tank of central domestic treatment plant of Bangkok Municipal, Thailand (Sripaya sewage treatment plant) was used as the inoculum of GAC-SBR system. The bio-sludge was fed with STWW without direct dyes in the reactor and acclimatized for 1 week.

2.5. *GAC-SBR system*

Six 10-L reactors, made from acrylic plastic (5 mm thick) as shown in Fig. 1, were used in the experiments. The dimension of each reactor was 18cm-diameter and 40 cm-height, and the working volume was 7.5 L. Low speed gear motors (model P 630A-387, 100 V, 50/60 Hz, 1.7/1.3 A, Japan Servo Co. Ltd., Japan) were used for driving the paddle-shaped impellers. The speed of impellers was adjusted to 60 rpm for complete mixing. One set of air pump system, model EK-8000, 6.0 W (President Co. Ltd., Thailand) was used for supplying air to each set of 2 reactors (the system had enough oxygen as evidenced by the dissolved oxygen in the system of about 2–3 mg/L). The excess sludge was drawn during draw and idle period to control mixed liquor suspended solids (MLSS) of the system as mentioned in Table 3.

Table 1
Types and properties of direct dyes that used in the experiments

Scientific name	Trade name	Color index no.	Type	Color	Wavelength at maximum absorption (nm)
Direct red 23	Hirus direct sarle 4BS	29160	Diazo dye	Red	505
Direct blue 201	Hirus Blue BRL	–	Azo dye	Blue	568
–	Textile wastewater[a]	–	–	Red-violet	550

[a] Wastewater sample was collected from the influent sump tank of the central wastewater treatment plant of a textile factory in Samutprakarn province, Thailand.

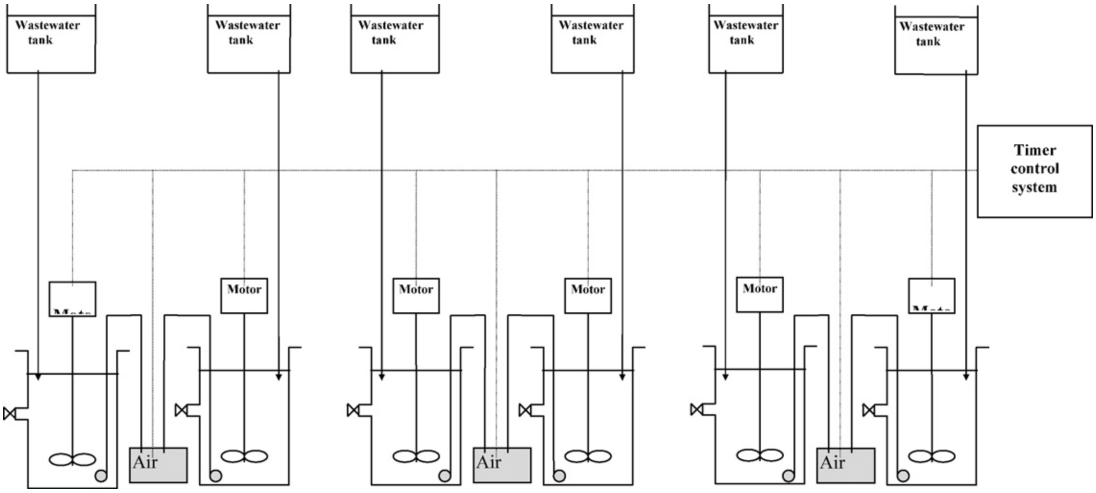

Fig. 1. Flow diagram of SBR treatment system. The physical operation controlling were 60 rpm of impeller speed, fully aeration with air-pump system model EK-8000, 6.0 W (one set of air pump was supplied for 2 sets of reactor the working volume of the reactor was 75% of total volume (7.5 L). The chemical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

2.6. *Operation of GAC-SBR systems*

A 1.4 L acclimatized sludge (10 g/L of SS) and 7500 mg GAC were inoculated in each reactor, and the TWW or STWW was added (final volume of 7.5 L) within 1 h. During feeding of the wastewater, the system had to be fully aerated and the aeration continued for 19 h. Aeration was then shut down for 3 h. After the sludge was fully settled, the supernatant was removed within 0.5 h and the system kept under idle conditions for 0.5 h (totally 3 h for anoxic step). Then, the raw wastewater was filled into the reactor to the final volume of 7.5 L and the above operation was repeated. The operation parameters of the GAC-SBR system with TWW and STWW are described in Table 3. In the excess bio-sludge discharging step, the mixture of bio-sludge waste was passed through the screener to collect the lost-GAC. The experiments were carried out for 12 months during January–December 2005.

2.7. *Chemical analysis*

Chemical oxygen demand (COD), biological oxygen demand (BOD_5), total kjeldahl nitrogen (TKN), and pH of influent and effluent and mixed liquor suspended solids (MLSS), sludge settled volume tested at 30 min (SV30) and sludge volume index (SVI) of the GAC-SBR system were determined using standard methods for the examination of water and wastewater [31]. The color intensity of STWW and TWW was determined as the absorbance at the optimum wavelength as shown in Table 1 after centrifugation at 6000 × *g* for 10 min. The SRT (solid retention time/sludge age) was determined as the ratio of total MLSS of the system to the amount of excess sludge wasted in a day.

2.8. *Statistical analysis method*

Each experiment was repeated at least 3 times. All the data were subjected to two-way analysis of variance (ANOVA) using SAS Windows Version 6.12 [32]. Statistical significance was tested using the least significant difference (LSD) at the $p < 0.05$ level and the results are shown as the mean ± S.D.

3. Results

3.1. *Effect of MLSS on the efficiency of GAC-SBR system*

The organic and dye removal efficiencies of GAC-SBR system with STWW were increased with the increase of MLSS or decrease of F/M ratio as shown in Table 4. GAC-SBR system with STWW containing 40 mg/L direct blue 201 showed high COD, BOD_5, TKN and dye removal efficiencies of 97.0 ± 2.3%, 98.6 ± 1.2%, 93.6 ± 2.2% and 95.0 ± 0.1%, respectively under MLSS of 3000 mg/L and HRT of 7.5 days as shown in Tables 4 and 5. The system also showed high COD, BOD_5, TKN and dye removal efficiencies of 94.8 ± 2.5%, 98.1 ± 1.6%, 96.8 ± 1.5% and 92.5 ± 1.0%, respectively with STWW containing direct red 23 under same operational condition with STWW containing direct blue 201. TKN and NH_4^+ concentrations

Table 3
The operating parameters of GAC-SBR system with STWW, TWW, TWW + glucose and TWW + TRNWW under various MLSS of 1000, 1500, 2000, 2500 and 3000 mg/L

Parameters	Types of wastewater was tested in GAC-SBR system							
	STWW					TWW	TWW + glucose[a]	TWW + TRNWW[b]
MLSS, mg/L	1000	1500	2000	2500	3000	3000	3000	3000
HRT, days	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Flow rate, mL/d	1000	1000	1000	1000	1000	1000	1000	1000
Hydraulic loading, m^3/m^3 d	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13
F/M ratio	0.83	0.55	0.41	0.33	0.27	0.22	0.5	0.5
BOD_5 loading, g/d	1.10	1.10	1.10	1.10	1.10	1.17	3.0	–[c]
Volumetric BOD_5 loading, kg/m^3 d	0.11	0.11	0.11	0.11	0.11	0.23	0.40	–[c]
Dye loading, g/d	0.04	0.04	0.04	0.04	0.04	–[c]	–[c]	–[c]
Volumetric dye loading, kg/m^3 d	0.004	0.004	0.004	0.004	0.004	–[c]	–[c]	–[c]

[a] TWW + glucose: TWW supplemented with 1.1 g/L of glucose.

[b] TWW + TRNWW: TWW supplemented with 10 mL/L of TRNWW.

[c] Cannot be calculated.

Table 4
Effluent qualities and removal efficiencies of GAC-SBR system with STWW[a] under variation of MLSS

Types of direct dye	MLSS of the system (mg/L)	F/M ratio	Chemical properties						Effluent SS
			Color		COD		BOD_5		
			Effluent (mg/L)	%Removal	Effluent (mg/L)	%Removal	Effluent (mg/L)	%Removal	
Direct red 23	1000	0.83	5.8 ± 0.5	85.5 ± 1.2	161 ± 19	92.0 ± 3.0	19 ± 2	97.1 ± 1.7	78 ± 18
	1500	0.55	5.5 ± 0.6	86.3 ± 1.3	122 ± 19	94.0 ± 3.0	20 ± 2	97.0 ± 2.5	54 ± 17
	2000	0.41	4.3 ± 0.4	89.3 ± 1.0	122 ± 14	94.5 ± 2.4	13 ± 1	98.0 ± 1.4	56 ± 13
	2500	0.33	4.0 ± 0.4	90.0 ± 1.0	120 ± 15	94.5 ± 3.0	12 ± 3	98.8 ± 1.2	64 ± 4
	3000	0.27	3..0 ± 0.3	92.5 ± 1.0	120 ± 11	94.8 ± 2.5	12 ± 1	98.1 ± 1.6	31 ± 8
Direct blue 201	1000	0.83	4.4 ± 0.3	89.0 ± 1.0	73 ± 10	96.4 ± 2.2	26 ± 3	97.3 ± 1.4	24 ± 9
	1500	0.55	3.5 ± 0.3	91.3 ± 1.0	66 ± 9	96.7 ± 2.8	19 ± 1	98.1 ± 1.2	19 ± 6
	2000	0.41	3.0 ± 0.3	92.5 ± 1.0	66 ± 5	96.6 ± 2.3	15 ± 2	98.5 ± 1.2	24 ± 7
	2500	0.33	2.5 ± 0.3	93.8 ± 1.0	65 ± 9	96.6 ± 2.6	16 ± 2	97.4 ± 1.5	21 ± 9
	3000	0.27	2.0 ± 0.3	95.0 ± 1.0	61 ± 7	97.0 ± 2.3	12 ± 1	98.6 ± 1.2	29 ± 6

[a] STWW containing 40 mg/L direct dyes.

of the wastewater were decreased while their NO_3^- concentration was increased after treated by GAC-SBR system as shown in Table 5. However, the effluent NO_3^- was decreased with the increase of MLSS. Then, TN removal efficiency was increased with the increase of MLSS. SVI of the system with both types of STWW was between 60 mL/g and 90 mL/g under MLSS between 1000 mL/g and 3000 mg/L as shown in Table 6. Also, sludge age or SRT was increased with the increase of MLSS. SRT of the system with both types of STWW under MLSS of 3000 mg/L was about 22 days as shown in Table 6.

3.2. *Effect of type and concentration of direct dyes on the efficiency of GAC-SBR system*

The COD and BOD_5 removal efficiencies were not effected by the dyes concentration or loading, even they were increased up to 160 mg/L or 0.016 kg/m^3 d, respectively. But, they effected to the dye removal yield as shown in Table 7. The COD, BOD_5 and TKN removal efficiencies were about 90–91%, 94–97% and 88–91%, respectively under dye concentration or loading of up to 160 mg/L or 0.016 kg/m^3 d, respectively. And direct red 23 was more effective than direct blue 201 to repress the dye and nitrogen removal efficiencies. The dye removal efficiency with STWW containing direct red 23 was reduced by 30% with the increase of dye concentration from 40 mg/L to 160 mg/L as shown in Table 7. And the effluent NO_3^- was higher than 40 mg/L with the dye concentration of higher than 100 mg/L as shown in Table 8. SVI and SRT were increased with the increase of dye concentration or loading as shown in Table 6. But, SVI of the GAC-SBR system was still less than 85 mL/g even the dyes concentration or loading was up to 160 mg/L or 0.016 kg/m^3 d, respectively.

3.3. *Effect of organic matter (BOD_5) on the efficiency of GAC-SBR system*

The experiments were carried out in GAC-SBR system with TWW containing glucose or TRWW to determine the system efficiency and performance as follows:

3.3.1. *Effect of glucose supplementation on the efficiency of GAC-SBR system*

The experiment was carried out in GAC-SBR system with TWW supplementing with and without 1.1 g/L glucose. The COD, BOD_5, TKN and dye removal efficiencies of the GAC-SBR system with raw TWW (BOD_5 of about 645 ± 5 mg/L) were only 84.7 ± 4.7%, 64.7 ± 4.9% 40.2 ± 4.2 and 50.2 ± 6.9%, respectively as shown in Tables 9 and 10. But the COD, BOD_5, TKN and dye removal efficiencies of GAC-SBR system were increased up to 84.8 ± 1.9%, 88.8 ± 2.4%, 87.5 ± 5.2 and 82.3 ± 5.7%, respectively when the TWW was supplemented with 1.1 g/L glucose: TWW + glucose (final BOD_5 of 1500 mg/L) as shown in Tables 9 and 10. TN removal efficiency of the system was only 50%. The NO_2^- and NO_3^- concentrations of TWW + glucose were increased after treated as shown in Table 10. The effluent SS of the system with TWW and TWW + glucose were quite high (50–70 mg/L). SRT of the system with TWW was 97 ± 3 days, while it was only 28 ± 1 with TWW + glucose. SVI of the system with TWW and TWW + glucose were lower than 50 mL/g (Table 6).

Table 5
Effluent qualities and nitrogen compounds removal efficiencies of GAC-SBR system with STWW[a] under variation of MLSS

Types of direct dye	MLSS of the system (mg/L)	TKN		NH_4^+ (mg/L)		NO_2^- (mg/L)		NO_3^- (mg/L)		TN (mg/L)		% TN removal
		Effluent (mg/L)	%Removal	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
Direct red 23	1000	3.6 ± 0.2	91.2 ± 5.2	6.3 ± 1.0	1.6 ± 0.2	9.9 ± 0.3	2.5 ± 1.1	1.6 ± 0.2	12.7 ± 1.7	49.8 ± 3.5	18.8 ± 1.6	53.0 ± 1.2
	1500	2.5 ± 0.3	93.2 ± 2.5	6.3 ± 1.0	1.6 ± 0.2	9.9 ± 0.3	2.1 ± 0.6	1.6 ± 0.2	13.7 ± 1.8	49.8 ± 3.2	18.2 ± 1.2	54.5 ± 1.4
	2000	2.4 ± 0.2	94.3 ± 3.1	6.3 ± 1.0	0.9 ± 0.3	9.9 ± 0.3	2.1 ± 0.4	1.6 ± 0.2	7.1 ± 0.9	49.8 ± 2.9	5.9 ± 0.2	85.2 ± 2.6
	2500	1.7 ± 0.1	95.4 ± 2.9	6.3 ± 1.0	0.8 ± 0.3	9.9 ± 0.3	2.4 ± 0.4	1.6 ± 0.2	7.3 ± 0.7	49.8 ± 3.1	11.4 ± 1.9	71.7 ± 3.8
	3000	1.2 ± 0.6	96.8 ± 1.5	6.3 ± 1.0	0.8 ± 0.3	9.9 ± 0.3	2.6 ± 0.3	1.6 ± 0.2	7.2 ± 1.3	49.8 ± 2.9	11.7 ± 1.1	71.8 ± 7.2
Direct blue 201	1000	2.6 ± 0.9	93.0 ± 2.6	9.9 ± 2.2	3.6 ± 2.6	13.3 ± 1.5	3.5 ± 0.8	1.1 ± 0.1	21.7 ± 1.4	52.2 ± 3.4	27.8 ± 1.1	46.6 ± 2.1
	1500	3.2 ± 0.8	91.6 ± 2.0	9.9 ± 2.2	2.5 ± 1.2	13.3 ± 1.5	3.7 ± 0.5	1.1 ± 0.1	25.4 ± 1.7	52.2 ± 3.5	32.2 ± 1.2	38.2 ± 1.9
	2000	2.1 ± 0.8	94.5 ± 2.4	9.9 ± 2.2	2.4 ± 1.6	13.3 ± 1.5	3.7 ± 0.8	1.1 ± 0.1	20.4 ± 2.0	52.2 ± 3.1	26.2 ± 1.6	49.8 ± 4.2
	2500	2.4 ± 0.8	93.5 ± 2.3	9.9 ± 2.2	1.79 ± 0.6	13.3 ± 1.5	3.5 ± 0.7	1.1 ± 0.1	15.5 ± 1.8	52.2 ± 3.2	21.4 ± 2.5	59.0 ± 6.2
	3000	2.4 ± 0.8	93.6 ± 2.2	9.9 ± 2.2	2.1 ± 0.5	13.3 ± 1.5	3.8 ± 1.0	1.1 ± 0.1	9.9 ± 0.4	52.2 ± 3.1	16.1 ± 2.0	69.3 ± 5.0

[a] STWW containing 40 mg/L direct dyes.

Table 6
The bio-sludge qualities of GAC-SBR system with STWW, TWW, TWW + glucoses and TWW + TRNWW

Types of wastewater	Types of dye	Initial dye concentration (mg/L)	MLSS (mg/L)	Excess sludge (mg/d)	SRT (d)	SVI (mL/g)
STWW	Direct red 23	40	1000	2.543 ± 218	4 ± 0	59 ± 18
			1500	1.290 ± 136	10 ± 1	71 ± 19
			2000	1.673 ± 126	10 ± 1	89 ± 20
			2500	1.266 ± 131	16 ± 1	85 ± 10
			3000	1.102 ± 159	22 ± 2	76 ± 3
	Direct blue 201	40	1000	1.603 ± 123	6 ± 1	56 ± 5
			1500	1.002 ± 86	13 ± 1	54 ± 3
			2000	1.256 ± 110	13 ± 1	76 ± 5
			2500	908 ± 68	22 ± 1	86 ± 4
			3000	1.050 ± 98	22 ± 1	81 ± 4
STWW	Direct red 23	40	3000	1.393 ± 156	18 ± 1	31 ± 3
		80		1.352 ± 110	18 ± 1	42 ± 5
		100		1.278 ± 108	19 ± 1	47 ± 6
		120		1.279 ± 125	19 ± 1	62 ± 8
		140		811 ± 74	29 ± 1	66 ± 4
		160		584 ± 62	40 ± 2	70 ± 2
	Direct blue 201	40	3000	1219 ± 105	20 ± 1	56 ± 3
		80		1.063 ± 91	23 ± 1	72 ± 4
		100		1.017 ± 105	24 ± 1	75 ± 4
		120		1.125 ± 114	22 ± 1	80 ± 5
		140		1.058 ± 105	23 ± 1	80 ± 6
		160		369 ± 29	62 ± 3	80 ± 6
TWW	Mixed colorants	N/A[a]	3000	229 ± 33	97 ± 3	28 ± 3
TWW + glucoses	Mixed colorants	N/A[a]	3000	848 ± 48	28 ± 1	33 ± 2
TWW + TRNWW	Mixed colorants	N/A[a]	3000	725 ± 60	31 ± 2	27 ± 2

[a] Cannot be calculated.

3.3.2. *Effect of TRWW supplementation on the efficiency of GAC-SBR system*

The result on the effect of supplemented-TRNWW on the efficiency of GAC-SBR system was shown in Tables 6, 9 and 10. The dye removal yield was 20% increased by adding TRNWW at the ratio of 10 mL/L of TWW. For the determination of nitrogen contents of TWW + TRNWW, treated by GAC-SBR system, both effluent TKN and NH_4^+ were decreased rapidly while effluent NO_2^- was in the high level (46.5 ± 3.2 mg/L) as shown in Table 9. The effluent SS of the system with TWW + TRNWW was also high (57 ± 5 mg/L). SRT and SVI of the system with TWW + TRNWW were 62 ± 2 days and 23 ± 1 mL/g, respectively as shown in Table 6.

4. Discussions

Our previous study [22,23] found that both SBR and GAC-SBR systems could be applied for treatment textile wastewater containing direct dyes, but GAC-SBR give higher dye removal efficiency than SBR system, because, the GAC-SBR system was operated under high total bio-sludge concentration resulting from the bio-film mass [8,17,23,24]. The SRT of the GAC-SBR system was thus longer than that of the conventional SBR system resulting in an increase dyes adsorption capacity of the bio-sludge [22–24,33–35]. However, the system showed quite low dye removal efficiency of only 57% [23]. The dye removal mechanism consists of dye adsorption and degradation [22–24,36]. Then, MLSS and bio-sludge age (SRT) might effect to both organic and dye removal efficiencies [24,34]. It was confirmed that the GAC-SBR system showed the highest dye removal efficiency (over 95%) with STWW containing 40 mg/L direct dyes under MLSS of 3000 mg/L and SRT of about 22 days. And it could explain that the bio-sludge of the system under high MLSS operation, was in the late log phase or early stationary phase state, showed high dye adsorption and degradation capacities [22,24,34,36]. However it was recommended that the further research regarding the determination

Table 7
Effluent qualities and removal efficiencies of GAC-SBR system with STWW containing various dyes concentrations of 40 mg/L, 80 mg/L, 120 mg/L and 140 mg/L

Types of direct dye	Initial dye concentration (mg/L)	Volumetric dye loading (kg/m³ d)	Chemical properties						Effluent SS
			Dye		COD		BOD_5		
			Effluent (mg/L)	%Removal	Effluent (mg/L)	%Removal	Effluent (mg/L)	%Removal	
Direct red 23	40	0.004	4.4 ± 0.4	90.3 ± 0.8	131 ± 18	93.2 ± 0.8	31 ± 2	96.9 ± 1.2	29 ± 3
	80	0.008	17.2 ± 4.3	76.7 ± 1.7	149 ± 28	92.9 ± 1.2	38 ± 4	96.5 ± 1.6	27 ± 4
	100	0.010	30.1 ± 3.8	70.2 ± 3.9	154 ± 37	92.8 ± 1.6	44 ± 2	96.3 ± 1.9	37 ± 7
	120	0.012	40.8 ± 4.6	66.2 ± 3.9	175 ± 59	91.9 ± 2.8	46 ± 2	96.4 ± 1.7	28 ± 2
	140	0.014	47.1 ± 5.0	66.5 ± 3.5	192 ± 60	91.6 ± 2.4	46 ± 2	96.5 ± 1.6	18 ± 3
	160	0.016	56.9 ± 10.1	64.4 ± 6.4	227 ± 64	90.2 ± 2.5	48 ± 2	96.5 ± 1.6	47 ± 3
Direct blue 201	40	0.004	6.6 ± 0.7	92.0 ± 0.8	131 ± 32	94.4 ± 1.6	35 ± 4	96.8 ± 1.2	24 ± 2
	80	0.008	9.8 ± 1.8	87.9 ± 2.2	136 ± 79	93.7 ± 3.6	53 ± 3	95.3 ± 2.0	32 ± 2
	100	0.010	12.8 ± 1.8	86.7 ± 1.6	165 ± 80	92.5 ± 3.4	74 ± 2	93.6 ± 1.6	27 ± 3
	120	0.012	14.8 ± 3.6	87.5 ± 2.9	182 ± 59	91.8 ± 2.5	77 ± 7	93.7 ± 2.9	26 ± 3
	140	0.014	19.8 ± 3.9	85.9 ± 2.7	184 ± 56	91.8 ± 2.3	55 ± 7	95.3 ± 2.2	33 ± 2
	160	0.016	27.9 ± 3.8	82.2 ± 2.9	225 ± 71	90.0 ± 3.2	77 ± 5	93.9 ± 2.4	36 ± 4

Table 8
Effluent nitrogen compounds and their removal efficiencies of GAC-SBR system with STWW containing various dyes concentrations of 40 mg/L, 80 mg/L, 120 mg/L and 140 mg/L

Types of direct dye	Initial dye (mg/L)	TKN(mg/L)		NH_4^+ (mg/L)		NO_2^- (mg/L)		NO_3^- (mg/L)		TN (mg/L)		% TN removal
		Effluent	%Removal	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
Direct red 23	40	7.4 ± 2.7	85.3 ± 7.2	8.7 ± 2.0	3.1 ± 2.8	6.7 ± 0.5	0.1 ± 0.0	2.0 ± 0.2	32.3 ± 2.0	53.0 ± 3.5	39.8 ± 1.2	24.9 ± 2.4
	80	4.8 ± 0.6	86.9 ± 6.5	9.1 ± 1.4	1.3 ± 0.5	7.5 ± 0.5	0.4 ± 0.0	1.9 ± 0.1	32.4 ± 2.0	53.6 ± 2.1	37.6 ± 2.3	29.8 ± 1.8
	100	8.0 ± 2.3	82.5 ± 6.1	9.6 ± 1.7	2.7 ± 1.3	7.7 ± 0.3	0.2 ± 0.0	2.0 ± 0.1	38.0 ± 3.4	52.8 ± 3.0	46.2 ± 2.1	12.5 ± 2.1
	120	7.2 ± 2.2	85.0 ± 7.6	8.9 ± 1.3	0.9 ± 0.3	8.2 ± 0.9	0.2 ± 0.0	2.5 ± 0.2	40.7 ± 6.0	54.6 ± 2.2	47.9 ± 2.1	13.0 ± 1.9
	140	5.6 ± 2.6	88.0 ± 6.7	8.9 ± 1.4	1.6 ± 0.6	7.8 ± 0.5	1.2 ± 0.1	2.1 ± 0.4	40.8 ± 6.3	55.5 ± 2.2	47.5 ± 2.0	14.4 ± 1.4
	160	5.2 ± 0.6	88.2 ± 1.6	9.2 ± 1.6	0.9 ± 0.3	10.6 ± 1.4	1.2 ± 0.2	1.8 ± 0.3	41.9 ± 2.6	57.8 ± 1.8	48.3 ± 2.4	16.4 ± 1.2
Direct blue 201	40	2.61 ± 0.6	94.5 ± 1.2	14.6 ± 2.2	0.7 ± 0.4	9.6 ± 1.1	0.8 ± 0.1	1.7 ± 0.1	7.9 ± 0.9	59.0 ± 1.7	11.3 ± 1.0	80.8 ± 2.4
	80	2.24 ± 0.0	95.3 ± 0.2	11.2 ± 1.1	0.9 ± 0.3	10.3 ± 0.5	0.9 ± 0.1	1.7 ± 0.3	10.4 ± 1.6	59.6 ± 2.4	12.8 ± 1.4	78.5 ± 2.0
	100	2.61 ± 0.6	94.6 ± 1.3	17.3 ± 1.9	1.3 ± 0.8	10.4 ± 0.4	0.8 ± 0.2	1.8 ± 0.2	8.1 ± 1.6	59.8 ± 2.2	11.5 ± 1.3	80.8 ± 1.8
	120	3.52 ± 0.3	91.3 ± 1.9	18.1 ± 1.2	1.2 ± 0.6	10.4 ± 0.4	0.7 ± 0.2	1.9 ± 0.2	6.2 ± 1.3	59.8 ± 2.3	10.4 ± 0.8	82.6 ± 1.9
	140	2.77 ± 0.9	92.8 ± 2.2	18.6 ± 3.3	1.8 ± 0.2	10.5 ± 0.3	0.7 ± 0.2	2.0 ± 0.2	6.6 ± 1.3	59.6 ± 2.1	10.1 ± 1.0	83.1 ± 1.6
	160	4.00 ± 0.9	91.25 ± 2.3	19.0 ± 3.2	1.57 ± 0.6	10.6 ± 0.5	0.81 ± 0.1	1.7 ± 0.1	6.1 ± 1.0	59.7 ± 1.9	11.0 ± 2.6	81.6 ± 1.7

of adsorbed dyes of bio-sludge should be conducted to further advance toward the understanding of the dye removal mechanism. The other advantages of the operation of GAC-SBR system under high MLSS were good bio-sludge quality and low effluent TKN and NH_4^+ [8,23–24]. SVI of the system under MLSS operation of 3000 mg/L was about 80 mL/g. And the effluent TKN and NH_4^+ were only 7–8 mg/L and 1–3 mg/L, respectively. It could explain that the long SRT bio-sludge showed high flocculation ability [8] and consisted of large number of nitrifying and denitrifying bacteria [8,17,20].

Under high dye concentration of 160 mg/L, The BOD_5 and COD removal efficiencies of the GAC-SBR system were still high (over 90%), but both dye and nitrogen removal efficiencies were effected by high dye concentration. The dye removal yield was reduced by 30% when the direct red 23 was increased from 40 mg/L to 160 mg/L. Also, direct red 23 was more effect than direct blue 201 to repress dye removal efficiency due to the dye structure. The direct red 23, a diazo dye, may be difficult to biodegrade whereas the direct blue201, being an azo dye, may be more amenable to biodegradation [17,18,24,25,32]. The effluent SS and SRT of the system was increased with the increase of dye concentration resulted by the effect of high dye concentration to kill bio-sludge [8,21,22,24].

From the above results, it could summarize that the dye concentration of up to 160 mg/L was not effected to BOD_5 and COD removal efficiencies, but it affected to the growth of bio-sludge (SRT of more than 22 days) [8,21,24]. However, the effluent NO_3^- of the system with direct red 23 was quite high (30–40 mg/L). This might be the toxic of direct red 23 on the denitrifying bacteria. It is therefore recommended that the further research regarding to effect of direct red 23 on the population of denitrifying bacteria should be conducted to further understanding of nitrogen removal mechanism. Also, the operating cycle of the system should be considered. According to the short operating period (4 h) of anoxic step, the number and activity of denitrifying bacteria might be repressed [8,37–39]. To decrease effluent NO_3^-, the period of anoxic step had to be extended resulted to increase number and activity of denitrifying bacteria [8,38].

For treatment of TWW, GAC-SBR systems showed quite low BOD_5, TKN and dye removal efficiencies of only 64.7 ± 4.9%, 40.2 ± 4.2% and 50.2 ± 6.9% resulted by low growth of bio-sludge (low excess sludge production of only 229 ± 33 mg/d) according to low organic concentration of 645 ± 25 mg/L. To increase the removal efficiencies, the external BOD_5 should be supplemented. The dye removal yield was increased by about 20–30% when the organic matter such as glucose or TRWW was supplemented to reach the final BOD_5 of 1500 mg/L. This was confirmed that both organic matter and direct dye could be rapidly removed with high efficiencies resulting by the growth of bio-sludge: growth association mechanism [8,24]. Both glucose and TRNWW could be use as the carbon source (BOD_5). However, glucose being a simple sugar is more suitable as a carbon source than TRNWW which contains variety of sugars and starchs which are probably more difficult to degrade [8].

Finally, it could suggest that the GAC-SBR system was suitable to apply for textile wastewater containing direct dye. The advantage of the using GAC in SBR system is that the GAC acts as the media for bio-film and the GAC will not adsorb the dyes on the surface [23]. Then, the GAC might be used for long time in SBR system without any regeneration and the GAC might be self bio-regenerated during operation by the attached bio-film [24,40,41]. The other advantage of GAC was to increase the MLSS of the system resulted to increase the number of nitrifying and denitrifying bacteria. But, the external carbon sources such as glucose, starch or wastewater containing high concentration of carbon source must be added to increase efficiency and performance of the system. Also, the operating period of anoxic step had to be extended resulting to stimulate activity of denitrifying bacteria.

Table 9
Effluent qualities and removal efficiencies of GAC-SBR system[a] with TWW, TWW + glucoses and TWW + TRNWW

Types of wastewater	Types of dye	Chemical properties						SS
		Dye (color)[b]		COD		BOD_5		
		Effluent OD_{550nm}	%Removal	Effluent (mg/L)	%Removal	Effluent (mg/L)	%Removal	
TWW	Mixed colorants	0.08 ± 0.01	50.2 ± 6.9	308 ± 85	84.7 ± 4.7	228 ± 19	64.7 ± 4.9	50 ± 4
TWW + glucoses[c]	Mixed colorants	0.03 ± 0.01	82.3 ± 5.7	271 ± 46	88.8 ± 2.4	236 ± 17	84.8 ± 1.9	69 ± 3
TWW + TRNWW[d]	Mixed colorants	0.05 ± 0.01	70.0 ± 2.3	211 ± 76	89.9 ± 5.3	222 ± 23	85.1 ± 3.0	57 ± 5

[a] GAC-SBR system under MLSS of 3000 mg/L.
[b] According to the mixed dyes in the TWW, they were detected as the optical density at 550 nm.
[c] TWW + glucose: TWW supplemented with 1.1 g/L of glucose.
[d] TWW + TRNWW: 1 L of TWW was supplemented with 10 mL of TRNWW.

Table 10

Effluent qualities and nitrogen compounds removal efficiencies of GAC-SBR[a] system with TWW, TWW + glucoses and TWW + TRNWW

Types of wastewater	Types of dye	Chemical properties									
		TKN		NH_4^+ (mg/L)		NO_2^- (mg/L)		NO_3^- (mg/L)		TN (mg/L)		
		Effluent	%Removal	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	%Removal
TWW	Mixed colorant	15.7 ± 1.3	40.2 ± 4.2	13.0 ± 1.0	3.8 ± 0.3	32.9 ± 3.2	38.2 ± 3.7	0.0 ± 0.0	0.2 ± 0.0	59.2 ± 4.2	57.7 ± 3.4	2.5 ± 0.5
TWW + glucoses[b]	Mixed colorant	3.6 ± 1.5	87.5 ± 5.2	18.1 ± 1.0	1.1 ± 0.7	40.6 ± 3.5	55.0 ± 4.3	0.0 ± 0.0	6.4 ± 0.3	63.3 ± 7.2	50.6 ± 4.7	20.1 ± 1.3
TWW + TRNWW[c]	Mixed colorant	6.3 ± 1.3	77.8 ± 4.1	17.7 ± 1.2	2.0 ± 0.9	73.8 ± 3.7	46.5 ± 3.2	0.0 ± 0.0	3.0 ± 0.6	102.0 ± 11.5	57.7 ± 6.1	42.4 ± 3.2

[a] GAC-SBR system under MLSS of 3000 mg/L.

[b] TWW + glucose: TWW supplemented with 1.1 g/L of glucose.

[c] TWW + TRNWW: One liter of TWW was supplemented with 10 mL of TRNWW.

5. Conclusion

GAC-SBR system could apply to treat textile wastewater containing direct dyes. The optimal operating conditions of the system were 3000 mg/L of MLSS, HRT of 7.5 days and 40 mg/L of direct dyes. The BOD_5 TKN and dye removal efficiencies of the system with STWW containing 40 mg/L of direct red 23 or direct blue 201 were around 98–99%, 94–97% and 94–99%, respectively. The system could also applied to treat textile wastewater containing direct dye of up to 160 mg/L without any effect to the COD and BOD_5 removal yields. But, it effected to dye removal efficiency and denitrifying bacteria resulted by the toxic of dye at the high concentration. The application of GAC-SBR to treat raw textile wastewater with high efficiency, the carbon source such as glucose or TRNWW have to be added resulting to increase influent BOD_5.

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