J. ENVIRONMENTAL SYSTEMS, Vol. 33(2) 121-131, 2011

EFFECT OF TERTIARY TREATMENT ON CHEMICALLY COMPLEX SECONDARY WASTEWATER*

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ABSTRACT

Biochemical characteristics of chemical secondary effluent in tertiary treatment were studied with a piloted system of biological contact aerators to meet national discharge limits. The results showed that biochemical characteristics of the secondary effluent had higher concentrations of residual COD and NH_3-N, as well as lower residual concentrations of BOD_5 and alkalinity. Residual COD in the effluent consisted mainly of three parts including the non-biodegradable COD presented by organic matter of toxicity, the soluble COD presented by BOD_5, and the particulate COD presented by SS. Under conditions of non-biodegradable COD concentration of 132.70 mg/L and less alkalinity, NH_3-N effluent concentrations were decreased from 30.44 mg/L to 14.79 mg/L, and a scientific basis of reference was provided for reforming the pulse flocculated clarifier system which can be a new dimension for wastewater treatment.

*This project was supported by a grant number 2009-13 from the Environmental Protection Bureau of Jilin Province and wastewater treatment plant of Jilin Chemical Industrial Corporation.

doi: 10.2190/ES.33.2.d
http://baywood.com

The wastewater treatment plant of Jilin Chemical Industrial Corporation is the largest plant in Asia for treating chemical wastewater; it adopts the anoxic/oxic (A/O) process in secondary treatment and the pulse-flocculated clarifier (PFC) process in tertiary treatment. The current loading of wastewater is 6000 m^3/h; the wastewater characteristics are very complicated, containing a great deal of non-biodegradable organic matter, such as benzene, pesticide, organic agrochemicals, petroleum processing wastes, complex aromatic substances, epoxy resin, dyestuffs, and intermediate pigments. The COD and NH_3-N concentration in effluent from the A/O process did not meet the national regulation effluent discharge limits because of serious insufficiencies in alkalinity and organic substances of non-biological degradation in the influent and the PFC used for treating secondary effluent from the A/O process. According to the results of previous research works, the removal efficiency of COD and NH_3-N was ineffective. In order to meet the national NH_3-N discharge standard, 15,000 tons of calcium oxide were added per year at an expense of 3 million Yuan (RMB).

With the operational parameters and influent fluctuations affecting A/O system performance [1-3], traditional operation of the PFC system often fails to have optimal results for solids, carbonaceous organic matter, and nutrient removal [4-6]. Moreover, stricter regulations for effluent, biological contact aerators (BCAs) and biological aerated filters (BAFs) have heightened the importance of modifying biological wastewater processes using a biochemical film process [7-12].

In the present study, in order to meet limits of national discharge and to provide the parameters for reforming the original PFC, a pilot bio-film test in BCAs was studied under various operational conditions for fluctuations of secondary effluent. The purpose was to investigate biochemical characteristics of residual and non-biodegradable COD and the effect of bio-film in the BCAs on organic matters and ammonia removal under conditions of reduced alkalinity, in order to offer an economical and practical environmental protection technology for a developing country. In the literature, no other report was found on the tertiary treatment for chemical secondary effluent with a bio-film in BCAs.

MATERIALS AND METHODS

Reactor Setup

A device on a pilot scale was designed according to the PFC characteristics, so that the PFC could be reformed effectively after success of the experiment. The testing process is shown in Figure 1. The influent wastewater was pumped to the bottom of a $\Phi 1.5$ m × 3.5 m cylinder, and wastewater with aerated air compatibly went up together. The depth of packing media is 1.5 m, the distance from the top of the media to the outlet of the device is 0.5 m, and to the bottom of cylinder is 1.5 m. The density of packing media is 14 kg/m^3 with a specific surface area of 1538.0 m^2/m^3. Diameter of the plastic wreath is 8.0 cm, and its distance between the spacer is 2.6 cm with fiber lengths of 6.0 ~ 7.0 cm. The rope-type of media is shown in Figure 2. A combined frame was affixed in the cylinder for supporting the fibers. Air was supplied to the reactor through four diffusers located at the height of 1.5 m of the reactor base; a valve connected to line of the air supply was used to initiate and cut off the air supply, and an airflow meter was used to control the sufficient aeration. A peristaltic pump, a valve and a water flow meter were used to control wastewater flux, and the dissolved oxygen and a pH probe were also used for continuous monitoring.

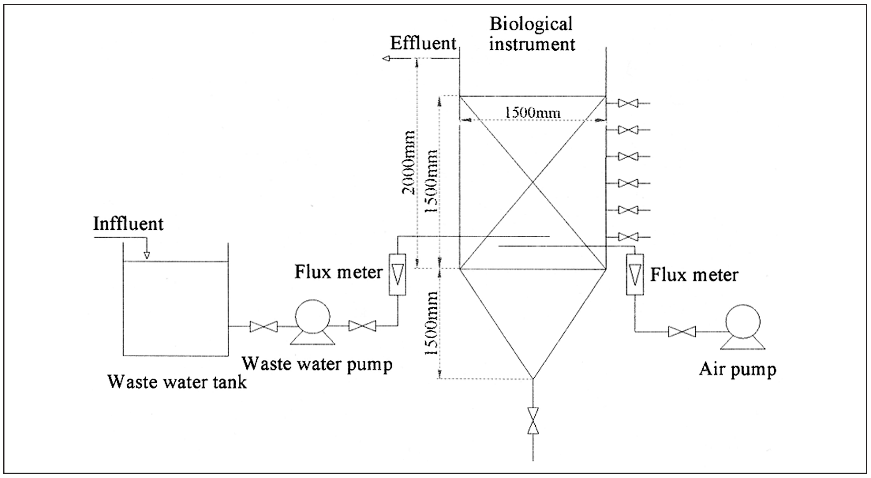

Figure 1. The testing process in pilot scale.

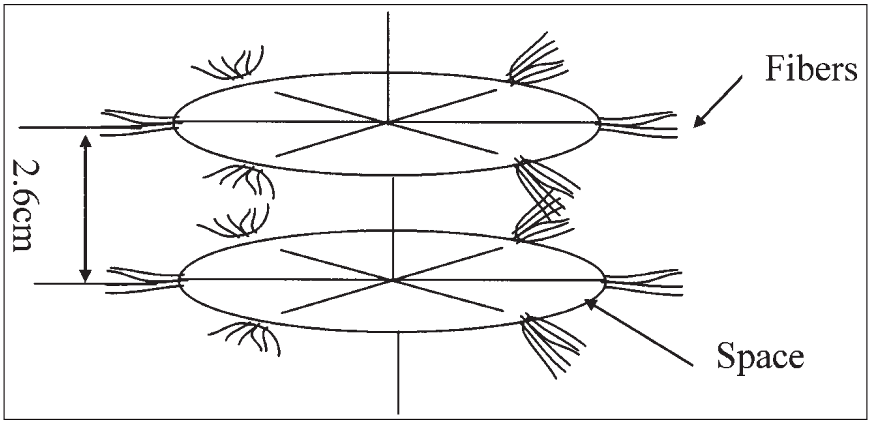

Figure 2. The rope-type of media used in this study.

The Feed Characteristics

After acclimation, a pilot scale test was conducted for the secondary effluent from A/O process. Trial results showed that the process for adopting BCAs to treat the secondary effluent was practical with the technique; its efficiency was obviously better than that of the PFC. The characteristics of experimental feed and limits of discharge are shown in Table 1. Ratio of BOD_5/COD of 0.11 ~ 0.16 is less than 0.3, with a lower ratio of carbon/nitrogen of 3.4; the highest alkalinity of 1.5 mmol/L in the secondary effluent can remove NH_3-N concentration of 10.5 mg/L in theory. Such secondary effluent belongs to difficult-to-treat biodegradable wastewater because of a high quantity of non-biodegradable organic matters, the key study is how to degrade COD and NH_3-N and meet the requirements of discharge limits in using an economic and practical bio-technology.

Analytical Methods

Most routine chemical parameters, such as COD, BOD_5, SS, NH_3-N, NO_x-N, pH, and alkalinity, were analyzed according to the standard methods [13].

RESULTS AND DISCUSSION

Biological Film in Acclimation

First, the raw chemical wastewater was entered, then the activated sludge was introduced to the experimental device at the concentration of 2 g/L. The biological film with the dust-color could be formed gradually after being aerated 5 days. Second, the raw chemical wastewater was entered continuously into the testing device under the conditions of influent flux of 0.5 m^3/h and an optimal ratio of 2.66:1 for the air to wastewater, until the removal rate of COD and NH_3-N reached 70% and 50%, respectively. The third step is that the secondary effluent from A/O process was entered under the condition of the same ratio of the air to wastewater, until the removal rate of COD and NH_3-N reached 20% and 10%, respectively. Finally, the biological film in acclimation was finished successfully.

The Relationships of Experimental Parameters

The experimental relationships of feed flux, hydraulic retention time (HRT), hydraulic loading rates (HLR), and volumetric loading rates (VLR) are shown in equation (1), (2), and (3), respectively. The experimental relationships of influent flux, HRT, and HLR are summarized under optimal conditions of ratio of 2.66:1 for the air-to-wastewater flux in Table 2.

$$\mathrm{HRT} = \mathrm{V/F} = \mathrm{H/HLR} \tag{1}$$

$$\mathrm{HLR} = \mathrm{F/S} \tag{2}$$

$$\mathrm{VLR} = 24\mathrm{F(Co\text{-}Ce)/1000V} \tag{3}$$

Table 1. The Experimental Influent Main Characteristics

Item	COD (mg/L)	BOD_5 (mg/L)	NH_3-N (mg/L)	SS (mg/L)	NO_x-N (mg/L)	pH	Alkalinity (mmol/L)	BOD_5/COD
Data of feed	67.49 ~ 147.00	6.95 ~ 23.52	6.34 ~ 39.36	46.80 ~ 63.00	14.62 ~ 22.52	6.10 ~ 7.50	0.00 ~ 1.50	0.11 ~ 0.16
Limits of discharge	100	20	15	70		6.0 ~ 9.0		0.20

Table 2. The Experimental Relationship of Influent Flux, HRT, and HLR

Terms	Quantitative value							
Feed flux (m^3/h)	0.3	0.4	0.5	0.6	0.75	1.00	1.25	1.50
HRT (h)	10.0	7.5	6.0	5.0	4.0	3.0	2.4	2.0
HLR [$m^3/(m^2 \cdot h)$]	0.170	0.226	0.283	0.339	0.425	0.566	0.707	0.849

where HRT is hydraulic retention time, h; V is volume of bioreactor, m^3; F is feed flux, m^3/h; HLR is hydraulic loading rates, $m^3/(m^2 \cdot h)$; S is cross-sectional area of bioreactor, m^2; VLR is volumetric loading rates, $kg/(m^3 \cdot d)$; Co is feed concentration, mg/L; and Ce is effluent concentration, mg/L.

Determination of the Optimum HLR

The corresponding parameters of COD VLR, HLR and removal efficiency are shown in Figure 3. While the COD VLR was increased from 0.062 $kg/(m^3 \cdot d)$ to 0.144 $kg/(m^3 \cdot d)$, COD removal efficiencies were decreased from 21.15% to 11.35% with the increase of HLR. The HRT was increased with the decrease of HLR or the wastewater velocity, so, the higher COD removal efficiencies were obtained while VLR was at the lower level. Because HRT of the PFC was 4 h, 0.425 $m^3/(m^2 \cdot h)$ was preferred as the HLR to reform PFC.

The Effect of Soluble COD on COD Removal Efficiency

Residual COD in the effluent consisted mainly of three parts, the non-biodegradable COD presented by toxic organic matter, the soluble COD presented by BOD_5, and the particulate COD presented by SS. Under conditions of the optimum ratio of air to wastewater and HLR, influent COD concentration ranged from 70.76 mg/L to 132.43 mg/L, and influent BOD_5 concentration ranged from 6.95 mg/L to 23.52 mg/L, the testing relationship between the influent COD

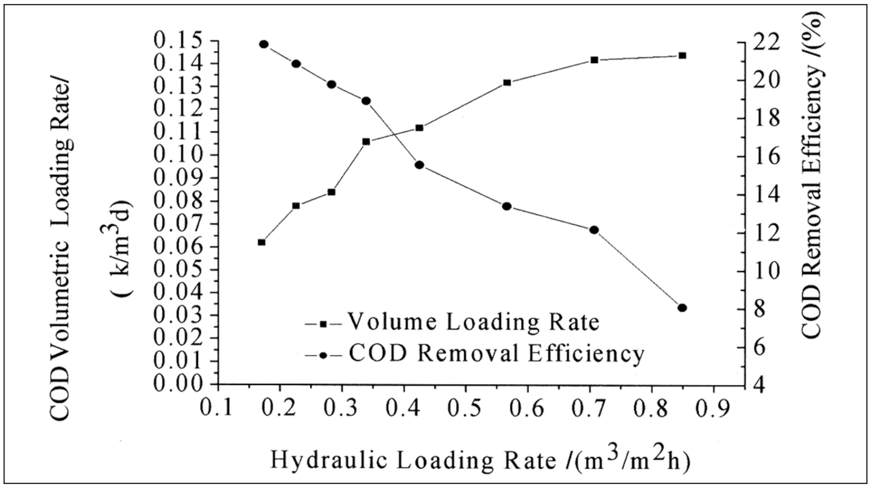

Figure 3. The effect of HLR on COD VLR and COD removal efficiency.

concentration and the correspondent BOD_5 concentration is shown in Figure 4. BOD_5 concentration of 1 mg/L delivers the soluble COD concentration range from 1.86 mg/L to 3.36 mg/L. Because some toxic organics exist, such as benzene, pesticide, and organic agrochemicals, non-biodegradable COD concentration in the secondary effluent varies from 54.17 mg/L to 80.56 mg/L. The relation between COD and BOD_5 is COD = (1.86 ~ 3.36) BOD_5 + 54.17 ~ 80.56. The higher removal of BOD_5 concentration, the higher COD VLR and its removal efficiency are obtained.

While BOD_5 concentrations were decreased from 23.52 mg/L to 6.00 mg/L, COD concentrations in effluent were degraded from 132.70 mg/L to less 100.24 mg/L, COD removal efficiencies were more than 24.46%.

The Effect of Particulate COD on COD Removal Efficiency

The particulate COD concentration is represented by SS concentration. The relationships between concentration of influent SS and correspondent COD were studied for determining drop concentrations of COD as compared with drop concentrations of SS after the wastewater was settled for 4 h at room temperature. As shown in Figure 5, the COD concentrations dropped from 20.99 mg/L to 14.01 mg/L while the correspondent SS concentrations dropped from 32.95 mg/L to 22.08 mg/L. SS concentration of 1 mg/L can deliver COD concentration of 0.58 mg/L, which was different from 1.42 mg/L COD concentration [13]. The SS VLR and its removal efficiencies are shown in Figure 6. The HLR did not influence SS removal efficiency. The SS concentration in effluent varied from

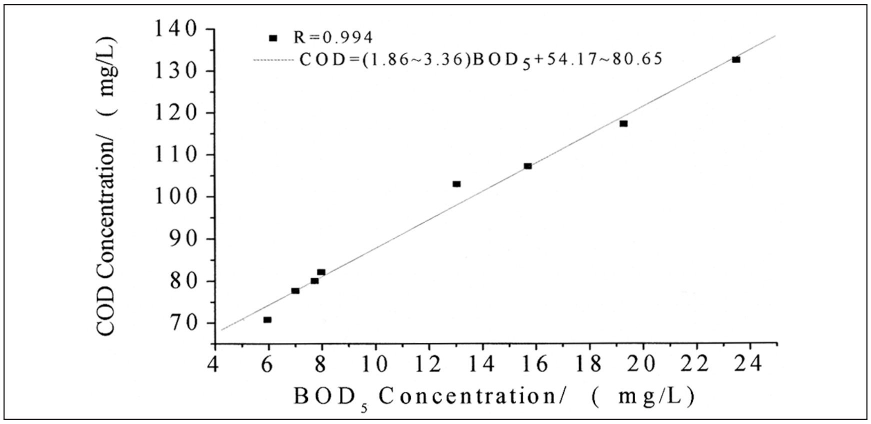

Figure 4. The relationship for the influent COD and BOD_5 concentration.

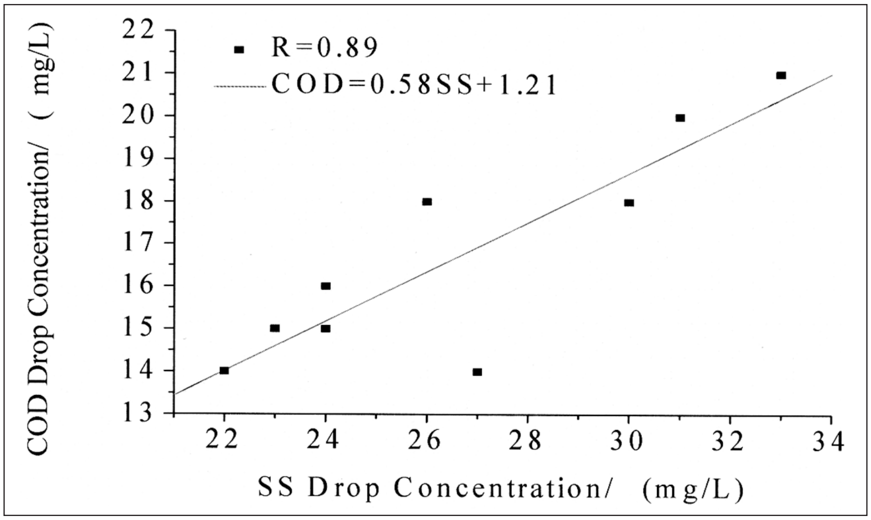

Figure 5. The relationship between influent SS and correspondent COD concentration.

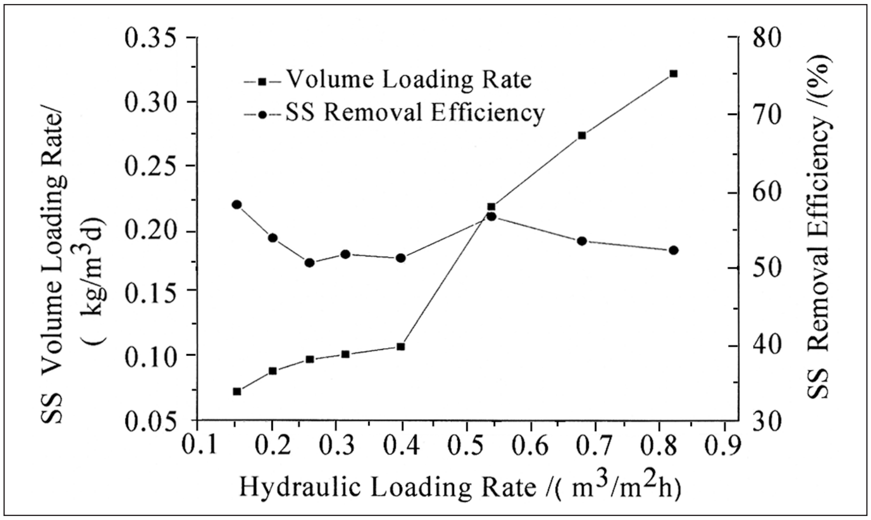

Figure 6. The effect of HLR on SS VLR and SS removal efficiency.

16.50 mg/L to 26.33 mg/L, but SS removal efficiencies changed only from 50.43% to 56.54%. The SS concentrations of main removal depended mainly on deposition. The COD VLR increased with the increase of SS concentrations and its removal efficiencies.

The Effect of NH_3-N Alkalinity on Its Removal Efficiency

Under optimal test conditions with influent residual alkalinity of 0 ~ 1.50 mmol/L, the relationships among influent alkalinity consumed, NH_3-N feed concentration, and NH_3-N removal efficiencies are shown in Figure 7. The higher the alkalinity in normal nitrification processes, the more NH_3-N substances are removed. Thus, alkalinity of 0.143 mmol/L can be consumed for theoretical removal rates of NH_3-N of 1 mg/L. The NH_3-N removal efficiencies were 51.41% and effluent concentrations were 14.79 mg/L at residual alkalinity of 1.50 mmol/L. The results were to apply to Cevat Yaman's data [15, 16].

The ratio of TB/NH_3-N ranges from 0.05 mmol/mg ~ 0.10 mmol/mg, which is less than theoretical value of 0.143 mmol/mg. The discrepancy was due to SND [17, 18]. It was found that maintaining sufficient alkalinity in the system was critical to nitrifying the ammonium wastewater [18-20].

CONCLUSIONS

Biochemical characteristics for a bio-film pilot test in a biological contact aerator were studied for chemical complex secondary effluent under various

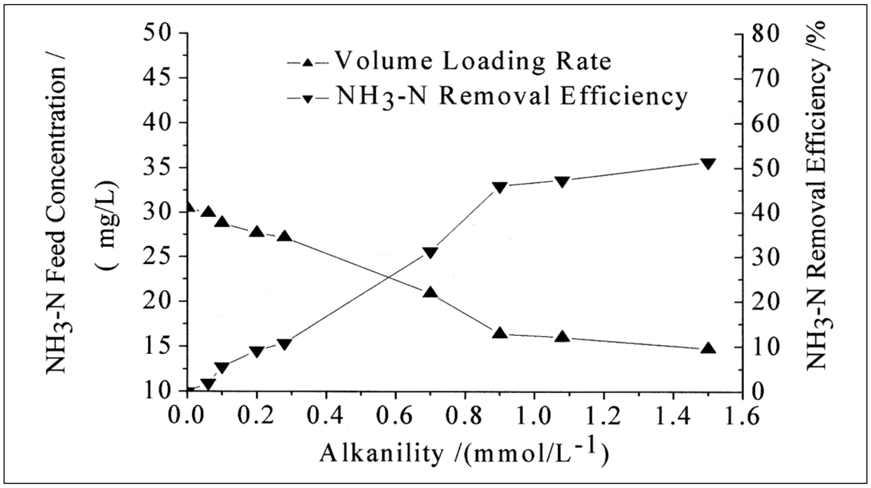

Figure 7. The effect of NH_3-N alkalinity on its removal efficiency.

operational conditions instead of PFC. The objective of this work has been attained to offer a practical model for estimating biochemical characteristics and finding a feasible technology to treat this kind of non-biodegradable wastewater, while complying with national discharge regulations.

Under optimal conditions of HRT of 4 h or HLR of 0.425 $m^3/(m^2 \cdot h)$, the effluent NH_3-N can be decreased from 30.44 m/L to 14.79 mg/L, and the COD can be cut from 132.70 mg/L to less 100.24 mg/L by the BCAs with a lower ratio of carbon/nitrogen of 3.4. NH_3-N and COD removal efficiencies of 51.41% and 24.46% in the BCAs respectively.

Non-biodegradable COD concentrations from toxic organic matter in the secondary effluent varies from 54.17 mg/L to 80.56 mg/L; BOD_5 concentration of 1 mg/L delivers a soluble COD concentration ranging from 1.86 mg/L to 3.36 mg/L. BOD_5 concentrations in effluent can be decreased from 23.52 mg/L to 6.00 mg/L; SS concentration of 1 mg/L can give COD concentration of 0.58 mg/L.

The ratio of $\Delta TB/\Delta NH_3$-N ranges from 0.05 mmol/mg ~ 0.10 mmol/mg, with the discrepancy due to SND. It was found that bio-film technology could save energy and alkalinity "resources" used in NH_3-N removal, and that maintaining a sufficient alkalinity in the system was critical to nitrate the ammonium wastewater. The effluent quality can meet the national discharge regulatory standards.

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