

JING-MING LIU^{***}, YAN XU^{*}, HUI LIU^{*}, ZHI-RONG ZHU^{**}, SHU-YUAN QIAO^{***}

PILOT STUDY ON CHEMICAL INDUSTRIAL WASTEWATER IN TERTIARY TREATMENT WITH BIOFILM FOR WASHING BELTS

The biochemical characteristics of chemical secondary effluent of the wastewater treatment plant of Jilin Chemical Industry Corporation have higher residual concentration of COD_{Cr} and $\text{NH}_3\text{-N}$, and lower residual concentration of BOD_5 and alkalinity. These biochemical characteristics of chemical secondary effluent in tertiary treatment were studied with a pilot system of biological contact aerators (BCAs) to meet national discharged limits and requirements for washing belts, particularly to meet national limits of ammonia and benzene substances, etc. in the air of a workshop. The highest removal efficiency was obtained in the BCAs system and a scientific basis of reference was provided for reforming the system of pulse flocculated clarifier which can constitute a new approach in tertiary wastewater treatment for washing belts.

1. INTRODUCTION

Jilin Chemical Industry Corporation (JCICWTP) adopts the anoxic/oxic (A/O) process in secondary treatment and PFC process in tertiary treatment. As the current loading of wastewater is $6000 \text{ m}^3/\text{h}$, the wastewater needs to be treated to meet national discharged limits and requirements for washing belts, especially to meet national limits of ammonia and benzene substances in the air of a workshop. The wastewater characteristics are very complicated, it contains a great deal of non-biodegradable organic matter such as benzene, pesticides, organic agrochemicals, petroleum processing waste, complex aromatic substances, epoxy resin, dyestuff, intermediate pigment, etc. The effluent $\text{NH}_3\text{-N}$ and COD_{Cr} concentration in the A/O process did not meet national limits on effluent discharged because of the more significant organic

* School of Chemical Engineering, Northeast Dianli University, Jilin, Jilin, P.R. China, 132012; corresponding author, e-mail: liujingmingmail@163.com

** Chemical Department, Tongji University, Shanghai, P.R. China, 200092.

*** Post-doctoral Scientific Research Station, Jiangsu Suzhou Purification Group Co., Ltd, Suzhou, Jiangsu, P.R. China, 215122.

content of non-biological substance in the influent. The PFC was used for treating secondary effluents of the A/O process, according to the results of previous studies; the removal efficiencies of COD_{Cr} and $\text{NH}_3\text{-N}$ were inadequate in the PFC.

As operating parameters and influent fluctuations affect the performance of the A/O system [1, 2], nitrogen and carbon removal is not at a satisfactory level under the traditional mode of A/O operation [3]. The traditional operation of the pulse-flocculated system often fails to attain optimum results for the removal of solids, carbonaceous organic matter, and nutrients. Moreover, stricter regulations on wastewater effluents, technical limitations on treatment site, and energy consumption issues have heightened the importance of modifying biological wastewater processes using biochemical film processes [4].

BCAs and biological aerated filters (BAFs) are biofilm systems used mainly for the tertiary treatment of wastewater [5]. When fibre spacers or granular media are used, the system is capable of removing organic matter, suspended solids, and nitrogen from wastewater at the same time; hence, there is no need to use a sedimentation tank. This kind of biofilm system can be used to a considerable extent for treating wastewater residues where simultaneous nitrification and denitrification (SND) can take place [6]. The SND reaction is much more advantageous when compared with the traditional method of nitrogen removal [7] because it can conserve energy sources, organic carbon, and alkalinity, shorten the reaction time, and curtail the production of sludge [8], [9]. Periodic backwashing in BAFs is necessary to avoid blockage of the system due to the entrapment of solids and biofilm growth. BCAs are much more advantageous in enhancing the original PFC, as they have the unique capability of achieving nutrient removal in a single reactor without requiring additional sedimentation [4].

In the present study, a BCAs biofilm pilot test was studied under various operating conditions for wastewater with varying secondary effluents. The purpose was to investigate the effect of BCAs biofilm on the removal of organic matter and ammonia and to provide the parameters in lieu of the PFC, especially to meet national limits of ammonia and benzene substances in the air of a workshop.

2. MATERIALS AND METHODS

2.1. REACTOR SETUP

The devices were designed according to the PFC characteristics so that the PFC was enhanced effectively after the success of the experiment. The pilot-scale test process is shown in Fig. 1. The influent wastewater was pumped to the bottom of a $\Phi 1.5 \text{ m} \times 3.5 \text{ m}$ cylinder and wastewater with aerated air raised together in a compatible manner. The depth of the packing media was 1.5 m, the distance between the me-

dia and the outlet of the treatment device was 0.5 m, and the distance from the media to the bottom of cylinder was 1.5 m. The density of the packing media was 14 kg/m^3 with the specific surface area of $1538.0 \text{ m}^2/\text{m}^3$. The diameter of the plastic wreath was 8.0 cm and the distance between adjacent spacers was 2.6 cm with the fibre length of 6.0–7.0 cm.

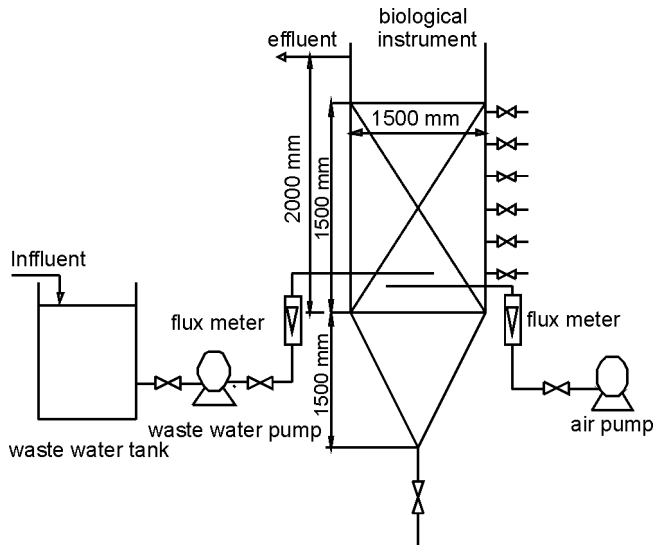


Fig. 1. The pilot-scale test stand

The rope-type of media is shown in Fig. 2. A combined support frame was affixed in the cylinder for supporting the fibres. Air was supplied to the reactor through four air screen diffusers located at height of 1.5 m from the reactor base. A valve connected to the air supply line was used to initiate and cut off the air supply and an airflow meter was used to control the aeration. A peristaltic pump, valve, and water flow meter were used to control the wastewater flux. The dissolved oxygen and a pH probe were used for continuous monitoring.

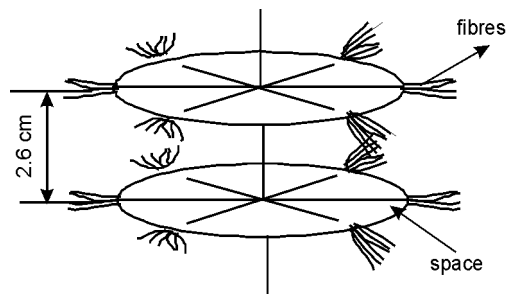


Fig. 2. The rope-type of media used in this study

2.2. THE INFLUENT CHARACTERISTICS AND OPERATION

After a run-in-period, the pilot scale test was conducted with respect to the secondary effluent of the A/O process. The results showed that the BCAs processes for wastewater were practical in terms of technique. The characteristics of the experimental influent are given in Table 1.

Table 1

Main characteristics of the experimental influent

Parameter	Influent	Effluent standard
COD _{Cr} , mg/dm ³	67.49–147.00	100
BOD ₅ , mg/dm ³	6.95–23.52	20
NH ₃ -N, mg/dm ³	6.34–39.36	15
SS, mg/dm ³	46.80–63.00	70
NO _x -N, mg/dm ³	14.62–22.52	–
pH	6.1–7.5	6.0–9.0
Alkalinity, mg/dm ³	0.00–1.50	–

2.3. ANALYTICAL METHODS

Most routine items of chemical analysis, such as COD_{Cr}, BOD₅, SS, NH₃-N, and alkalinity, were conducted according to the standard of APHA [10].

3. RESULTS AND DISCUSSION

3.1. BIOLOGICAL FILM IN ACCLIMATION

Firstly, untreated chemical wastewaters, then activated sludge were introduced to the experimental devices at the concentration of 2 g/dm³. The biological film with the dust colour could form gradually after five days of aeration. Secondly, untreated chemical wastewater was continuously introduced to the test devices under influent flux of 0.5 m³/h and optimum ratio of 2.66:1 for the air to wastewater, until the removal efficiency of COD_{Cr} and NH₃-N reached 70% and 50%, respectively. The third step, the input of effluent wastewater from the A/O process was combined at the same ratio of air to wastewater until the removal efficiency of COD_{Cr} and NH₃-N reached 20% and 10%, respectively. Finally, the biological film was developed successfully under acclimation.

3.2. INFLUENCE OF THE VOLUMETRIC LOADING RATE ON COD_{Cr} AND THE REMOVAL EFFICIENCY

The experimental relationships between the influent flux, hydraulic retention time (HRT), and hydraulic loading rate (HLR) under the optimum ratio of the air to wastewater flux of 2.66:1 is summarized in Table 2. The volumetric loading rate (VLR) of COD_{Cr} and the removal efficiency are shown in Fig. 3.

Table 2

Experimental relationships between the influent flux, HRT, and HLR

Influent 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

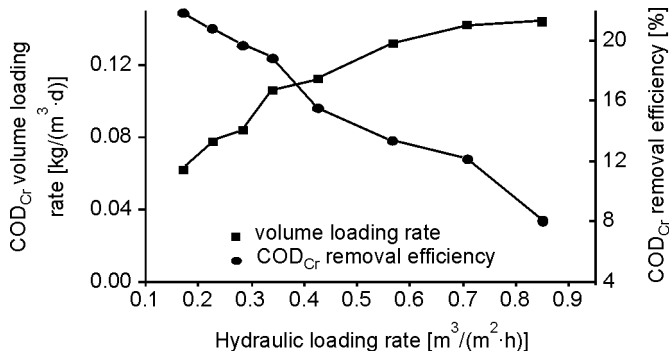


Fig. 3. Dependences of the volume loading rate and removal efficiency of COD_{Cr} on the hydraulic loading rate

As the HLR increased, the COD_{Cr} VLR increased from $0.062 \text{ kg}/(m^3 \cdot d)$ to $0.144 \text{ kg}/(m^3 \cdot d)$ and the COD_{Cr} removal efficiency decreased. The HRT increased when either the HLR or the wastewater velocity decreased, so that higher removal efficiency for COD_{Cr} was obtained while the VLR was at a lower level. Since the HRT of the PFC was 4 h, $0.425 \text{ m}^3/(m^2 \cdot h)$ was preferred as the HLR for reforming the PFC (Table 2, Fig. 3).

The influence of the VLR and the removal efficiency for COD_{Cr} on the influent organic concentration are shown in Fig. 4. The COD_{Cr} VLR increased with the COD_{Cr} concentration, it increased from the initial value of $0.062 \text{ kg}/(m^2 \cdot d)$ to $0.214 \text{ kg}/(m^2 \cdot d)$ because the COD_{Cr} concentration show a linear correlation with the BOD_5 concentration; further, higher the removal of BOD_5 , higher the VLR and removal efficiency of COD_{Cr} were obtained. When the BOD_5 effluent concentration decreased from

23.52 mg/dm³ to 6.00 mg/dm³, the COD_{Cr} effluent concentration decreased from 132.70 mg/dm³ to 100.24 mg/dm³ and the COD_{Cr} removal efficiency was 24.46%, respectively (Fig. 4).

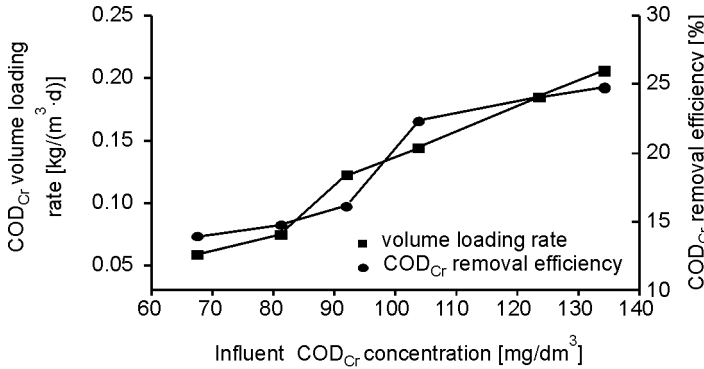


Fig. 4. Dependences of the volume loading rate and removal efficiency of COD_{Cr} on the influent organic concentration

The SS VLR and removal efficiency are shown in Fig. 5. The HLR did not influence the SS removal efficiency but the concentration of the principal SS removal depends on deposition. The concentration of the effluent SS was 16.50–26.33 mg/dm³, and the SS removal efficiency was 50.43–56.54%.

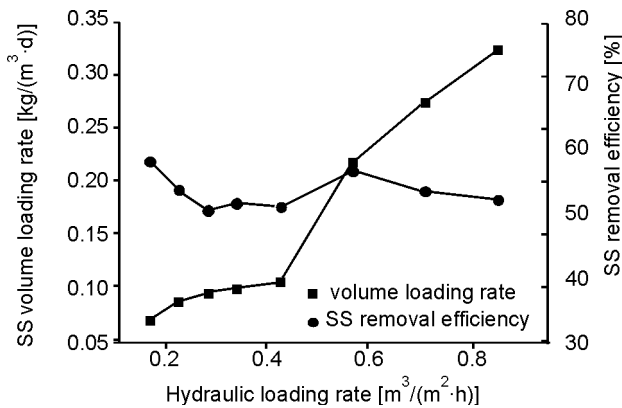


Fig. 5. Dependences of the SS volume loading rate and removal efficiency on the hydraulic loading rate

Relationship between the concentration of the influent SS and the corresponding COD_{Cr} was studied by determining the decrease of the COD_{Cr} concentration in relation to the increase of the SS concentration after the wastewater was allowed to settle for 4 h at room temperature. Such relationship is shown in Fig. 6. The SS concentration

decreased and the removal efficiency increased with the increase of COD_{Cr} VLR. The COD_{Cr} concentration decreased to the range of 14.01–20.99 mg/dm^3 , while the corre-

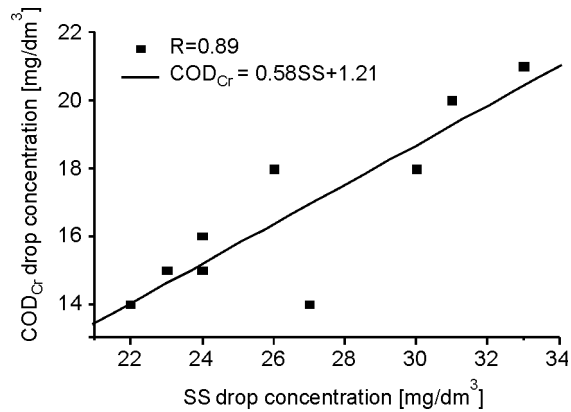


Fig. 6. Dependence of the COD_{Cr} concentration on the influent SS concentration

sponding SS concentration decreased in the range of 22.08–32.95 mg/dm^3 . SS concentration of 1 mg/dm^3 yielded the COD_{Cr} concentration of 0.58 mg/dm^3 which was different from the estimated COD_{Cr} concentration of 1.42 mg/dm^3 [11].

3.3. INFLUENCE OF THE VLR OF $\text{NH}_3\text{-N}$ AND THE REMOVAL EFFICIENCY

The VLR and removal efficiency of $\text{NH}_3\text{-N}$ are shown in Fig. 7. While the $\text{NH}_3\text{-N}$ VLR increased from 0.011 $\text{kg}/(\text{m}^3 \cdot \text{d})$ to 0.016 $\text{kg}/(\text{m}^3 \cdot \text{d})$, the $\text{NH}_3\text{-N}$ VLR did not change much more comparing to the change of the HLR. The $\text{NH}_3\text{-N}$ VLR was

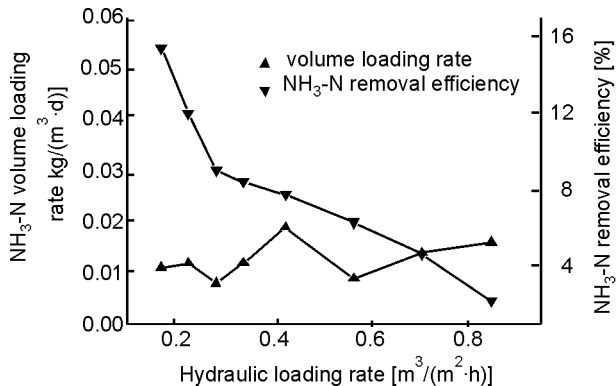


Fig. 7. Dependences of the $\text{NH}_3\text{-N}$ volume loading rate and removal efficiency on the hydraulic loading rate

changed more as the influent alkalinity (Table 3) is changed, and the $\text{NH}_3\text{-N}$ removal efficiency decreased as the HLR increased. When the HLR is $0.425 \text{ m}^3/(\text{m}^2\cdot\text{h})$, the $\text{NH}_3\text{-N}$ removal efficiency was 7.75% and the effluent concentration was $18.62 \text{ mg}/\text{dm}^3$ respectively, the $\text{NH}_3\text{-N}$ VLR was subject to the limit of the reactive condition and was basically unchanged with the HLR. The wastewater velocity and/or HLR increased as the HRT decreased; hence, the $\text{NH}_3\text{-N}$ removal efficiency was in the lower range because the pollutants were not totally degraded and had already left the reactor [12].

Table 3

Relationships between the influent alkalinity consumed, $\text{NH}_3\text{-N}$ removal, and increased in $\text{NO}_x\text{-N}$

ΔTB [mmol/dm ³]	$\Delta\text{NH}_3\text{-N}$ [mg/dm ³]	$\Delta\text{NO}_x\text{-N}$ [mg/dm ³]	$\Delta\text{TB}/\Delta\text{NH}_3\text{-N}$	$\Delta\text{NO}_x\text{-N}/\Delta\text{NH}_3\text{-N}$
0.00	0.00–1.12	1.07–2.04	0	0.95–1.82
0.06	0.00–1.12	1.68–2.58	0.00–0.05	1.50–2.33
0.10	1.12–2.24	2.07–2.68	0.05–0.09	0.54–1.19
0.20	2.12–3.43	2.97–3.09	0.06–0.09	0.90–1.40
0.28	2.68–3.87	3.51–3.67	0.07–0.10	0.95–1.31
0.70	7.85–11.21	5.9–12.24	0.06–0.09	0.75–1.09
0.90	13.45–14.57	9.41–12.63	0.06–0.07	0.70–1.06
1.08	15.65–18.69	11.11–16.57	0.06–0.07	0.71–1.06

Higher the alkalinity in normal nitrification processes, more $\text{NH}_3\text{-N}$ substances is removed and the $\text{NO}_x\text{-N}$ substances produced. Thus, the alkalinity concentration of $0.143 \text{ mmol}/\text{dm}^3$ would be consumed and $\text{NO}_x\text{-N}$ concentration of $1 \text{ mg}/\text{dm}^3$ would be produced for the theoretical removal of $\text{NH}_3\text{-N}$ of $1 \text{ mg}/\text{dm}^3$ [13]. The residual alkalinity of the influent was $0\text{--}1.50 \text{ mmol}/\text{dm}^3$. The relationships between the influent alkalinity consumed, $\text{NH}_3\text{-N}$ removal, and increase of $\text{NO}_x\text{-N}$ are given in Table 3. From Table 3, the ratio of $\Delta\text{TB}/\Delta\text{NH}_3\text{-N}$ is $0.05\text{--}0.10 \text{ mmol}/\text{mg}$ (less than the theoretical value of $0.143 \text{ mmol}/\text{mg}$) and the ratio of $(\Delta\text{NO}_x\text{-N})/(\Delta\text{NH}_3\text{-N})$ is $0.54\text{--}2.33$.

The results show that parts of $\text{NH}_3\text{-N}$ were used to form microbiological cells in function of assimilation, while the alkalinity concentration consumed was lower than $0.10 \text{ mmol}/\text{dm}^3$. Parts of $\text{NH}_3\text{-N}$ were consumed as a part of the main function of nitrification when the alkalinity concentration consumed was higher than $0.10 \text{ mmol}/\text{dm}^3$ and lower than $0.70 \text{ mmol}/\text{dm}^3$. When the alkalinity concentration consumed was higher than $0.70 \text{ mmol}/\text{dm}^3$ or even when the concentration was lower than 1.08, the ratio of $(\Delta\text{NO}_x\text{-N})/(\Delta\text{NH}_3\text{-N})$ was $0.70\text{--}1.09$. The results were applied to Yaman's data [14]. The discrepancy was due to SND [15]. It was found that a sufficient alkalinity in the system was critical for nitrifying the ammonium wastewater.

3.4. INFLUENCE OF COD_{Cr} AND NH₃-N REMOVAL ON THE STUFFING HEIGHT

The quantities of COD_{Cr} and NH₃-N removed varied with the stuffing height. The optimum stuffing height was measured for the best quantities of removal of COD_{Cr} and NH₃-N at lower ratio of C/N of 4.4. The dependence of COD_{Cr} and NH₃-N removal on various stuffing heights is shown in Fig. 8.

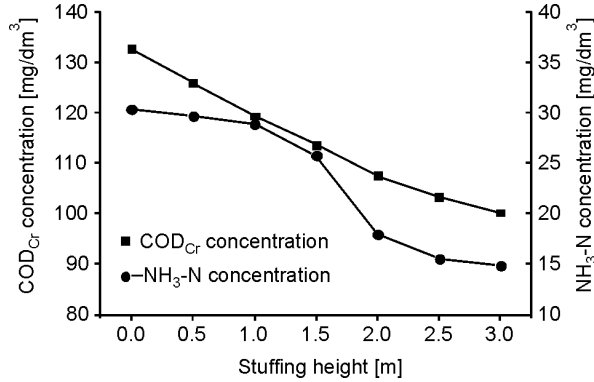


Fig. 8. Dependences of the COD_{Cr} and NH₃-N removal on the stuffing height

At the distance of 1 m from the bottom of the reactor, the removal of the COD_{Cr} concentration increased to 10.02%, while the removal of the NH₃-N concentration increased to only 5.14%. These shows that bacterial carbonaceous oxidation was more active than bacterial nitrification below the stuffing height of 1m when the wastewater just entered the instrument. The removal of NH₃-N concentration was 15.37% at the height of 1.5 m, thus, the nitrifying bacteria began to work well once the concentration of degradable carbon reached a lower level. The filler height of 3 m could meet demands for treating the wastewater (Fig. 8).

The best-fit mathematical model for COD_{Cr} removal was obtained for the related parameters from Figs. 4 and 8 for yielding the best representation of Jinbao's design [16]. An empirical depth parameter equation for NH₃-N removal was found for application to the Gujer–Boller model [11]. Two appropriate mathematical models represent Eqs. (1) and (2). The results show that a suitable HLR and a suitable height of the reactor were necessary to achieve the effective removal of both COD_{Cr} and nitrogen

$$\ln \frac{\rho_{so}}{\rho_s} = K (\rho_{so})^m \left(\frac{q_v}{A} \right)^n h \quad (1)$$

$$\frac{Haj_{N,max}}{\frac{q_v}{A}} = \rho_{sno} - \rho_{sne} + M \ln \frac{\rho_{sno}}{\rho_{sne}} \quad (2)$$

The issues and performance parameters regarding Eqs. (1) and (2) are presented in Table 4.

Table 4

Summary of the fit performance parameters

Parameter	Value
Influent COD _{Cr} concentration, ρ_{so}	132.70 mg/dm ³
Range of the effluent COD _{Cr} (over various heights), ρ_s	126.10–100.24 mg/dm ³
Constant concerning the influent concentration, m	1.065
Constant concerning the hydraulic loading rate, n	–0.490
Hydraulic loading rate, q_v/A	0.425 m ³ /(m ² ·h)
Range of the height of the reactor, h	0.0–3.0 m
Constants concerning influent concentration and hydraulic loading rate at 20 °C, K	0.000337
Height of the reactor, H	3.0 m
Specific surface area of the stuffing, a	1538 m ² /m ³
Maximum specific rate of removal of NH ₃ -N, $j_{N,max}$	0.0015 g/(m ² ·h)
Influent NH ₃ -N concentration, ρ_{sno}	30.44 mg/dm ³
Effluent NH ₃ -N concentration, ρ_{sne}	30.44–14.79 mg/dm ³
Half-saturation NH ₃ -N coefficient, N	0.8729 mg/dm ³

3.5. APPLICATION OF THE EFFECT OF TREATED WASTEWATER

Through technological improvements and actual operating results of several years, the treated wastewater of reuse by BCAs can meet the needs of sludge dewatering belts. The influence of filtrated water for sludge dewatering belts with the groundwater and reused wastewater, and the influence of the air of a workshop for the groundwater and reused wastewater are shown in table 5 and table 6, respectively. In the reuse of tertiary wastewater, while reducing the costs of wastewater treatment of sludge dewatering belts, annual costs with flocculant dosing can reduce 200 000 yuan RMB per pool

Table 5

Influence of filtrated wastewater on groundwater and reused wastewater

Item	COD _{Cr} [mg/dm ³]		SS [mg/dm ³]	
	Groundwater	Wastewater	Groundwater	Wastewater
1	2829.57	1562.91	1283	894
2	1020.27	1377.48	339	585
3	1160.89	1422.10	986	649
4	1235.19	1736.86	754	1071
5	1267.58	1247.68	1025	1062
Average	1249.18	1469.41	877.4	852.2

Table 6

Influence of air of workshop on groundwater and reused wastewater

Item	Groundwater [mg/m ³]	Wastewater [mg/m ³]	National standards [mg/m ³]
Benzene	0.58	0.68	5
Ammonia	0.95	1.15	30
Aniline	0.22	0.27	5
Toluene	0.41	0.21	5
Nitrobenzene	0.19	0.32	1
Styrene	0.23	0.28	40
Xylene	0.41	0.53	100

and the groundwater of 876 000 t cannot be consumed each year, the annual cost of 360 000 yuan RMB can be saved each year.

4. CONCLUSIONS

A biofilm pilot test in a biological contact aerator was studied for complex chemical secondary effluent wastewater with biochemical characteristics and various operational conditions in lieu of the PFC.

The effluent COD_{Cr} could decreased from 132.70 mg/dm³ to 100.24 mg/dm³ and the NH₃-N could declined from 30.44 mg/dm³ to 14.79 mg/dm³ through the BCAs under a lower ratio of C/N of 4.4. The SS concentration of 1 mg/dm³ yielded a COD_{Cr} concentration of 0.58 mg/dm³. The ratio of (Δ NO_x-N)/(Δ NH₃-N) was 0.7 and the discrepancy was due to SND. The removal efficiency through the BCAs for COD_{Cr} and NH₃-N was 24.46% and 51.41% respectively, under HLR of 0.425 m³/(m²·h). Since two appropriate mathematical models and parameters were obtained for achieving the effective removal of both COD_{Cr} and nitrogen, the effluent quality can satisfy national discharged limits and the requirements of washing belts, particularly to meet national limits of ammonia and benzene substances, etc. in the air of a workshop.

ACKNOWLEDGEMENT

This study was sponsored by the wastewater treatment plant of Jilin Chemical Industry Corporation and was financially supported from foundations of Technological Bureau of Suzhou City, Jiangsu Province (No. SG201024).

REFERENCES

- [1] SAMUELSSON P., CARLSSON B., *Water Sci. Technol.*, 2001, 43 (1), 115.
- [2] CHO J.H., SUNG S.W., LEE I.B., *Water Sci. Technol.*, 2002, 45 (5), 53.
- [3] YONGZHEN P., ZHIHUI W., SHUYING W., *J. Environ. Sci.*, 2005, 17 (3), 425.
- [4] GUO H., ZHOU J., SU J., ZHANG Z., *Biochem. Eng. J.*, 2005, 23, 57.

-
- [5] LEKANG O.-I., KLEPPE H., *Aquacult. Eng.*, 2000, 21, 181.
- [6] XIA S., LI J., WANG R., *Ecol. Eng.*, 2008, 32, 2562.
- [7] KHIN T., ANNACHATRE A.P., *Biotechnol. Adv.*, 2004, 22, 519.
- [8] VAN DONGEN U., JETTEN M.S.M., VAN LOOSDRECHT M.C.M., *Water Sci. Technol.*, 2001, 44 (1), 153.
- [9] CHUANG H.P., OHASHIA A., IMACHIB H., TANDUKAR M., HARADA H., *Water Res.* 2007, 41, 295.
- [10] *Standard methods for the examination of water and wastewater*, 19th Ed., American Public Health Association, APHA, Washington, DC, 1995.
- [11] EVANS E.A., ELLIS T.G., GULLICKS H., RINGELESTEIN J., *J. Environ. Eng.*, 2004, 130 (11), 1280.
- [12] SEONG J.L., YEONG H.A., EUN Y.K., HO N.CH., *Biotechnol. Bioprocess Eng.*, 2006, 11 (6), 538.
- [13] MULLER A.W., WENTZEL M.C., EKAMA G.A., *Water SA*, 2006, 32 (5), 611.
- [14] YAMAN C., MARTIN J.P., KORKUT E., *J. Environ. Eng.*, 2005, 131 (12), 1667.
- [15] WEISSENBACHER N., LODERER CH., LENZ K., MAHNIK S.N., WETT B., FUERHACKER M., *Water Res.*, 2007, 41, 397.
- [16] JINBAO W., HUI L., XUEPING H., *J. Nanchang Coll. Water Cons. Hydroelect. Power*, 2004, 23 (2), 42 (in Chinese).