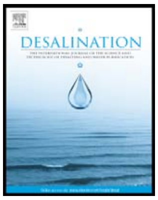
Desalination 254 (2010) 149–153

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal



Study of municipal wastewater treatment with oyster shell as biological aerated filter medium

Yao-Xing Liu, Tong Ou Yang *, Dong-Xing Yuan, Xiao-Yun Wu

State Key Laboratory of Marine Environmental Science, Environmental Science Research Center, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history:
Received 1 September 2009
Received in revised form 25 November 2009
Accepted 1 December 2009
Available online 8 January 2010

Keywords:
Biological aerated filter
Oyster shell
Municipal wastewater
pH
Total phosphorus

ABSTRACT

Oyster shell and plastic ball were applied as the media of biological aerated filters (BAF) to treat municipal wastewater in two lab scale upflow BAFs. The results indicated that oyster shell BAF and plastic ball BAF had average chemical oxygen demand (COD) removals of 85.1% and 80.0%, when hydraulic retention time (HRT) was longer than 4 h, and 65.7% and 68% with HRT of 2 h, respectively. In terms of removing ammonia nitrogen (NH_3-N), oyster shell BAF and plastic ball BAF had average removals of 98.1% and 93.7% for HRT longer than 4 h, and 47.2% and 65.1% for HRT of 2 h, respectively. Total phosphorus (TP) removals of oyster shell BAF were increased to 79.9% and 90.6% as the pH increased to 9 and 10, respectively, while no improvement was observed for plastic ball BAF. The effluent pH of oyster shell BAF was higher and buffered compared with that of the influent, mainly due to the $CaCO_3$ released from the shell. The oyster shell may also be the main reason to support the BAF a higher NH_3-N removal efficiency when HRT was longer than 4 h, compared with plastic ball BAF.

1. Introduction

Biological aerated filter (BAF) is a novel, flexible and effective bioreactor that provides a small footprint process at various stages of wastewater treatment [1]. BAF was first developed in Europe and then widely applied all over the world as a wastewater treatment system due to its advantages compared to other systems [2]. Stensel and Reiber [3] found that the land required for a BAF system was approximately only one fifth of that needed for plastic medium trickling filters and one tenth of that needed for activated sludge plants. BAF technology is based on the principle of biofiltration through a submerged granular medium that serves two purposes: biological conversion of organic matter by the biomass attached onto the large support medium surface and physical removal of suspended particles by medium filtration. As a promising technology for the decentralisated wastewater treatment, BAF removes organic matter, solids and NH_3-N in one reactor unit. It can be utilized at both secondary and tertiary stages of wastewater treatment, wastewater reclamation engineering and pretreatment process of newly developed membrane techniques, particularly when low land usage is required in urban areas [4].

Foremost BAFs, as defined by Stephenson [5], contain a granular medium that provides a large surface area per unit volume for biofilm development. The initial purpose of these processes was to obtain carbon oxidation and solid filtration [6]. In recent years, several technologies using BAF have been developed to treat wastewater from slaughterhouses, pulp, mill industries [7,8], and refractory wastewater such as textile and oil field wastewater [6,9]. In addition, some BAF combination techniques have been studied to treat formalin wastewater and remove nitrogen from low carbon-to-nitrogen wastewater [10,11]. Several model studies have been carried out to improve the performance and theoretical knowledge [12,13].

Medium selection is important for BAF to achieve effluent quality requirements. The media play a key role in maintaining a high amount of active biomass and a variety of microbic populations. The most frequently studied biofilm support media include clay-, schist- or plastic-based ones of various types, such as polyethylene, polystyrene, and polyesterene [14].

Oyster shells are waste product from mariculture and cause a major disposal problem in coastal regions, e.g. southeast China. Shellfish-farming is a large part of the regional economy, since the custom of taking shellfish as a major part of the diet creates a large market of marine products. A large amount of oyster shell is produced every year. Shellfish farms have faced to the problem of disposing oyster shell waste. Oyster shell waste dumped into coastal water or reclaimed land produces a potent smell and disserves surrounding environments. Some of the waste oyster shells are used as limestone in fertilizers and chicken feed, but the usages are limited. The waste oyster shells lead to severe problem of solid waste pollution. Thus, recycle has arisen as an imminent issue in mariculture areas. The ideal solution is to convert the waste oyster shells to a product that is both beneficial and economically viable.

---

* Corresponding author. Fax: +86 592 2181613.
E-mail address: yz3t@xmu.edu.cn (T.O. Yang).

0011-9164/$ – see front matter. Crown Copyright © 2009 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2009.12.003

Table 1
Influent characteristics.

Parameter	Average	Standard deviation ($n = 30$)
Chemical oxygen demand (COD) (mg/L)	110.4	37.3
NH_4-N (mg/L)	28.1	12.4
Total phosphorus (TP) (mg/L)	2.4	0.7
PO_4-P (mg/L)	1.7	0.3
pH	7.25	0.2

The purpose of the present research is to study the use of waste oyster shells as a BAF medium. Oyster shell is selected due to its availability, the characteristic shape, good rigidity, outstanding chemical constitutes and biological stability. It is possible that oyster shell releases $CaCO_3$ into wastewater, since more than 96% of its component is $CaCO_3$ [15]. The shells supply sufficient alkalinity to enhance the decreasing pH caused by nitrification in BAF. Oyster shell is also good for removing phosphorus from wastewater by producing calcium phosphate precipitation. Moreover, its high roughness surface makes the microorganisms grow and adhere easily. To our best knowledge, this is the first time that oyster shell is used as biofilm carrier in the field of municipal wastewater treatment.

2. Materials and methods

2.1. Wastewater characteristics

The municipal wastewater was collected from a wastewater treatment plant, located at Xiamen University, China. The raw influent was characterized as shown in Table 1.

2.2. Reactor description

Two parallel lab-scale BAF reactors were made of Plexiglas. The reactors were packed with oyster shell and plastic ball, respectively. Waste oyster shells (Fig. 1A) were obtained from a temporary storage near the workplace where oysters were separated from shells. Plastic ball medium (Fig. 1B) was purchased from Tongji University, Shanghai, China. The characteristics of media are listed in Table 2. The reactors (Fig. 2) had an upflow configuration with 1.15 m in height and 0.10 m in inner diameter. The medium was 1.0 m height, with an effective volume of 7.8 L. Since the air was introduced into the reactors with an air diffuser, located at 0.3 m from the downside inlet, an anaerobic area between the air diffuser and downside inlet was formed. The air flow rate was controlled, using an air flowmeter. The raw wastewater was pumped into BAF with a peristaltic pump and flowed upward through the filter medium layer. The flow rate ratio of air to water was controlled at 5:1.

Table 2
The characteristics of the media.

Medium	Diameter (cm)	Packed density (kg/m^3)	Actual density (kg/m^3)	Porosity (%)
Oyster shell	2.0–5.0	250	1390	88
Plastic ball	1.0	95.6	797	82

The two BAFs were backwashed using a counter-current manner to remove the accumulated suspend solid (SS) and the excess biomass periodically. Backwashing process was designed as follows: after shutting off the feeding valves of the BAFs at the first washing step, air was introduced for 3 min from the bottom of the filter; in the second step, the effluent was transported into the BAFs from the top and the air was sent into the BAFs from the bottom for 5 min; then in the third step the effluent was again introduced back into the top of BAFs for 3 min. The backwash air and water velocities of two BAFs were 13–15 L $(m^2 s)^{-1}$ and 4–5 L $(m^2 s)^{-1}$, respectively.

2.3. Analytical methods

During the study, influent and effluent samples were taken regularly and the concentrations of COD, NH_3-N, and TP were tested according to the standard methods [16]. A pH meter (CyberScan pH510, Eutech Co., U.S.A.) was used to measure temperature and pH. A prober (HI9146, Hanna Co., Italy) was used to measure dissolved oxygen (DO).

3. Results and discussion

Throughout the study, the two BAFs were operated at the conditions of water temperature ranging from 17.3 °C to 23 °C and DO ≥ 2 mg/L. Four HRTs, 12 h, 8 h, 4 h and 2 h were adopted, coincided with hydraulic loadings 0.071, 0.11, 0.22 and 0.44 m^3/m^2 h, respectively. The changing trends of COD, NH_3-N, TP and pH of the influent and effluent are shown in Figs. 3–7.

3.1. COD reduction in two BAFs

From Fig. 3, it was found that two BAFs both processed excellent removals towards COD. Oyster shell BAF had a slightly higher COD removal efficiency compared with plastic ball BAF at HRT longer than

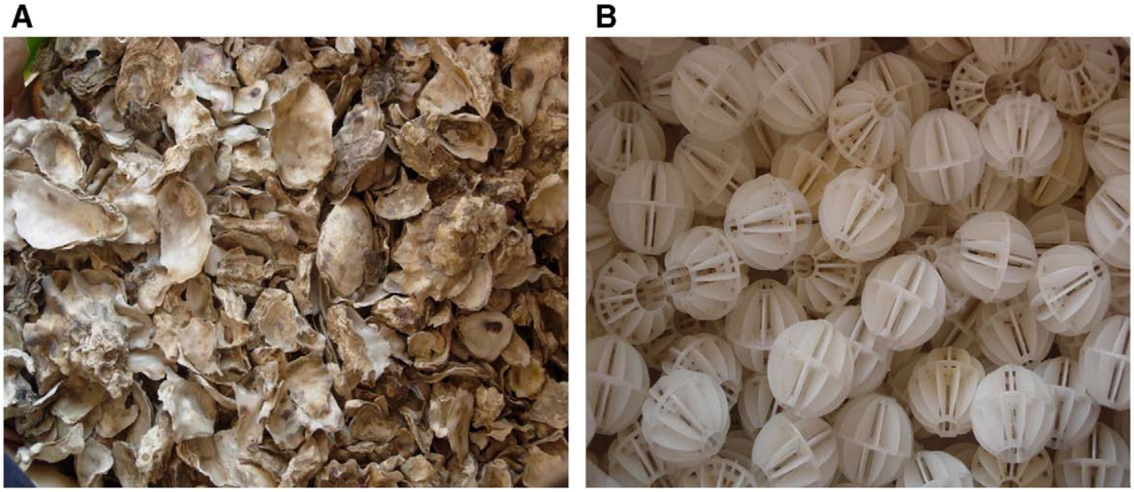


Fig. 1. Photos of media. A: Oyster shell. B: plastic ball.

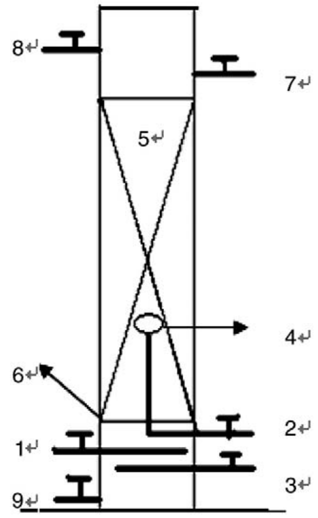


Fig. 2. Diagram of BAF (1, influent; 2, air inlet; 3, backwashing air inlet; 4, diffusor; 5, medium; 6, backstop; 7, effluent and sampling port; 8, backwashing water inlet; 9, backwashing outlet).

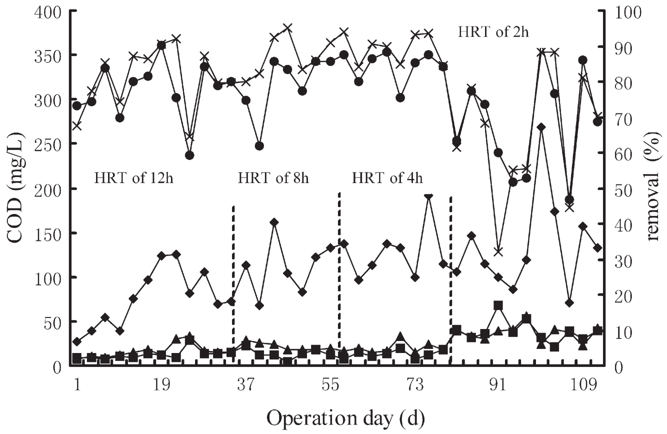


Fig. 3. COD concentrations and removals in influent and effluent of BAFs. OS: oyster shell BAF. PB: plastic ball BAF. —◆— influent. —■— OS-effluent. —▲— PB-effluent. —×— OS-removal. —●— PB-removal.

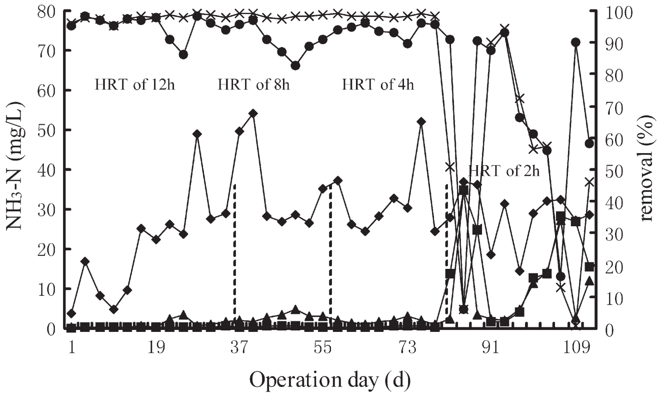


Fig. 4. NH_3-N concentrations and removals in influent and effluent of BAFs. OS: oyster shell BAF. PB: plastic ball BAF. —◆— influent. —■— OS-effluent. —▲— PB-effluent. —×— OS-removal. —●— PB-removal.

4 h. COD removal of both BAFs decreased remarkably when HRT was 2 h, and oyster shell and plastic ball BAFs had average COD removals of 65.7% and 68.0%, respectively. The concentrations of COD in the effluent of oyster shell and plastic ball BAFs were in the ranges of 8.0–29 mg/L (on average, 13.0 mg/L) and 7.2–33.4 mg/L (on average, 18.6 mg/L), respectively. COD removals varied from 64% to 94.0% (on average, 85.1%) and 59.3% to 90.1% (on average, 80.0%) at HRT longer than 4 h, respectively. When HRT was 2 h, the concentrations of COD in the effluent of oyster shell and plastic ball BAFs were 20.6–67.4 mg/L (on average, 38.9 mg/L) and 22.0–56.2 mg/L (on average, 36.9 mg/L), respectively, and COD removals of these two BAFs were 31.9–88.2% (on average, 65.7%) and 51.6–90.84% (on average, 68.0%), respectively. These observations confirmed that HRT could affect COD removal efficiency. With shorter HRT, organic substrates were not fully degraded before being discharged from the BAF. Moreover shorter HRT led to higher hydraulic loading thus stronger scour on medium surface, and lower biomass on medium surface thus lower COD removal.

3.2. NH_3-N reduction in two BAFs

As shown in Fig. 4, both BAFs had excellent NH_3-N removal when HRT was longer than 4 h, and manifested a decrease of NH_3-N removal while HRT was at 2 h. The NH_3-N in the effluent ranged from 0.14 to 0.67 mg/L with an average of 0.44 mg/L for oyster shell BAF, and from 0.19 to 4.9 mg/L with an average of 1.75 mg/L for plastic ball BAF. NH_3-N removals of oyster shell and plastic ball BAFs varied from 95.3% to 99.2% (on average, 98.1%) and 82.8% to 98.5% (on average, 93.7%), respectively, when HRT was longer than 4 h. When HRT was 2 h, the effluent of oyster shell BAF had NH_3-N concentrations of 1.87–34.7 mg/L (on average, 16.1 mg/L) and plastic ball BAF 2.11–34.7 mg/L (on average, 10.6 mg/L). NH_3-N removals of oyster shell and plastic ball BAFs varied from 6.2% to 94.4% with an average of 47.2%, and 6.2% to 93.3% with an average of 65.1%, respectively. The results indicated when HRT was 2 h that NH_3-N was not fully nitrified before being discharged from BAF compared with HRT longer than 4 h. This can be explained by the following reasons. Firstly, when HRT was 2 h, the time wastewater retained in the BAF was short, and nitrobacteria did not have sufficient time to nitrify NH_3-N. Secondly, hydraulic load increased as the HRT decreased. Impulsive force of water and gas was also increasing with the augment of hydraulic load. The enhanced impulsive force could force some biofilm to be out of BAFs, resulting in lower NH_3-N removal efficiency. Thirdly, with HRT of 2 h DO in effluent was a little lower compared with HRT longer than 4 h. Thus, relative lower DO in effluent could cause a little decrease of NH_3-N removal efficiency. Fourthly, there was competition between heterotrophic bacteria and autotrophic bacteria in BAFs for the substrates, DO and inhabitation area of the medium. A higher organic loading induced by the increase of hydraulic loading could be favorable to heterotrophic bacteria against autotrophic bacteria [17]. As a result, nitrification was inhibited and NH_3-N removal decreased rapidly.

From Fig. 4, it was also found that oyster shell BAF had a slightly higher NH_3-N removal compared with plastic ball BAF when HRT was longer than 4 h. On the other hand, contrary results were obtained when HRT was 2 h. There were two main reasons. Firstly, HRT of 4 h was sufficiently long to allow biomass to degrade NH_3-N in the BAFs. Secondly, due to the contribution of the oyster shell to the buffer capacity, H^+ generated during nitrification in the oyster shell BAF could be easily removed. Therefore the BAF processed a higher reduction of NH_3-N. Theoretically, nitrification is pH-sensitive and the rate declines significantly at pH values below 6.8. Optimal nitrification occurs at a pH range of 7.5–8.0 [18,19]. Fig. 5 shows that higher pH in the effluent of oyster shell BAF was observed, compared with that of plastic BAF. When HRT was 2 h, the pH of plastic ball BAF effluent had a slight increase. Therefore, it had limited effect on nitrification. Another possibility to cause higher NH_3-N removals at 2 h in plastic BAF might be the larger amount of biomass.

3.3. TP reduction in two BAFs

In terms of removing TP, oyster shell BAF did not show higher TP removal compared with plastic ball BAF, as shown in Fig. 6. The TP

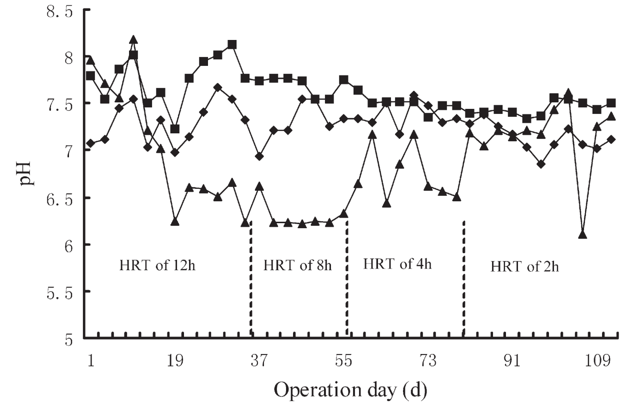


Fig. 5. pH value in influent and effluent of BAFs. OS: oyster shell BAF. PB: plastic ball BAF. —◆— influent. —■— OS-effluent. —▲— PB-effluent.

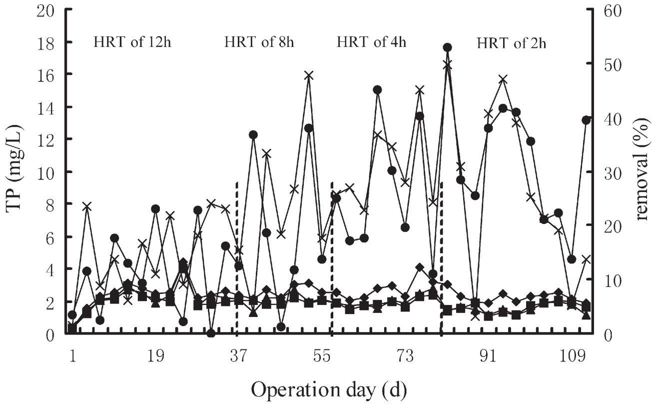


Fig. 6. TP concentrations and removals in influent and effluent of BAFs. OS: oyster shell BAF. PB: plastic ball BAF. —◆— influent. —■— OS-effluent. —▲— PB-effluent. —✕— OS-removal. —●— PB-removal.

removals of oyster shell and plastic ball BAFs were 1.6%–49.8% (on average, 23.2%) and 0%–52.84% (on average, 21.7%), respectively. The result indicated that there might be no precipitation of calcium phosphate produced in oyster shell BAF during the process. The phosphorus was removed mainly as the nutrition consumption for microorganism. According to the study of Carlsson [20], calcium phosphate precipitation occurred in all the systems at sufficiently high concentrations of calcium (at least 100 mg/L) and phosphate (at least 50 mg/L) at neutral pH. The wastewater in this study did not contain so much high phosphate concentrations, and thus no precipitation was produced in oyster shell BAF. However as shown in Fig. 7, once the effluent pH of two BAFs was increased to 9 or 10, the TP removal did not improve for plastic ball BAF. On the other hand, in oyster shell BAF the TP removal reached 79.9% and 90.6% in average, respectively. This result confirmed that PO_4^{3-} in oyster shell effluent could be removed by producing calcium phosphate precipitation at higher pH.

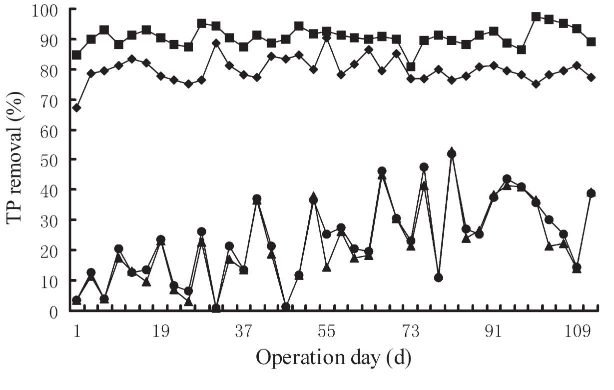


Fig. 7. TP removal after increasing effluent pH of BAFs. OS: oyster shell BAF. PB: plastic ball BAF. —◆— OS-pH9. —■— OS-pH10. —▲— PB-pH9. —●— PB-pH10.

3.4. Influent and effluent pH in two BAFs

The influent and effluent pHs of two BAFs are shown in Fig. 5. Effluent pH of oyster shell BAF was constant and higher, mainly due to its buffer ability to neutralize H^+ produced during NH_3-N nitrification. The effluent pH of plastic ball BAF was lower than that of oyster shell BAF when HRT was longer than 4 h, resulting from H^+ accumulation during the process of NH_3-N nitrification. When HRT was 2 h, with the lower NH_3-N nitrification (shown in Fig. 4) the effluent pH of plastic ball BAF was higher obviously (Fig. 5).

4. Conclusions

During the study, the raw wastewater was fed into upflow BAFs and the performance of BAFs packed with oyster shell and plastic ball, respectively, was observed at different hydraulic loads. Because plastic ball is a common and superior filter medium for BAF, the efficiencies of these two BAFs were compared for simultaneous removal of organic pollutants, NH_3-N and TP from raw wastewater. The results are summarized as follows:

(1) Both BAFs had excellent COD and NH_3-N removal efficiency when HRT was longer than 4 h, and oyster shell BAF had higher removal efficiency than plastic ball BAF.
(2) When the pH of oyster shell BAF effluent was changed from neutral to 9 and 10, the TP removal efficiency could be increased from 23.2% to 79.9% and 90.6%, respectively.
(3) Oyster shell is a good medium of BAF to treat municipal wastewater, especially those with higher concentration of phosphorus.

Acknowledgements

This work was supported by the Guangdong-HK Technology Cooperation Funding Scheme through grant no. 08Lh-04.

References

[1] L. Qiu, J. Ma, L. Zhang, Characteristics and utilization of biologically aerated filter backwashed sludge, Desalination 208 (2007) 73–80.
[2] M. Allan, M.E. Leopoldo, S. Tom, A comparison of floating and sunken media biological aerated filters for nitrification, Chem. Technol. Biotechnol. 72 (1998) 273–279.
[3] H.D. Stensel, S. Reiber, Industrial wastewater treatment with a new biological, Environ. Prog. 2 (1983) 110–115.
[4] L. Qiu, J. Ma, L. Zhang, Y. Yang, Nitrification performance and its kinetic characteristic of biological aerated filter (BAF), Conference of the International-Water-Association (IWA), Future of Urban Wastewater Systems (FUWWS) — Decentralization and Reuse, Xi'an, China, 2005, pp. 769–777.
[5] T. Stephenson, High rate aerobic wastewater treatment processes—what next? Proceedings of the Third International Symposium on Environmental Biotechnology, vol. 1, April 21–23 2007, pp. 57–66, Ostend, Belgium.
[6] W. Chang, S. Hong, J. Park, Effect of zeolite media for the treatment of textile wastewater in a biological aerated filter, Process Biochem. 37 (2002) 693–698.
[7] A. Kantardjieff, J.P. Jones, Aerobic biofilter treatment of slaughterhouse effluent, Proceedings of 51st Purdue Industrial Waste Conference, Ann Arbor, MI, 1996, pp. 595–600.
[8] A. Kantardjieff, J.P. Jones, Practical experiences with aerobic biofilters in thermo-mechanical pulping (TMP), sulfite and fine paper mill in Canada, Water Sci. Technol. 35 (1997) 227–234.
[9] X. Zhao, Y. Wang, Z. Ye, Oil field wastewater treatment in biological aerated filter by immobilized microorganisms, Process Biochem. 41 (2006) 1475–1483.
[10] J.A. Herrera Melián, A. Ortega Méndeza, J. Araña, O. González Díaza, E. Tello Rendóna, Degradation and detoxification of formalin wastewater with aerated biological filters and wetland reactors, Process Biochem. 43 (2008) 1432–1435.
[11] H. Ryu, D. Kim, H. Lim, S. Lee, Nitrogen removal from low carbon-to-nitrogen wastewater in four-stage biological aerated filter system, Process Biochem. 43 (2008) 729–735.
[12] C. Wang, J. Li, B. Wang, G. Zhang, Development of an empirical model for domestic wastewater treatment by biological aerated filter, Process Biochem. 41 (2006) 778–782.

[13] A.T. Mann, T. Stephenson, Modelling biological aerated filters for wastewater treatment, Water Res. 31 (1997) 2443–2448.

[14] M. Rozic, S.C. Stefanonvic, S. Kuranjica, V. Vancina, E. Hodzic, Ammoniacal nitrogen removal from water by treatment with clays and zeolites, Water Res. 34 (2000) 3675–3681.

[15] C.L. Yoon, B.T. Kim, B.O. Kim, S.H. Han, Chemical–mechanical characteristics of crushed oyster-shell, Waste Manage. 23 (2003) 825–834.

[16] State Environmental Protection Administration of China, Monitoring and Analysis Methods of Water and WastewaterFourth ed, China Environmental Science Press, Beijing, 2002.

[17] F. Liu, C.C. Zhao, D.F. Zhao, G.H. Liu, Tertiary treatment of textile wastewater with combined media biological aerated filter (CMBAF) at different hydraulic loadings and dissolved oxygen concentrations, J. Hazard. Mater. 160 (2008) 161–167.

[18] S.J. Park, J.W. Oh, T.I. Yoon, The role of powdered zeolite and activated carbon carriers on nitrification in activated sludge with inhibitory materials, Process Biochem. 39 (2003) 211–219.

[19] M. Sarioglu, Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite, Sep. Purif. Technol. 41 (2005) 1–11.

[20] H. Carlsson, N. Aspergen, N. Lee, A. Hilmer, Calcium phosphate precipitation in biological phosphorus removal systems, Water Res. 31 (1997) 1047–1055.