

# Using a zeolite medium biofilter to remove organic pollutant and ammonia simultaneously

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**Abstract:** A pilot scale zeolite medium biological aerated filter (ZBAF) was designed and used to treat municipal wastewater. It showed that ZBAF could simultaneously remove chemical oxygen demand (COD), ammonia-N and turbidity to satisfied degree at a hydraulic retention time (HRT) of 0.95 h. Their average removal efficiencies were 73.9%, 88.4% and 96.2% with the corresponding average effluent concentrations of 43.4 mg/L, 3.5 mg/L and 3.7 NTU, respectively. These effluent items met with the water quality standard of the treated water reused for cooling water. The COD removal volumetric loading rate increased proportionally with its applied volumetric loading rate with its maximum of 7.1 kg/(m<sup>3</sup>·d). Ammonia-N removal loading rate also increased proportionally with its applied loading rate at HRT of longer than 0.95 h and the feasible maximum removal loading rate was 0.9 kg/(m<sup>3</sup>·d). The COD loading rate did not affect the ammonia-N removal efficiency significantly when it was lower than 5.5 kg/(m<sup>3</sup>·d). ZBAF has good application prospect for its low cost and high removal efficiency in the future.

**Keywords:** ammonia-N removal; biological aerated filter; hydraulic retention time; natural zeolite; volumetric loading rate

## Introduction

Water shortage problem is quite serious in many cities of China. The reuse of municipal wastewater is one of the key methods to release this problem. Makeup water for recirculating cooling system is the largest water usage in many factories. The water quality standards for reclaimed water using as makeup water of cooling system are very strict. For example, chemical oxygen demand (COD), ammonia-N and turbidity standards are 60 mg/L, 5 mg/L and 5 NTU, respectively (Dong, 2000).

Biological aerated filters (BAFs) are one type of the attractive choices to treat municipal wastewater to be reusable water for cooling system for their high nitrification efficiency. The high nitrate concentration in effluent does not harm the cooling system. Moreover, BAFs have the advantages of lower capital costs, no secondary clarifiers, smaller footprint, fewer odors, no solid bulking issues, modular construction and automated operation, and so on (William, 1997). For example, eight full-scale up-flow aerated Biofor biofilters installed at West Basin Recycling Plant (California, USA) have continuously produced reliable high quality ammonia-free water, which has been reused as cooling water in oil refineries for more than 5 years (Lazarova, 1999).

The filter medium in BAFs represents a significant proportion of the initial capital outlay. It greatly affects daily running costs such as energy consumption cost for backwashing (Letterman, 1980). At present, the widely used medium is expanded clay that is manufactured at high temperature. The manufacture process consumes great energy and occupies large land resource that results in a high price for clay medium.

Natural zeolite is a potential filter medium for BAF. It is a nonmetallic mineral with the characteristics of high porosity and large specific surface area. Additionally, it has preferential ammonium ion exchange capability and has been used to enhancing the nitrification of biofilters and equalizing the ammonia peaks from secondary effluent (Oldenburg, 1995; Baykal, 1996; 1998). However, it has not been

found the reports on removing organic pollutants and ammonia nitrogen simultaneously from wastewater by using zeolite medium biofilter.

Natural zeolite is abundant and widely exists in China. Our previous studies (Tian, 2003) indicate that the characteristics of zeolite are similar to that of expanded clay in density, porosity and minimum fluidization velocity. The surface of the zeolite is very coarse so that it shows good biofilm attachment properties. Therefore, zeolite might be a good filter medium to replace clay for BAF. The price of zeolite is only 1/4—1/6 of that of expanded clay. Therefore, it could greatly decrease the cost of biofilter by using zeolite as the medium.

This paper studied the feasibility of using a ZBAF to simultaneously remove COD and ammonia-N from domestic wastewater and to make the effluent quality meet with the water quality standards for cooling water. Performance of the ZBAF was evaluated at various hydraulic retention times (HRTs). The feasible operational parameters, such as HRT, maximum volumetric removal loading rate were obtained. The influence of COD loading rate on ammonia-N removal loading rate was also examined.

## 1 Materials and method

### 1.1 Experimental setup

The experiment was done with a down-flow ZBAF. The ZBAF was an organic glass cylinder of 5.5 m in height and 0.2 m in diameter (Fig. 1). The medium was natural zeolite of 4—6 mm in diameter that was from Zhejiang Province of China. Characteristics of the zeolite are shown in Table 1. The diameter of the column was nearly 50 times of that of the filter medium to limit the wall effect (Moore, 2001). The bioreactor was packed with zeolite of 3.0 m in height and it was divided into two zones by the air diffuser: aeration zone (2.1 m) and filtration zone (0.9 m). Sewage from Tsinghua University was settled in a sewage tank firstly and then pumped by a metering pump to the reactor. A fine screen was fixed at the inlet of the pump to prevent clogging.

### 1.2 Experimental conditions and methods

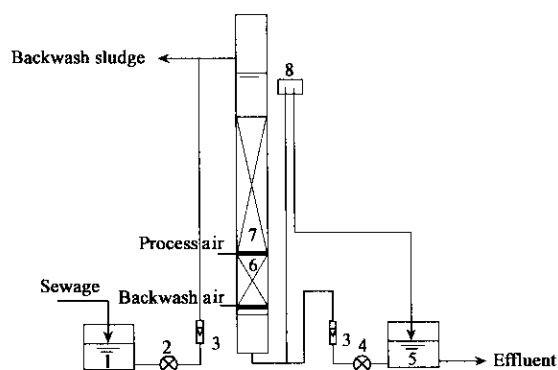


Fig.1 Schematic description of the process

1. sewage tank; 2. metering pump; 3. flow metric; 4. backwash pump;
5. effluent tank; 6. filter section; 7. oxidation section; 8. effluent weir

To shorten the startup time, the ZBAF was seeded with the sludge

Table 1 Characteristics of the zeolite

Size range, Mm	Density, kg/m <sup>3</sup>	Bulk density, kg/m <sup>3</sup>	External porosity, %	Internal porosity, %	SSA*, m <sup>2</sup> /g	V <sub>mf</sub> **, m/h	Mohn hardness	Stable temperature, °C	Silicon/alumina
4—6	2266	944	43.9	12.3	6.66	179	3—4	750	4.3—5.3

Notes: \* specific surface area; \*\* minimum fluidization velocity

Table 2 Experimental conditions

Experimental run	I	II	III	IV
Sewage flow, L/h	30	60	90	120
Hydraulic loading rate, m/h	1.1	2.2	3.3	4.4
HRT of aeration zone, h	1.9	0.95	0.64	0.48
HRT of filtration zone, h	0.82	0.41	0.27	0.20
Total HRT, h	2.72	1.36	0.91	0.68

## 2 Results and discussion

### 2.1 System performance

Table 3 shows the average removal efficiencies of COD, ammonia-N and turbidity under different HRTs. The average removal efficiencies of COD, ammonia-N and turbidity were 87.8%, 95.3% and 97.3% respectively when the HRT of aeration zone was 1.9 h. Their removal efficiencies reached 73.9%, 88.4% and 96.2% as HRT was decreased to 0.95 h. It indicates that ZBAF can remove COD, ammonia-N and turbidity efficiently within only 1 h. At HRT of 0.95 h, the average effluent concentrations were 43.4 mg/L for COD, 3.5 mg/l. for ammonia-N and 3.7 NTU for turbidity, respectively. The effluent quality items met with the standards of the treated water reused for cooling water.

Table 3 Average removal efficiency of COD, ammonia-N and turbidity at different HRT

Experimental run	I	II	III	IV
COD removal efficiency, %	87.8	73.9	66.9	60.9
Ammonia-N removal efficiency, %	95.3	88.4	43.3	32.8
Turbidity removal efficiency, %	97.3	96.2	84.0	79.6

The removal efficiencies of the three pollutants decreased sharply to 66.9%, 44.3% and 84.0%, respectively as HRT was decreased to 0.64 h. Their removal efficiencies decreased further to 60.9%, 32.8% and 79.6% when HRT decreased to 0.48 h. This suggests that HRT affected the removal efficiency considerably.

### 2.2 Influence of HRT on the removal of COD, ammonia-N and

from other BAF in the Lab. The effluent was recirculated back to the inlet of the ZBAF to avoid the loss of biomass at the first three days. Then the ZBAF was operated with a flow rate of 1.1 m/h. After 35 d operation, ammonia-N in the effluent was constantly low, which signed that nitrobacteria biofilm was firmly formed in the ZBAF (Tian, 2002). Then four runs of experiments were conducted with the hydraulic loadings of 1.1, 2.2, 3.3 and 4.4 m/h and the corresponding HRTs of 1.90, 0.95, 0.64 and 0.48 h for the aeration zone. The ratio of gas to water was 4:1 and DO in water maintained at above 2 mg/L to supply enough oxygen for the nitrobacteria. The temperature was 23—29°C. COD, ammonia-N (NH<sub>4</sub><sup>+</sup>-N) and turbidity were measured once daily by using the standard methods when the ZBAF operational state was stable (APHA/AWWA/AWEF, 1995). The experimental conditions are summarized in Table 2. The filter was backwashed using water and air scour simultaneously when the head loss reached 1.2 m.

### turbidity

HRT is a very important parameter that determines the system performance and the construction cost. Figs. 2, 3 and 4 depict the daily operational data of COD, ammonia-N concentration and turbidity in influent and effluent at different HRTs, as well as the corresponding removal efficiency. The decrease of HRT had much greater effects on the removal of ammonia-N than those of COD and turbidity. Ammonia-N concentration in effluent increased sharply as HRT was decreased from 0.95 h to 0.64 h. However, the change of COD concentration and turbidity in effluent were not so great.

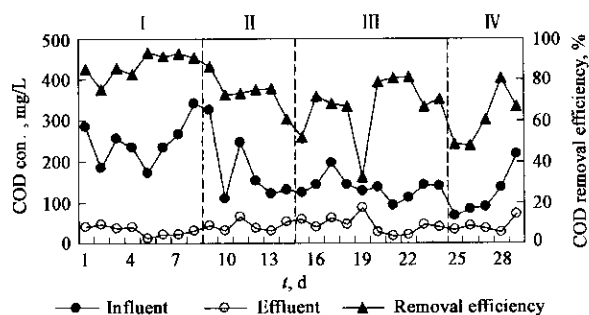


Fig.2 Influence of HRT on COD removal efficiency

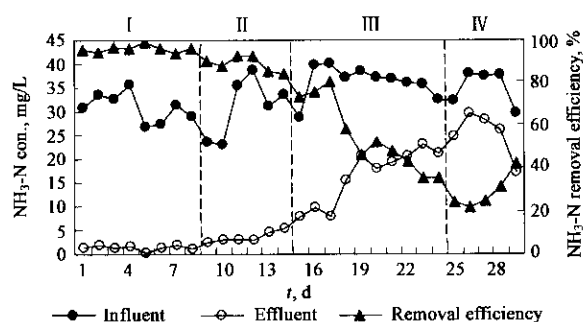


Fig.3 Influence of HRT on ammonia-N removal efficiency

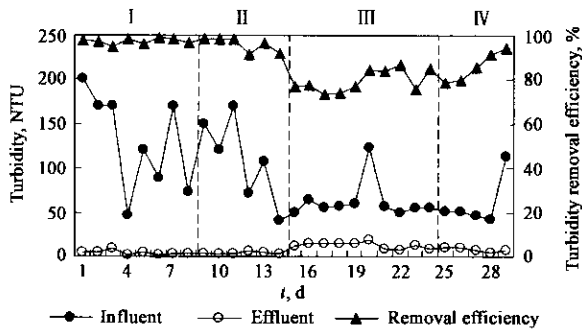


Fig. 4 Influence of HRT on turbidity removal efficiency

Shorter HRT means smaller footprint, which can save the construction cost of ZBAFs. Since ammonia-N is one of the major removal targets and the most sensitive parameter to the decrease of HRT for this ZBAF, a special attention should be paid to the removal efficiency and effluent concentration of ammonia-N to determine the feasible HRT. The feasible HRT was about 1 h and the ammonia-N could effectively removed and its effluent concentration met with the value of the standards of the treated water reused for cooling water.

### 2.3 Relationship between applied volumetric loading rate and removal loading rate

Besides HRT, another important parameter for BAF is the maximum removal volumetric loading rate (volumetric loading rate is shortened as loading rate in the following discussion). Loading rate is expressed as the amount of pollutant per cubic meter of the medium per day. Fig. 5 shows the relationship between the COD removal loading rate and its applied loading rate at different HRTs. It indicated that COD removal loading rate increased proportionally with its applied loading rate, the slope varied with the HRT. The maximum removal loading rate reached 7.1  $\text{kg}/(\text{m}^3 \cdot \text{d})$  with the applied loading rate of 8.2  $\text{kg}/(\text{m}^3 \cdot \text{d})$  and the removal efficiency of 86.6%.

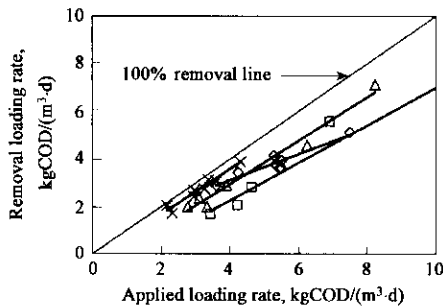


Fig. 5 Relationship between COD removal loading rate and its applied loading rate

I.  $\times$ :  $y = 0.959x - 0.269$ ,  $R^2 = 0.949$ ; II.  $\triangle$ :  $y = 0.918x - 0.722$ ,  $R^2 = 0.977$ ; III.  $\diamond$ :  $y = 0.531x + 1.014$ ,  $R^2 = 0.887$ ; IV.  $\square$ :  $y = 0.782x - 0.836$ ,  $R^2 = 0.945$

Fig. 6 shows the relationship between the ammonia-N removal loading rate and its applied loading rate at different HRTs. The ammonia-N removal loading rate increased proportionally with its applied loading rate at HRT of 0.95 h and the removal efficiency was close to 100%. But the ammonia-N removal loading rate was no longer proportionally increased with its applied loading rate and decreased as HRT below 0.95 h. The feasible maximum ammonia-N removal loading rate was 0.9  $\text{kg}/(\text{m}^3 \cdot \text{d})$  when the applied ammonia-N loading rate was

1.0  $\text{kg}/(\text{m}^3 \cdot \text{d})$  and the corresponded removal efficiency was 90%, though the maximum removal loading rate was able to reach 1.21  $\text{kg}/(\text{m}^3 \cdot \text{d})$ .

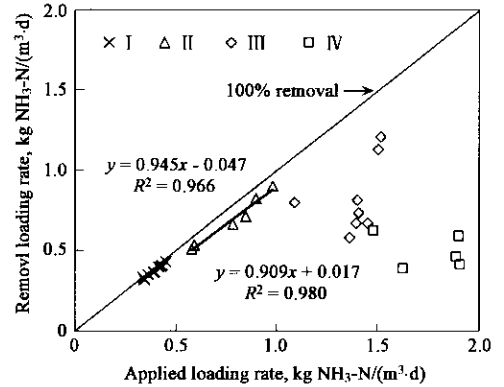


Fig. 6 Relationship between ammonia-N removal loading rate and its applied loading rate

### 2.4 Influence of COD applied loading rate on ammonia-N removal loading rate

Fig. 7 shows the change of ammonia-N removal loading rate with the COD applied loading rate. There was no apparent relationship between them. Previous studies (Gilmore, 1999; Fdz-Polanco, 2000) suggested that COD loading rate had adverse influence on ammonia-N removal. Having short generation time, heterotrophic bacteria grow fast and often dominate in the competition with other biological species in mixed culture. Nitrobacteria have long generation time and they are easily affected by the circumstance. So there was competition between them for oxygen and space in the aerated microfilm bioreactor. It appears that COD applied loading rate was not too high enough to prohibit the nitrifier activity significantly in this study. Another reason was that ZBAF had good performance to resist ammonia-N shock loading. The ammonia-N removal loading rate was not affected when the COD applied loading rate was below 5.5  $\text{kg}/(\text{m}^3 \cdot \text{d})$ .

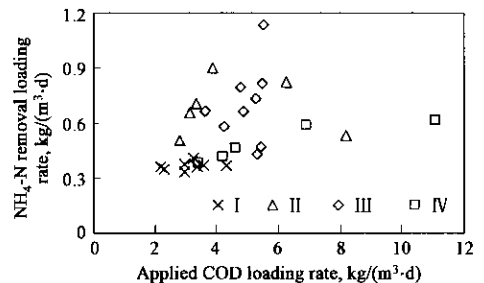


Fig. 7 Influence of COD applied loading rate on ammonia-N removal loading rate

### 2.5 Evaluation on the ZBAF performance

The feasible maximum ammonia-N removal loading rate reached 0.9  $\text{kg}/(\text{m}^3 \cdot \text{d})$  when COD applied loading rate was below 5.5  $\text{kg}/(\text{m}^3 \cdot \text{d})$  at 0.95 h HRT and the effluent item's quality met with the standards of the treated water reused for cooling water. The high COD and ammonia-N removal efficiencies were due to the good performance of ZBAF. Zeolite medium with large available surface for biofilm formation played good role in this performance. The biomass attached on the surface of the zeolite reached 4—5  $\text{kgVSS}/\text{m}^3$  in decarbonization zone and 0.5—2.0

kgVSS/m<sup>3</sup> in nitrification zone. The ZBAF high resistance to ammonia-N shock loadings was due to higher ammonia-N exchange capacity of zeolite that reached 1.67 mg/g (Tian, 2003). The zeolite can still exchange ammonia after having biofilm attached on its surface. Since its low price and high pollutant removal efficiency, ZBAF has good application prospect in the future.

The shortage of ZBAF is that zeolite shape is not regular so that it is easier to abrade in backwash. High intensity and proper size zeolite is ideal for application.

### 3 Conclusions

ZBAF can simultaneously remove COD, ammonia-N and turbidity effectively at HRT of 1 h. Their average removal efficiencies were 73.9%, 88.4% and 96.2% with the corresponding average effluent concentration of 43.4 mg/L, 3.5 mg/L and 3.7 NTU, respectively. These effluent items quality met with the water quality standards of the treated water reused for cooling water.

HRT had much greater effect on the removal of ammonia-N than those of COD and turbidity. The feasible HRT was about 1 h for the removal of COD and ammonia-N simultaneously.

COD removal loading rate increased proportionally with its applied loading rate and its maximum removal loading rate reached 7.1 kg/(m<sup>3</sup>·d). Ammonia-N removal loading rate increased proportionally with its applied loading rate when the HRT was longer than 0.95 h. The feasible maximum ammonia-N removal loading rate was 0.9 kg/(m<sup>3</sup>·d).

COD applied loading rate did not prohibit nitrification significantly when it was below 5.5 kg/(m<sup>3</sup>·d).

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### References:

APHA /AWWA/AWEF, 1995. Standard methods for the examination of water and

wastewater[M]. 19th edn. Washington D. C.: American Public Health Association.

- Baykal B B, Guven D A, 1996. Performance of clinoptilolite alone and in combination with sand filters for the removal of ammonia peaks from domestic wastewater[J]. *Wat Sci Technol*, 35: 47—54.
- Baykal B B, 1998. Clinoptilolite and multipurpose filters for upgrading effluent ammonia quality under peak loads[J]. *Wat Sci & Tech*, 37: 235—242.
- Dong F X, Dong X D, 2000. Theory of city and industrial water saving[M]. Beijing: China Architecture Industry Press. 232—237.
- Fdz Polanco F, Méndez E, Urtiaga M A *et al.*, 2000. Spatial distribution of heterotrophs and nitrifiers in a submerged biofilter for nitrification[J]. *Wat Sci & Tech*, 34: 4081—4098.
- Gilmore K R, Husovitz K J, Holst T, 1999. Influence of organic and ammonia loading on nitrifier activity and nitrification performance for a two-stage biological aerated filter system[J]. *Wat Sci & Tech*, 39: 227—234.
- Lazarova V, Perera J, Bowen M, 1999. Application of aerated biofilters for production of high quality water for industrial reuse in West Basin[J]. *Wat Sci & Tech*, 41: 417—424.
- Letterman R A, 1980. Economic analysis of granular bed filtration[J]. *J Env Eng (ASCE)*, 106: 279—291.
- Moore R, Quarmby J, Stephenson T, 2001. The effects of medium size on the performance of biological aerated filters[J]. *Water Res*, 35: 2514—2522.
- Oldenburg M, Sekoulov I, 1995. Multipurpose filters with ion exchanger for the equalization of ammonia peaks[J]. *Wat Sci Technol*, 32: 199—206.
- Tian W H, Wen X H, Qian Y, 2003. Study on the feasibility of zeolite as biological aerated filter (BAF) medium[J]. *Environmental Engineering*(in press).
- Tian W H, Wen X H, Qian Y, 2002. Characteristics of zeolite medium biological aerated filter during startup [J]. *Technique and Equipment for Environmental Pollution Control*, 3(12): 38—42.
- William S M, 1997. Biological aerated filters: a new alternative [J]. *Water Environment and Technology*, 9: 39—43.

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