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Investigation of Characteristics and Mechanism for Removal of Ammonia by a Suspended Medium-zeolite Biological Aerated Filter

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This paper aimed to investigate characteristics and mechanism of the suspended medium-zeolite biological aerated filter (SZBAF) in micro-polluting source water ammonia removing and provide a reference for SZBAF optimization. Different ammonia concentration of raw water (about 2 mg/l and about 4 mg/l) and different zeolite size (1-3mm and 3-5mm) were investigated. Results showed different environment could change the ammonia removing mechanism and microbial community. Higher ammonia loading was beneficial to nitrobacteria proliferation and could enhance nitrification performance. Otherwise, smaller grain size was beneficial to adsorbing ability.

1. Introduction

Ammonia contamination in drinking water attracts much attention due to its serious perniciousness and degradation-resistant to regular water treatment. Too much ammonia exist in source water will lead to many disinfection by-products (Hong et al., 2008). Also incomplete oxidation will generate nitrite that is related to several diseases such as methmoglobinemia and carcinogenesis. Furthermore, ammonia will feed autotrophic bacteria and deteriorate water quality in municipal pipe (Han et al., 2013).

The current methods of removing ammonia in drinking water mainly include ion exchange method (Li et al., 2011; Hedstrom, et al., 2011) and biological method (Bond et al., 2011; Rožić et al., 2000). As the limitation of adsorbing capacity, ion exchanger needs to be regenerated periodically and that leads to a higher investment and a complicated operation. Hence, ion exchange method generally deals with micro-polluted water and applies in small scale water works. Biological method is a green technology in consideration of its low cost, sustainability, easy operation and non-secondary-pollution.

Nitrobacteria is the predominant functional bacteria in biological ammonia removing but it is sensitive to many factors such as influent composition, process configuration and parameters (Chen et al., 2017). As the main nutrient of nitrobacteria proliferation, ammonia feed is the dominant component. Different NH^{4+}-N and organic loading could change the community structure of ammonia oxidizing bacteria (AOB) under-loaded of ammonia nitrogen would lead to less proliferation of AOB (Young et al., 2017). Also sudden change of influent could influence the microbial community (Jr K W et al., 2010). Microbial community structure varies greatly in different process configuration. Furthermore, even in the same process configuration, microbial community could be different in different operating parameters. The cultivating environment should provide a restrict aerobic condition, enough inorganic carbon for autotrophic organisms proliferation (Rittmann et al., 2001), a proper pH (an optimal range of 7-8) (Sharma et al., 1977) and a suitable packing medium to support fixed biomass (Andersson et al., 2001).

This paper investigated the SZBAF characteristics and mechanism for removal of ammonia in different ammonia loading (about 2 mg/l and about 4 mg/l) and different zeolite size (1-3mm and 3-5mm). Different operating condition could influence the removing mechanism (adsorption and nitrification) and the microbial community. Adjustment of macroscopic parameters for achieving a higher ammonia removal rate and an

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advantage of nitrobacteria in microbial community is significant in technology implementation. In previous study, SZBAF is proved to be an effective process for ammonia removing (Han et al., 2013), this paper provides a reference for SZBAF optimization.

2. Materials and methods

2.1 Experimental set-up

Four identical reactors (Fig 1) were applied in the experiment. Each reactor had a height of 1600mm, with an upper layer of 1000mm (packed with 90% fill of zeolite), a lower layer of 500mm (packed with 80% fill of suspended media made of polyvinyl chloride) and a water distribution layer of 100mm at the bottom, inner diameter was 70mm. Six sampling points were distributed along the column every 200mm intervals from the bottom to the top. Both water and air were upward flow. 1# and 2# reactor were packed with zeolite size of 1-3mm, 3# and 4# reactor were packed with zeolite size of 3-5mm.

2.2 Raw water

Raw water used in the experiment was collected from the lake in the Logistical Engineering University, Chongqing, China. During the experiment, pH of the water was 6.8-7.9, turbidity was 5.2-11, TOC was 9-11 mg/l, TN was 1.2-1.8 mg/L, ammonia was 0.2-0.6 mg/l, nitrite was below 0.01mg/l, nitrate was 0.4-0.6mg/l, dissolved oxygen was 5.1-6.2 mg/l. NH_4Cl was dosed in raw water to maintain different ammonia concentration. 1# and 3# reactor were about 2 mg/l, 2# and 4# reactor were about 4 mg/l.

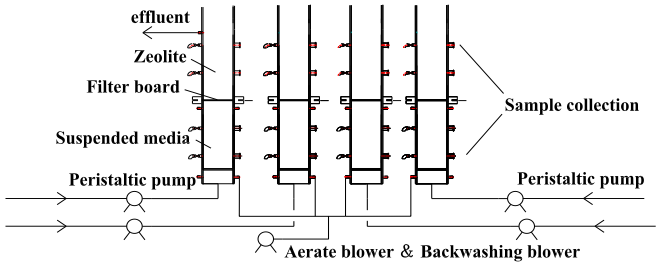

Figure 1: Schematic diagram of the system

2.3 Operating condition

Stage 1: Natural inoculation. The temperature of raw water was 18-20°C, aeration rate was 200mL/min, flow rate was 2.9L/h, hydraulic retention time was 2h.
Stage 2: Natural inoculation failed to inoculate nitrobacteria into the system. Then seed sludge was collected from a neighboring ammonia heavily polluted river and spread it out evenly on the bottom of raw water tank. The temperature of raw water was 18-20°C, aeration rate was 200mL/min, flow rate was 2.9L/h, hydraulic retention time was 2h. Self-circulation was adopted to promote the attachment of sediment on the zeolite. Ammonia concentration was also maintained at about 2 mg/L and 4 mg/L respectively everyday.
Stage 3: Continuous flow. Seed sludge was still remained in raw water tank to keep the consistency of water quality. The temperature of raw water was 18-20°C, aeration rate was 200mL/min, flow rate was 2.9L/h, hydraulic retention time was 2h.
Stage 4: The temperature of raw water was 11-15°C(as the winter coming), aeration rate was 200mL/min, flow rate was 2.9 L/h, hydraulic retention time was 2h. Seed sludge was still remained in raw water tank.

2.4 Analytical methods

Ammonia nitrogen, nitrite, nitrate and TN of influent and effluent were analyzed everyday according to standard methods. TOC was determined by the TOC analyzer (multi N/C 2100S, JENA, German). DO, pH and temperature were detected by the multi-analyzer (mutiHQ40d, HACH, America). All the samples were pretreated by a 0.45 μm micro-filtration membrane.

2.5 Polymerase chain reaction (PCR) amplification and denaturing gradient gel electrophoresis (DGGE)

The V3 region of 16S rRNA genes were amplified by using primers of F357GC (5'- CGC CCG CCG CGC GCG GCG GGC GGG GCG GGGGCA CGG GGG GCC TAC GGG AGG CAG CAG -3') and R518 (5'-ATTACC GCG GCT GCT GG -3'). The final PCR mixture (50μL) contained 41.25μL double distilled H_2O, 5μL

10× PCR buffer (including2.0 mM $MgCl_2$), 1μL deoxynucleoside triphosphates (10 mM), 1μL F357-GC (10μM), 1μL R518 (10μM), 0.25μL Taq polymerase (5U/μL), 0.5μL model DNA. Negative control was set. The touchdownPCR protocol included 4 min of initial denaturation at 94 °C, 30 cycles of 94°Cfor 0.5 min, 56°C for 1 min, 72°C for 0.5 min; followed by final extension of 72 °C for 7 min. PCR products (3μL) were detected by electrophoresis on a 1.5% agarose gel stained with 5% gold view.

DGGE was performed on a D-code mutation detection system. Samples containing approximately equal amounts of PCR amplicons were loaded onto 8% (wt/vol) polyacrylamide gels (37.5:1, acrylamide: bisacrylamide) using a denaturing gradient ranging from 30% to 60% denaturant (100% denaturant contains 7 M urea and 40% (v/v) formamide in 1×TAE). Electrophoresis was performed at 60 °C and 180V for 4h. Bacterial community structures were visualized and photographed using UVI system (Gene Genius, England).

3. Results and discussion

3.1 Nitrogen transformation

Nitrogen transformation revealed the ammonia removal mechanism of SZBAF. Ammonia, nitrite and nitrate were the three main forms of nitrogen in the SZBAF. Variation of the three forms were presented in Fig.2-4 to depict nitrogen transformation. TN concentration was also investigate considering the adsorption effect.

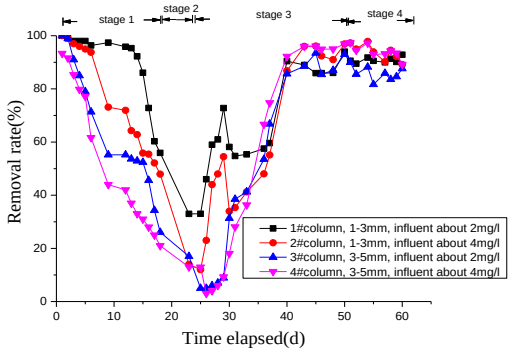

Figure 2: Ammonia removal of each column

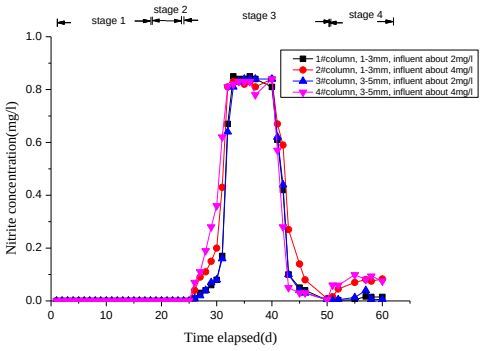

Figure 3: Nitrite accumulation of each column

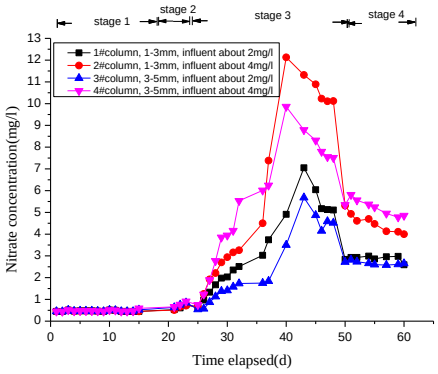

Figure 4: Nitrate concentration of each column

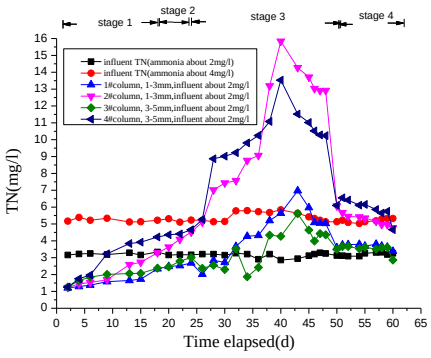

Figure 5: TN concentration of each column

Before the inoculation of seed sludge, ammonia removing mainly depended on adsorption of zeolite. However, disadvantage of adsorption was obvious. Adsorbing ability would decrease with the increasing of operation time. Ammonia removal rate of 1-4# column were 92.23%, 62.79%, 52.91%, 33.12% in 10th day and decreased to 33.28%, 12.72%, 5.61%, 2.93% in 25th day. Higher ammonia concentration would add load to zeolite and led to lower removal rate, so ammonia removal rate of 1# and 3# column (about 2 mg/l) were higher than 2# and 4# column (about 4 mg/l). Otherwise, smaller zeolite size could have a lager specific surface area, which was beneficial to ammonia adsorption. So ammonia removal rate of 1# and 2# (1-3mm) column were higher than 2# and 4# (3-5mm) column.

After the successful inoculation of nitrobacteria in stage 2, biological nitrification gradually increased. Ammonia removal rate of 1-4# column reached to an average of 87.82%, 92.82%, 89.27%, 94.81%, respectively (Fig 2).

Effluent ammonia concentration was always below 0.3 mg/l, which was within the standard limitation in China (0.5mg/l). After the saturation of zeolite adsorption, biological nitrification was the dominant part in ammonia removing. Results showed the advantage of its sustainability and high efficiency for ammonia removing. Notably, after 30th days, desorbed ammonium was degraded into nitrate by nitrobacteria again and led to the higher nitrate concentration and TN of effluent than influent (showed in Fig 4 and Fig 5). This suggested that intense nitrification could recover adsorbing ability of zeolite. Results revealed the relationship of biological nitrification and zeolite adsorption. Biological nitrification was the dominant part and adsorption was a favorable additional supplement for ammonia removing, corporation and mutual transformation of the two effects helped to build the ammonia removing system. Otherwise, nitrification of 2$^{\#}$ column and 4$^{\#}$ column (about 4 mg/l) were much more intense than 1$^{\#}$ column and 3$^{\#}$ column (about 2 mg/l). The reason was that increase of ammonia loading could promote proliferation of nitrobacteria and increase the proportion in the biofilm.

In stage 4 (11-15 °C), a significant decrease of nitrate transformation was observed (Fig 4). Decrease of temperature could inhibit nitrobacteria activity (Bae et al., 2001). However, ammonia removal rate was not influenced (showed in Fig. 2). The average ammonia removal rate of 1$^{\#}$ - 4$^{\#}$ column were 91.19%, 92.63%, 86.68% and 94.33%, respectively. Effluent ammonia concentration of each column was still below 0.4 mg/l. Statistics showed system had much stability in temperature decreasing shock.

3.2 Variation along the BAF

Variation of ammonia removing rate and DO concentration along the BAF was investigated in this experiment. 0-400mm was the lower layer (suspended medium), 400mm above was the upper layer (zeolite). Fig. 6 reflected condition of stage 1-4 and data were collected in the end of each stage.

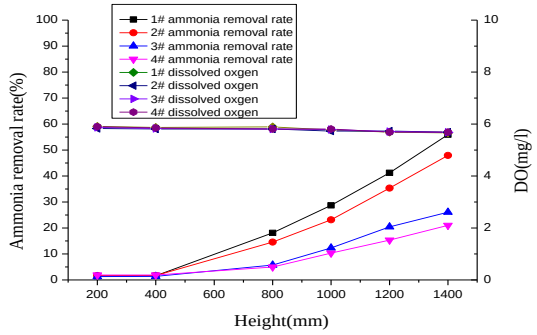

Figure 6: Variation along the BAF of stage 1

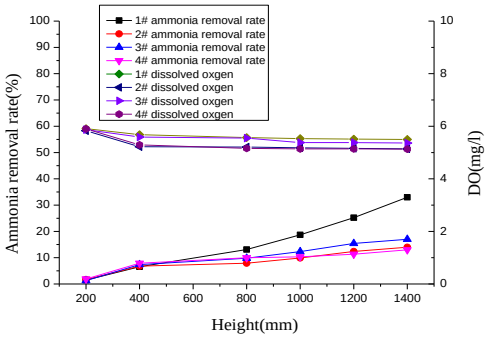

Figure 7: Variation along the BAF of stage 2

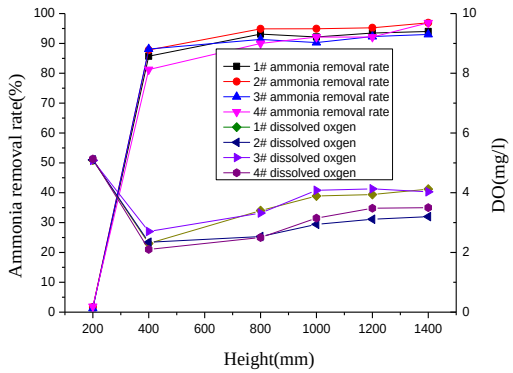

Figure 8: Variation along the BAF of stage 3

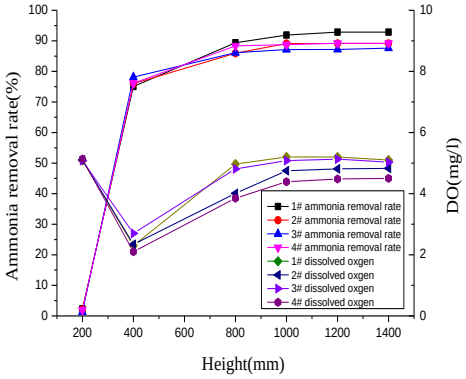

Figure 9: Variation along the BAF of stage 4

Stage 1 was the dynamic adsorption stage and mainly occurred in the zeolite layer (400mm above), so ammonia removal well-distributed along 400-1400mm BAF. Advantages of smaller grain size and lower ammonia loading were obvious in each subsection. In stage 2 weak nitrification existed in the lower layer and DO concentration began to decrease. However, ammonia removal still mainly depended on the adsorption of

zeolite. After long term system operation, zeolite adsorption reached to its saturation. Noticeably, with the lower influent ammonia concentration (2mg/l) and the smaller grain size (1-3mm), 1# column showed a much higher efficiency in ammonia adsorbing than others. Stage 3 and stage 4 were quite the same in ammonia removing, which mainly focused in the lower layer. Nevertheless, DO concentration was different. DO concentration of stage 3 of 400mm above was much lower than stage 4. In stage 4, adsorption and desorption tended to an equilibrium state. But in stage 3, dramatical ammonia desorption of zeolite along with the upper layer was oxidized by nitrobacteria again, which led to DO consumption along the upper layer.
This provided an optimization model of packing medium height. Generally, biological ammonia removal occurred at the height of 0-800 mm while physical adsorbing ammonia removal well-distributed along with the zeolite medium. Increasing of packing medium height would add investment and operation complication. 800mm was enough for micro ammonia contaminated raw water (below 4 mg/l) in normal temperature (above 10 °C) in this experiment. In the following experiment we would make some improvements in the column design.

3.3 Microbial community diversity analysis

Microbial community diversity were based on samples from biofilm of zeolite (upper layer) named as 1-4S and suspended medium (lower layer) named as 1-4X.
Alpha diversity measured the diversity of the microbial community within each column. Ace index estimated the total number of unique species. Ace of upper layer and lower layer tended to the same in one column (Fig.7), which indicated that different kind of packing medium had less influence in community diversity. Overall, 1# column and 3# column showed a higher community diversity. Higher ammonia loading promoted proliferation of nitrobacteria and helped them to outcompete in surviving. Limited resources such as dissolved oxygen and other micro-nutrients decreased for other micro bacteria, so community diversity of higher ammonia loading was lower. Results indicated ammonia loading was a key factor in community diversity.

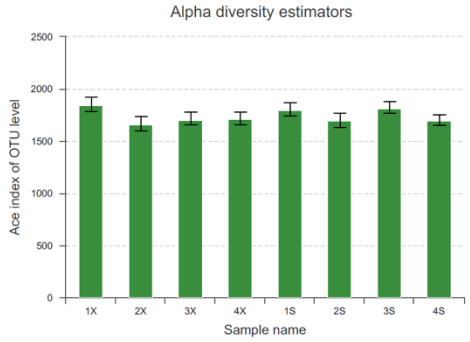

Figure 10: Ace index of each column

Color intensity was used to intuitively represent the similarities and differences among the various biomes clustering in the heatmap. Overall, there were two main clusters, one was 1# column and 3# column (2mg/l), the other was 2# column and 4# column (4mg/l). The same ammonia loading tended to a higher similarities of microbial community.
Promoting effect of high ammonia loading was noticeable on genus level analysis. Nitrosomonas and Nitrospira were the dominant nitrobacteria (Regan et al., 2003; Siripong et al., 2007). Community Percent of Nitrosomonas of 1-4# column were 6.17%, 10.47%, 5.23%, 8.57% (suspended medium) and 4.11%, 7.44%, 3.96%, 8.84% (zeolite), respectively. Nitrospira percent of 1-4# column were 1.03%, 2.12%, 1.12%, 1.29% (suspended medium) and 2.18%, 2.76%, 3.62%, 3.73% (zeolite), respectively. Candidatus_Nitrotoga was also found in the system, in previous study it was found as a nitrobacteria in sequencing batch reactor activated sludge process of 10°C (Alawi et al., 2007). and many wastewater treatment plant at a temperature about 7-16°C (Lu et al., 2012). In stage 4 the temperature was 11-15°C, which was in the same range as previous study. Community Percent of Candidatus_Nitrotoga of 1-4# column were 0.52%, 2.28%, 0.57%, 1.51% (suspended medium) and 1.07%, 1.54%, 0.35%, 1.63% (zeolite). This provided an explanation of the higher nitrate transformation and ammonia removal rate of 2# column and 4# column. Meanwhile, bigger grain size achieved a limited better nitrobacteria proliferation. The possible reason was that a bigger grain size could have a bigger interspace and pore width. Transferability of nutriment, oxygen and ammonia nitrogen could reach a higher sufficiency.

4. Conclusions

SZBAF could remove ammonia effectively. Adsorption and nitrification were the two main mechanisms in ammonia removing. Biological nitrification was the dominant part and adsorption was a favorable additional supplement for ammonia removing. Corporation and mutual transformation of the two mechanisms helped to build the ammonia removing system.

Biological ammonia removal occurred at the height of 0-800 mm while physical adsorbing ammonia removal well-distributed along with the zeolite medium. Decrease of packing medium could be an improvements in the column design in the following experiment.

Different operation condition could influence the removing mechanism and microbial community structure. Higher influent ammonia concentration would add load to zeolite adsorption and decrease ammonia removal, but it also would promote the proliferation of nitrobacteria and enhance the proportion in microbial community. Bigger zeolite grain size achieved a limited better nitrobacteria proliferation. Smaller zeolite grain size achieved a better adsorbing ability.

Acknowledgment

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