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Reduction of Precursors of Chlorination By-products in Drinking Water Using Fluidized-bed Biofilm Reactor at Low Temperature[1]

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Objective To investigate the reduction of chlorination by-products (CBPs) precursors using the fluidized-bed biofilm reactor (FBBR). **Methods** Reduction of total organic carbon (TOC), ultraviolet absorbance (UV_{254}), trihalomethane (THM) formation potential (THMFP), haloacetic acid (HAA) formation potential (HAAFP), and ammonia in FBBR were evaluated in detail. **Results** The reduction of TOC or UV_{254} was low, on average 12.6% and 4.7%, respectively, while the reduction of THMFP and HAAFP was significant. The reduction of ammonia was 30%-40% even below 3℃, however, it could quickly rise to over 50% above 3℃. **Conclusions** The FBBR effectively reduces CBPs and ammonia in drinking water even at low temperature and seems to be a very promising and competitive drinking water reactor for polluted surface source waters, especially in China.

Key words: Chlorination by-products; Low temperature; Drinking water; Fluidized-bed biofilm reactor

INTRODUCTION

Virtually all raw surface waters contain natural organic matter in which humic substances are important components. Humic substances in natural waters have been shown to be especially reactive with a variety of oxidants and disinfectants that are used for the purification of drinking water. These substances react with chlorine to produce carcinogenic THMs, HAAs, and other CBPs, a number of which have been shown to cause cancers in laboratory animals. However, chlorination of drinking water is still widely used for disinfection, especially in China, which poses toxicological threat to the safety of drinking water. Therefore, the reduction of CBP precursors is usually necessary in order to minimize the production of CBPs. Moreover, ammonia is one of the most important water quality parameters for assessing a water supply source. Since ammonia affects the disinfection process, the amount of chlorine has to be increased to ten times the concentration of ammonia in the raw water. This large amount of chlorine used in water treatment then generates THMs; therefore, ammonia elimination is also necessary before chlorination process.

In China, the predominant drinking water treatment process is still the conventional treatment process, which consists of sedimentation, coagulation/flocculation, phase separation, rapid sand filtration, and disinfection, in order to remove turbidity, color, and pathogens. Since it cannot remove the ammonia and THM precursors effectively, advanced water treatment has to be considered for the production of safer and cleaner drinking water. Nowadays in China, great attention has been paid to biological pretreatment of drinking water owing to the deterioration of surface water quality and the increasingly more stringent drinking water regulation. Biological pretreatment process (prior to conventional treatment chain) is considered as an economic and effective treatment process to remove pollutants from raw water. Among various kinds of bioreactors for pretreatment of water the biological contact oxidation reactor (BCOR) and bioceramic filter (BF) have been most widely studied in China, especially in the warm southern regions. It has many advantages, such as improvement of sequential treatment chain, reduction of chlorine demand, less production of THMs, and increased biological stability of finished water[1]. However, for various

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reasons, mainly difficult management, their application to practical projects is limited. Therefore, it is urgent to carry out studies on novel bioreactors for drinking water pretreatment.

FBBR is an innovative biofilm reactor and has two obvious advantages: no need for backwashing and easy management, which has gained increasing attention from wastewater treatment industry. It has been successfully employed in full-scale treatment of municipal and industrial wastewater. FBBR is a continuously operating non-cloggable biofilm reactor with no need for backwashing, low head-loss, and high specific biofilm surface area. This can be achieved by making the biofilm grow on small carrier elements that move along with the water in the reactor. The movement is normally caused by aeration in the aerobic version of the reactors[2-4]. However, the data concerning the operating characteristics of FBBR at low temperature (below 10℃) are not available. Moreover, this innovative biofilm reactor has not been introduced for drinking water treatment.

Yellow River is one of the largest drinking water sources in China but it is now faced with serious problems caused by pollution. The tap water quality of most water supply systems that pump water from Yellow River does not meet increasingly stringent drinking water quality criteria due to limitation of conventional drinking water treatment. Unfortunately, for many reasons researches on the improvement of drinking water quality, especially on reduction of CBP precursors, by advanced water treatment processes including biological pretreatment in Yellow River Basin are very few. Moreover, low water temperatures (below 10℃) prevail for extended periods (about four months per year) and the temperature effect on biological treatment must be seriously considered. Therefore, the investigation on reduction of the CBP precursors and ammonia using the FBBR at low temperature was the objective of this study. Moreover, this study provides fundamental data for the design of novel and safe water supply sources.

MATERIALS AND METHODS

Experimental Setup

The pilot-scale FBBR was a cuboid made of stainless steel with a total liquid volume of 6 m^3. The reactor was filled with hollow polypropylene plastic ball media (density 0.98 g/cm^3, diameter 100 mm, specific surface area 360 m^2/cm^3), occupying 11.5% of the total volume of the reactor. Mixing and aeration were provided by pressurized air through aerators in the bottom of the reactor.

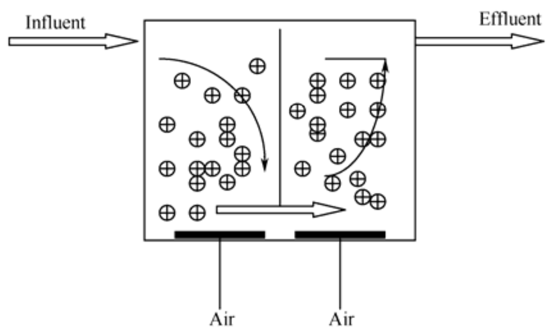

FIG. 1. Experimental setup of FBBR.

The raw water was directly taken from the source water of Shiyuan Waterworks in Zhengzhou City, namely Yellow River water after sedimentation for sand removal. The inflow for FBBR was 4 m^3/h. The pH value of raw water ranged from 8.0-8.5. Oxygen was supplied through aeration at a volume ratio of 0.25:1 (air to water) in both reactors and oxygen concentration was keep at 4-5 mg O_2/L. The study lasted for about three months in 2005. During this study the water temperature ranged from 1.2℃-10℃ (Fig. 2). Before this study the biofilm reactors were in operation for more than one year.

Analysis

UV_{254} was measured in an 1-cm quartz cell with

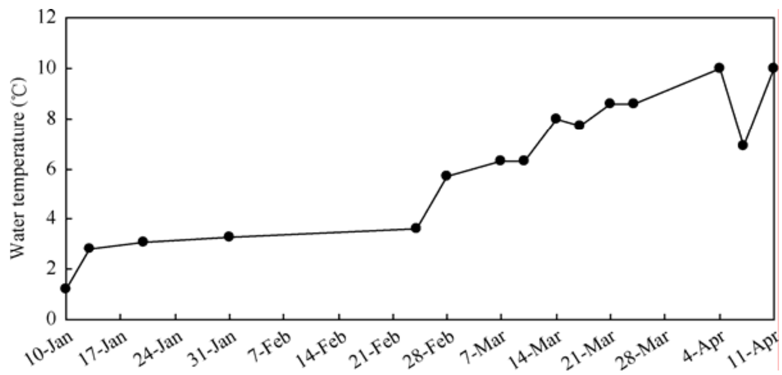

FIG. 2. Change of water temperature.

a spectrophotometer (Shimadzu UV-1200) and TOC was determined using a TOC analyzer (Shimadzu TOC-5000). Dissolved oxygen (DO), pH, and water temperatures were determined using selective electrodes. Ammonia and nitrite concentrations were measured following the standard methods[5].

The formation potential (FP) experiments for THMs and HAAs in raw water and FBBR effluent were conducted with a 7-day incubation period following the introduction of the NaOCl solution and phosphate buffer (pH 7.0). The applied chlorine concentration for formation potential experiments was about 50 mg/L, which was determined from preliminary studies and would provide a free residual chlorine of at least 3 mg/L at the end of the incubation period. The analysis of residual chlorine was preformed using the DPD (N, N-diethyl-*p*-phenylene-diamine) ferrous titration method[5]. THMs formed were extracted with *n*-pentane and the extract was then analyzed using a GC with a fused silica capillary column (DB-5, 30 m × 0.25 mm ID, 1.0 μm film thickness) and an electron capture detector. A microextraction procedure (extracting with methyl tert-butyl ether, esterifying with diazomethane) was used for HAA analysis). The esterified extract was analyzed using the same GC setup. All the analyses were performed by the QA/QC programs following the standard methods[5].

RESULTS

Removal of Precursors of CBPs

The most common indicators for natural organic matter are TOC and UV_{254}. As regards the prevention of THM generation, the TOC level is more important than that of easily biodegradable organic matter in water[6]. The reduction of TOC by the FBBR is shown in Fig. 3. During this study the TOC concentrations varied between 4.9 and 6.3 mg/L (5.5 mg/L average), and the reduction in the FBBR was 7.7%-19% (12.6% average). However, the effect of temperature rise on reduction of TOC was not obvious during this study.

UV_{254} usually shows good correlation with THM precursor and thus it is also regarded as a surrogate parameter of THM precursor although it is originally a general parameter[1]. The reduction of UV_{254} in the FBBR is shown in Fig. 4. During this study the UV_{254}

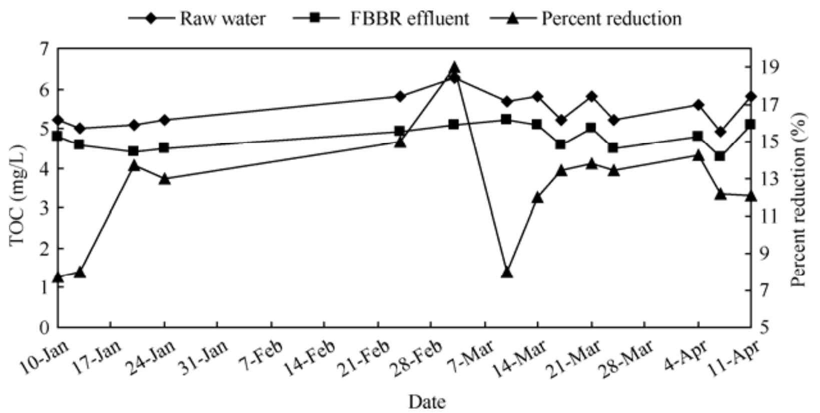

FIG. 3. TOC reduction in the FBBR.

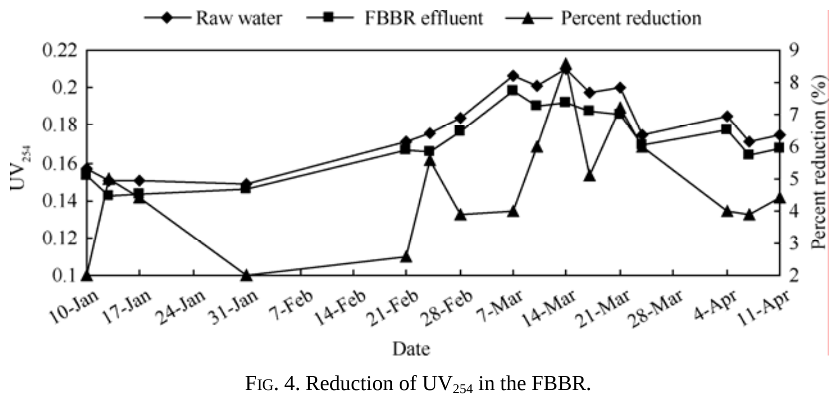

FIG. 4. Reduction of UV_{254} in the FBBR.

varied between 0.149 and 0.210 (0.179 on average), and the average reduction of UV_{254} in the FBBR was 4.7%, much lower than that of TOC (12.6% on average). Moreover, the effect of temperature rise on reduction of UV_{254} was also not obvious during this study.

The amount of precursors of CBPs in waters is usually indirectly measured by formation potential in water research. Five CBP species, including chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), DCAA, and TCAA were the major compounds detected in raw water or/and FBBR effluent after a 7-day incubation period for the measurement of THM formation potential (THMFP). The five CBP species were all regulated by China Sanitary Standard for Drinking Water Quality.

The reductions of $CHCl_3$FP, $CHCl_2Br$FP, and $CHClBr_2$FP in the FBBR were 21.5%-28.3% (25.1% on average), 19%-31.8% (26.0% on average), and 37.1%-53.3% (44.9% on average) respectively (Figs. 5-7). It was obvious that the percent reduction of $CHClBr_2$FP was much higher than that of $CHCl_3$FP or $CHCl_2Br$FP. The reduction of THMFP was 25.3%-31.2% (29.4% on average) (Fig. 8).

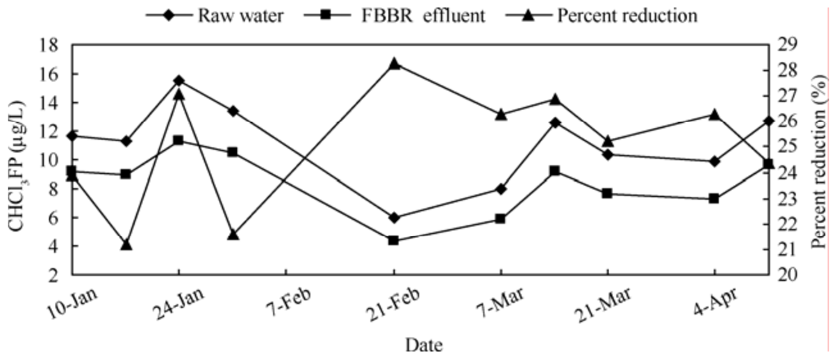

FIG. 5. Reduction of $CHCl_3$FP in the FBBR.

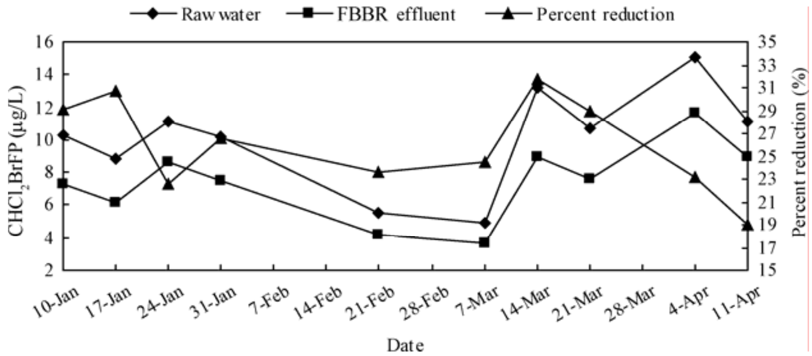

FIG. 6. Reduction of $CHCl_2Br$FP in the FBBR.

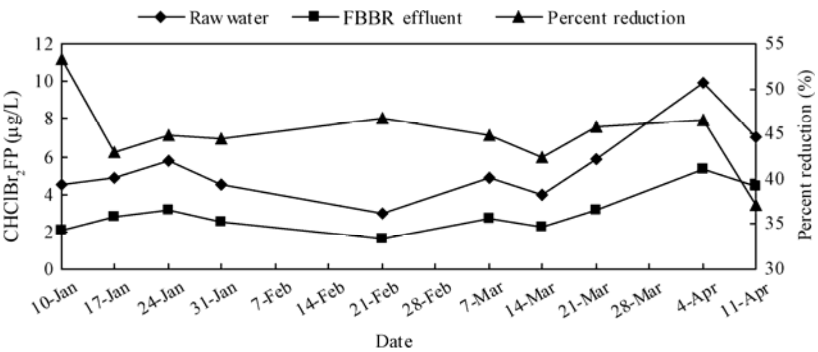

FIG. 7. Reduction of $CHClBr_2$FP in the FBBR.

The reductions of DCAAFP and TCAAFP in the FBBR were 19.5%-29.2% (22.9% on average) and 33.3%-38.9% (35.6% on average) respectively (Figs. 9 and 10). It was also obvious that the percent reduction of TCAAFP was much higher than that of DCAAFP.

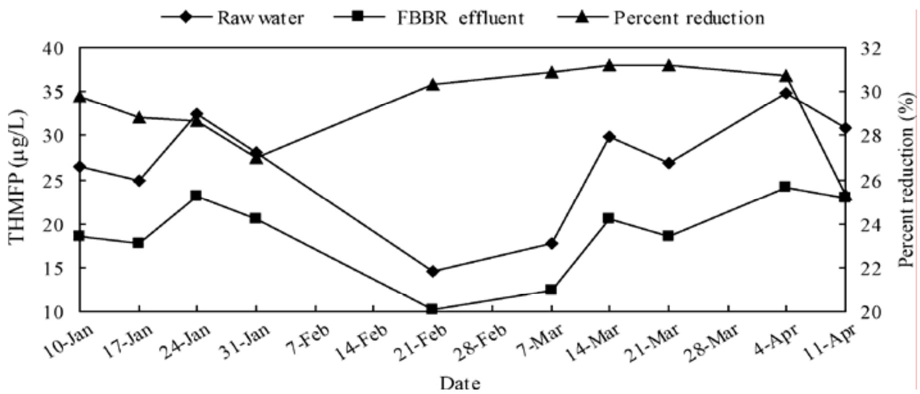

FIG. 8. Reduction of THMFP in the FBBR.

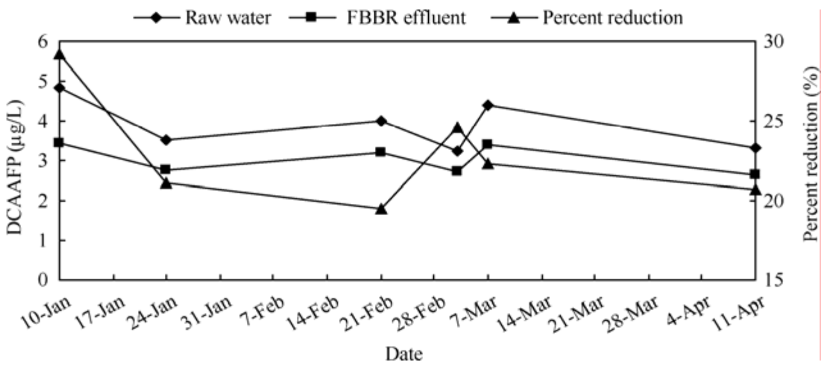

FIG. 9. Reduction of DCAAFP in the FBBR.

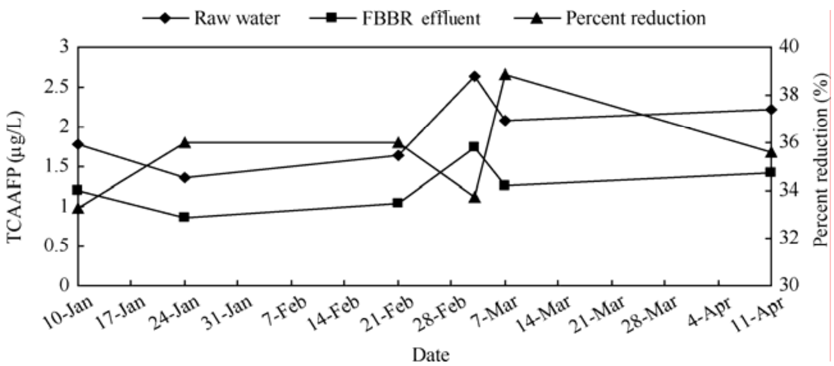

FIG. 10. Reduction of TCAAFP in the FBBR.

Removal of Ammonia and Nitrite

Biological nitrification is carried out in two steps: conversion of ammonia to nitrite by *Nitrosomonas* followed by further conversion of the nitrite to nitrate by *Nitrobacter*. Both groups of bacteria are autotrophic, using CO_2 as the carbon source for biosynthesis and oxidation of nitrogen compounds as the energy source. The rate-limiting step in nitrification is usually the growth of *Nitrosomonas*. It is generally accepted that the biological reaction rate coefficients of biological wastewater treatment processes are temperature dependent, which can be expressed by a simplified Arrhenius equation. The influence of low temperature on nitrification in activated sludge process and pure culture was significant. Some studies indicate a little or no growth below 5℃[7]. In activated sludge processes, temperature has two adverse effects on nitrification: readucing ammonia removal rates and increasing sludge age. The adverse effect of low temperature can be alleviated through attached growth in biofilm reactor. Euiso *et al.*[8] reported that the temperature effects on nitrification in activated sludge process can be reduced by addition of media. Rogalla *et al.*[9] investigated the removal rates of ammonia using aerobic filter at different temperatures and reported a removal rate of 85% at 5℃.

The reduction of ammonia in the FBBR is shown in Fig. 12. It could be observed that the reduction of ammonia was 30%-40% even below 3℃. The reduction of ammonia rose quickly to higher than 50% when the water temperature was only slightly above 3℃.

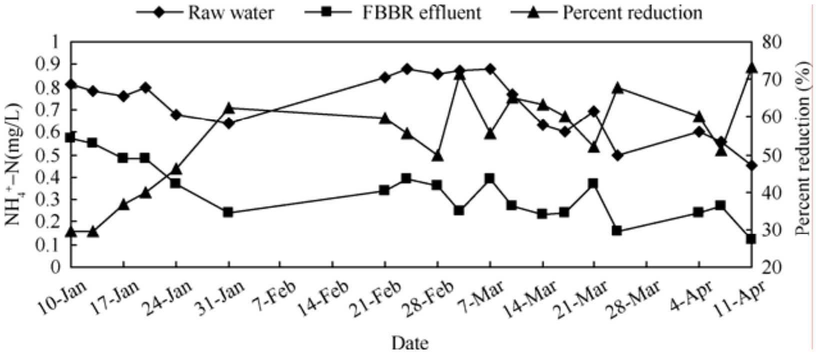

FIG. 11. Reduction of ammonia in the FBBR.

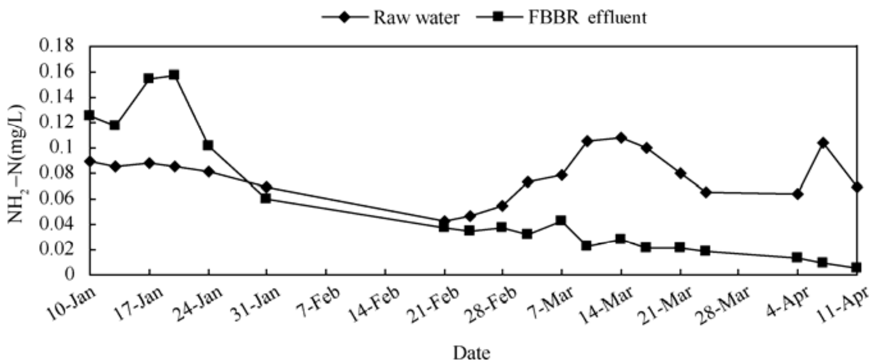

FIG. 12. Reduction of nitrite in the FBBR.

As nitrite is a cause of methemoglobinemia, its concentration must be kept low. The reduction of nitrite in the FBBR is shown in Fig. 12. It could be observed that the nitrite concentration in the FBBR effluent was higher than that in the raw water below 3℃. The nitrite concentration in the FBBR effluent was lower than that in the raw water soon after the water temperature was only slightly above 3℃. When the water temperature was about 10℃ the nitrite concentration in the FBBR effluent was very low.

DISCUSSION

It was reported that the attached biomass in biofilm reactors even at low temperature is excessive and the increase of attached biomass due to the temperature rise brings no obvious effect on reduction of TOC[10]. The percent reduction of TOC is closely related to the amount of biodegradable matters in raw water[11]. Moreover, the quality of raw water varies greatly, especially the ratio of the amount of biodegradable matters to the TOC, which may sometimes cover the apparently positive effect of temperature rise on biological treatment. Therefore, to some degree, the ratio of the amount of biodegradable matters to the TOC in raw water seems more important in determining the percent reduction of TOC even at varying temperatures, which partly accounts for no obvious effect of temperature rise on reduction of TOC.

Humic substances have a complicated molecular structure and poor biodegradability. Therefore, humic substances in biofilm reactors are reduced mainly by adsorption[12]. In the FBBR the media are in state of free-floating motion and thus biological flocculation of biofilm and interception of filter layer are very poor. Therefore, humic substances or UV_{254} can not be effectively reduced.

Although the percent reduction of TOC or UV_{254} is low, the FBBR can very effectively reduce THMFP, suggesting that TOC or UV_{254} may not be a suitable indicator for THMFP with regard to Yellow River water treatment using the FBBR. Moreover, the FBBR can also effectively reduce HAAFP.

Generally, the rise of temperature increases specific substrate utilization, specific growth rate, and affinity of nitrifiers for substrates during nitrification owing to softening of the lipids of the membrane[13]. However, the percent reduction of ammonia could not continuously increase with the rise of water temperature (ranged from 50%-73.3%). One possible reason is that the growth of nitrifying biomass as the result of temperature rise is limited by hydraulic disturbance and/or competition of heterotrophic biomass. The reduction of ammonia is 30%-40% below 3℃ but more than 50% above 3℃. Moreover, compared with the nitrite concentration in raw water, the nitrite concentration in the FBBR effluent is higher below 3℃ while lower above 3℃. Therefore, the water temperature of approximately 3℃ seems to be a critical point for nitrification in the FBBR. However, the reason is not fully understood.

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