Performance of Combined Pre-Ozonation and Biofiltration for the Purification of Water from China's Yellow River

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Abstract

Combined pre-ozonation and biofiltration was used for the treatment of source water from China's Yellow River. The combined methods were ineffective at reducing THMFP (trihalomethane formation potential) and in some cases increased THMFP in waters. The reduction of DCAAFP (dichloroacetic acid formation potential) in the combined pre-ozonation and biofiltration was limited, however, TCAAFP (trichloroacetic acid formation potential) was effectively reduced, even with high concentrations in raw water, when the combined methods were used. There was no obvious relationship between the change of CODMn (chemical oxygen demand) and THMFP or HAAFP (haloacetic acid formation potential) from combined treatment. Individually, pre-ozonation had little effect, if any, on ammonia and nitrite levels, whereas biofiltration effectively reduced these compounds. In conclusion, combined pre-ozonation and biofiltration was not suitable for reducing THMFP or DCAAFP; however, TCAAFP was effectively reduced by the combined approach, and at the biofiltration stage, effectively reduced ammonia and nitrite levels.

Keywords: Pre-ozonation, biofiltration, chlorination by-products.

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Introduction

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, particularly chlorine. These substances react with chlorine to produce carcinogenic THMs (trihalomethanes), HAAs (haloacetic acid), and other CBPs (chlorination by-products). Despite this potential public health hazard, chlorination of drinking water supplies is still widely used for disinfection. Therefore, technologies aimed at reducing CBP precursors are of extreme value for reducing the public health risks from exposure to chlorinated drinking water.

The amount of CBP precursors in water is usually indirectly measured by formation potential in water research. Reduction in THMFP upon ozonation is significant due to degradation of humic substances into low molecular weight compounds that are less reactive towards chlorine (1). The combination of ozonation and biofiltration using sand- or GAC (granular activated carbon) filters has been shown to be effective at reducing THMFP (2) and HAAFP (3). In China, biological pretreatment processes, applied prior to conventional treatment chains, use a bio-ceramic filter (BF), which is considered an economically effective process for removing pollutants from raw water. However, the scientific support for pre-ozonation and biofiltration using BF to reduce CBPs is limited to the work of Wu et al. (2000). In their report, the authors demonstrated an effective reduction of THMFP and HAAFP by the combined pre-ozonation and

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biofiltration methods using BF in the treatment of lake water (4).

Yellow River is one of the largest drinking water sources in China and is plagued with the continual introduction of pollution. In China, the predominant drinking water treatment process consists of sedimentation, coagulation/flocculation, phase separation, rapid sand filtration, and disinfection, in order to remove turbidity, color and pathogens. However, these processes do not effectively remove ammonia and CBPs. Therefore, the tap water quality of most water supply systems, which abstract water from Yellow River, cannot meet increasingly stringent drinking water quality criteria, due to limitation of conventional drinking water treatment. Unfortunately, China's emphasis on technologies aimed at improving the drinking water quality by advanced treatments including pre-ozonation or the combined pre-ozonation and biofiltration method are limited. Only Chen et al. (2004) recently reported high reduction of CODMn and ammonia in the combined pre-ozonation and biofiltration using GAC for the purification of Yellow River water (5). To the authors' knowledge there have been no reports concerning the reduction of CBPs in Yellow river water by pre-ozonation or the combined pre-ozonation and biofiltration. Therefore, the performance of combined pre-ozonation and biofiltration using BF was first introduced for the purification of Yellow River water in this study. The objective of this study was to investigate the feasibility of reducing the ammonia, THMFP and HAAFP by the combined pre-ozonation and biofiltration using a BF in Yellow River water. Moreover, the changes of various CBPFP were evaluated in detail. Low water temperatures (below 10^{o}C) prevail for extended periods (about four months per year) and so the temperature effect on the performance of the pre-ozonation and biofiltration was also considered in this study.

Materials & Methods

Experimental setup

The schematic diagram of the experiment setup is shown in Figure 1. The ozonation column consisted of a stainless steel cylinder with dimensions of 3 m high and 0.35 m of inside diameter. The ozone dosage was about 1 mg/L. The biofilter was a Plexiglas cylinder with dimensions of 3 m high and 0.5 m of inside diameter. The filter was filled with ceramic particles up to a depth of 2 m. Ceramic particles had an average diameter of 3-5 mm, a porosity of 0.09, a density of 1.56 g/cm^3, and a specific surface area of 2.5 m^2/cm^3. Liquid and gas phases flowed up through the filter in counter-current mode. The raw water was Yellow River water after sedimentation for sand removal and the inflow was 1 m^3/h. The pH values of raw water ranged between 8.0-8.5. The operating parameters of the pre-ozonation and biofiltration units are shown in Table 1. This experimental period experienced a fall and then a rise of water temperature (Figure 2).

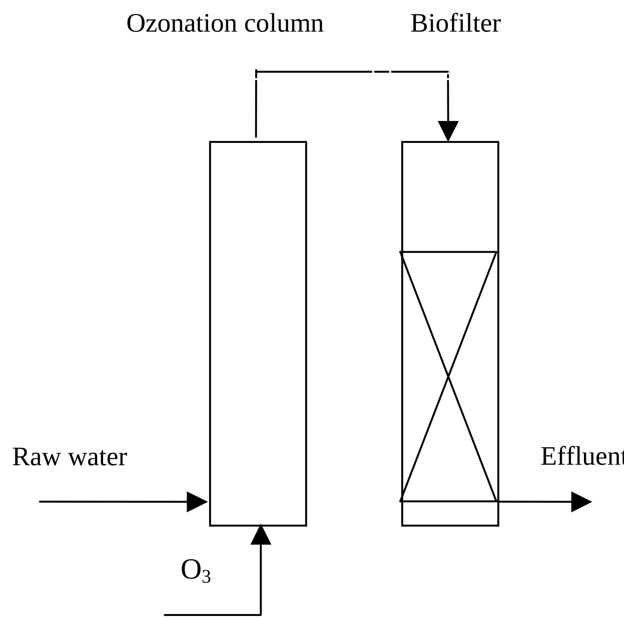

Figure 1. Schematic diagram of the experiment setup.

Analysis

UV_{254} was measured in a 1-cm quartz cell with a spectrophotometer (Shimadzu UV-1200). Dissolved oxygen (DO), pH and water temperatures were determined using a selective electrode. Ammonia and nitrite concentrations were measured according to standard methods (6). The analysis of residual chlorine was preformed using the DPD (N, N-diethyl-p-phenylene-diamine) ferrous titration method (7). Applied and utilized ozone concentrations were determined by the iodometric method (7). Permanganate consumption (CODMn) was determined according to the Chinese standard methods (6).

The formation potential (FP) experiments for THMs and HAAs were conducted with a 7-day incubation period following the introduction of the

Table 1. Operating parameters of the pre-ozonation and biofiltration units

Reactor	**Dimension ($D \times H$ mm^2)**	**Filter layer height (mm)**	**Filling particle size(mm)**	**Empty-bed contact time (min)**	**Flowrate (m/h)**
Ozonation column	350×3000			17.3	10.4
Biofilter	500×3000	2000	2~5	23.6	5.1

NaOCl solution and phosphate buffer (pH 7.0). The applied chlorine concentration was about 50 mg/L, which was determined from preliminary studies and would provide free residual chlorine of at least 3 mg/L at the end of the incubation period. 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 detailed analysis followed the QA/QC programs set forth in Standard Methods (7).

Results & Discussion

COD_{Mn} and UV_{254} reduction

COD_{Mn} as a surrogate parameter representing the concentration of organic substances in water is widely used in the field of drinking water treatment in China. The reductions of COD_{Mn} in the combined pre-ozonation and biofiltration were shown in Figure 3. The total reduction rate of COD_{Mn} in the combined pre-ozonation and biofiltration was 9~24.2% (average 14.1%). The effect of pre-ozonation on the reduction of COD_{Mn} was very poor and sometimes even no obvious reduction was shown. However, the reduction of COD_{Mn} in biofiltration was significant. The applied ozone dosage in pre-ozonation was low, and the pre-ozonation could only incompletely reduce some high molecular weight compounds to low molecular weight compounds and to some degree improve the biodegradability of water. Moreover, the effect of temperature on the reduction of COD_{Mn} in pre-ozonation and biofiltration was not obviously observed.

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 (8). The reductions of UV_{254} in the combined pre-ozonation and biofiltration were shown in Figure 4. Both pre-ozonation and biofiltration played an obvious role in reduction of UV_{254}. The total reduction rate of UV_{254} in the combined pre-ozonation and biofiltration was 17.2~42.7% (average 25.7%). However, the reduction mechanism of UV_{254} in the two reactors was different. Humic substances have complicated and large molecular structure, and poor biodegradability. The reduction of UV_{254} in pre-ozonation was due to a removal of aromatic structure and double bonds of the natural organic matters (9). In biofilm reactors humic substances are removed mainly by adsorption (10). In the BF, biological flocculation of biofilm and interception of filter layer could effectively absorb suspended matters and colloids that contain large amounts of humic substances, which played an important role in the removal of humic substances or UV_{254} (11).

Change of THMFP and HAAFP

Five CBP species, including chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), DCAA and TCAA, were the major compounds detected in raw water and/or effluent after a 7-day incubation period for the measurement of THM formation potential (THMFP). The five CBP species are all regulated in current China Drinking Water Standard. The changes of $CHCl_3$FP, $CHCl_2Br$FP and $CHClBr_2$FP in the combined pre-ozonation and biofiltration were shown in Figure 5, 6 and 7 respectively.

Fulvic and humic acids were usually regarded as major precursors of THMs. Pre-ozonation was often applied to reduce THM precursors (9). However, algae were also important THM precursors (8). An increase in the dissolved organic carbon content of the algal suspension caused by pre-ozonation may be responsible for the increase of THMFP in waters (12). High level of algae usually occurred in the raw water (11). The applied ozone dosage was low (1 mg/L) in this study, so pre-ozonation may increase in the dissolved organic carbon content of the algal suspension by breaking up the algal cells, instead of completely mineralizing them in raw waters.

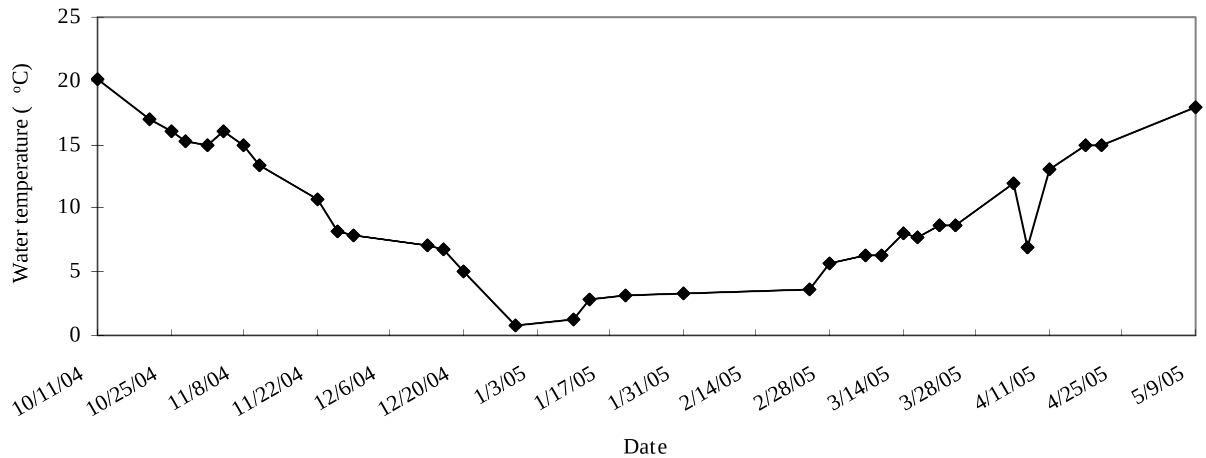

Figure 2. Change of water temperature.

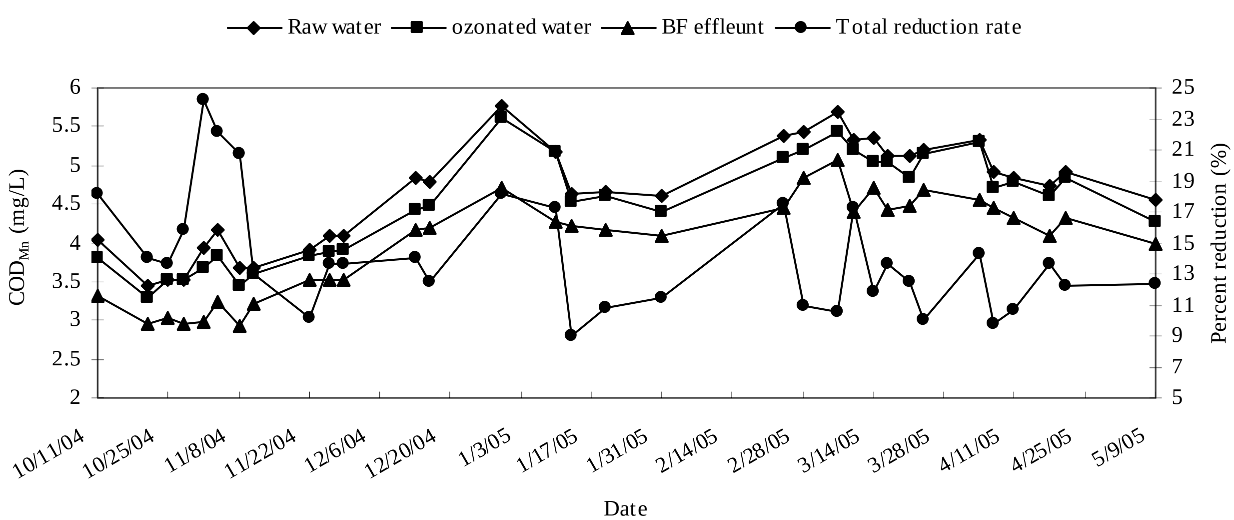

Figure 3. Reduction of COD_{Mn} in the combined pre-ozonation and biofiltration.

As shown in Figure 5, the $CHCl_3$FP in raw waters varied greatly, from 6.9 to 32.4 μg/L. To different degree the pre-ozonation increased $CHCl_3$FP in waters. However, the change of $CHCl_3$FP in the biofiltration was very complicated, and both a decline and rise of $CHCl_3$FP after biofiltration were observed. Therefore, after the treatment of pre-ozonation followed by biofiltration the $CHCl_3$FP in waters was usually increased. The $CHCl_2Br$FP in raw waters also varied greatly, from 6.9 to 17.9 μg/L and the $CHCl_2Br$FP in waters was increased both in the pre-ozonation and the biofiltration (Figure 6).

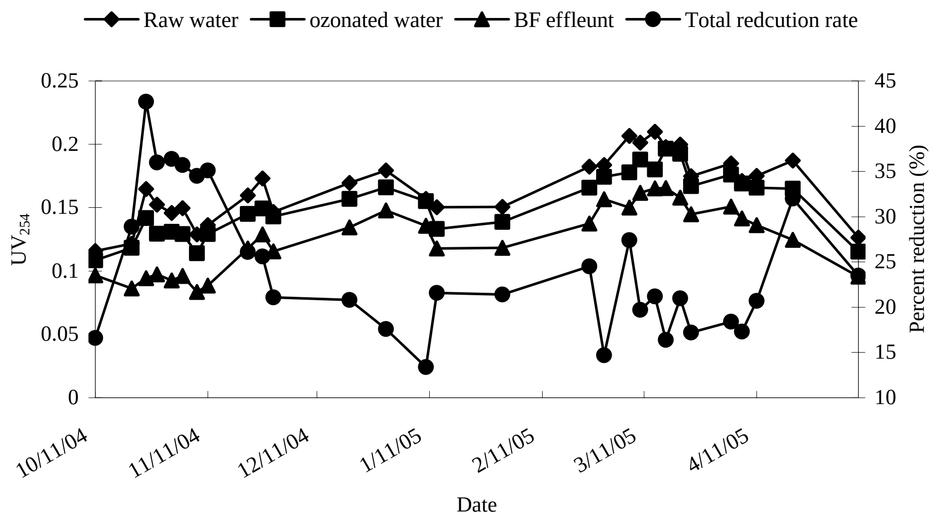

Figure 4. Reduction of UV_{254} in the combined pre-ozonation and biofiltration.

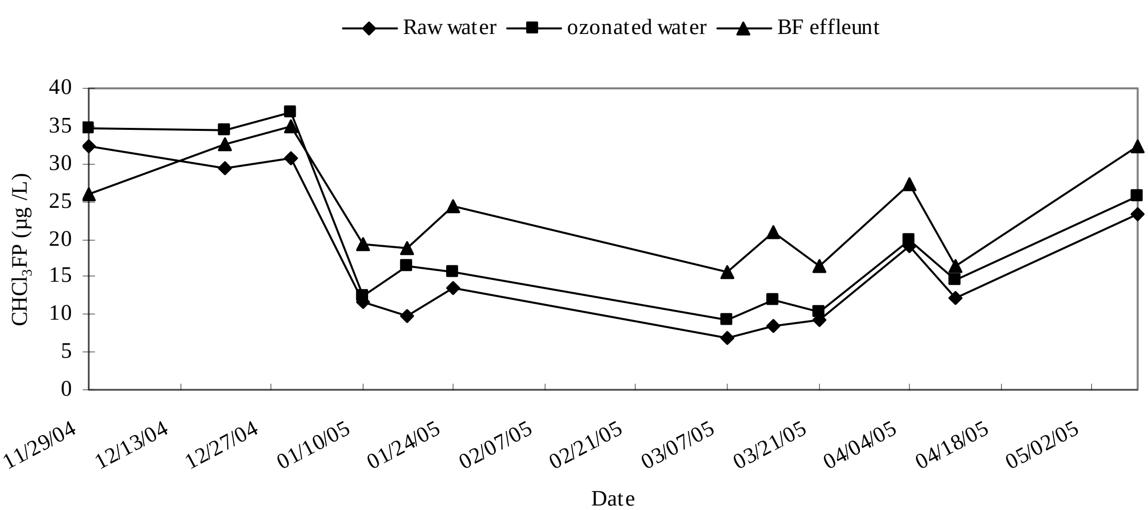

Figure 5. Change of $CHCl_3$FP in the combined pre-ozonation and biofiltration.

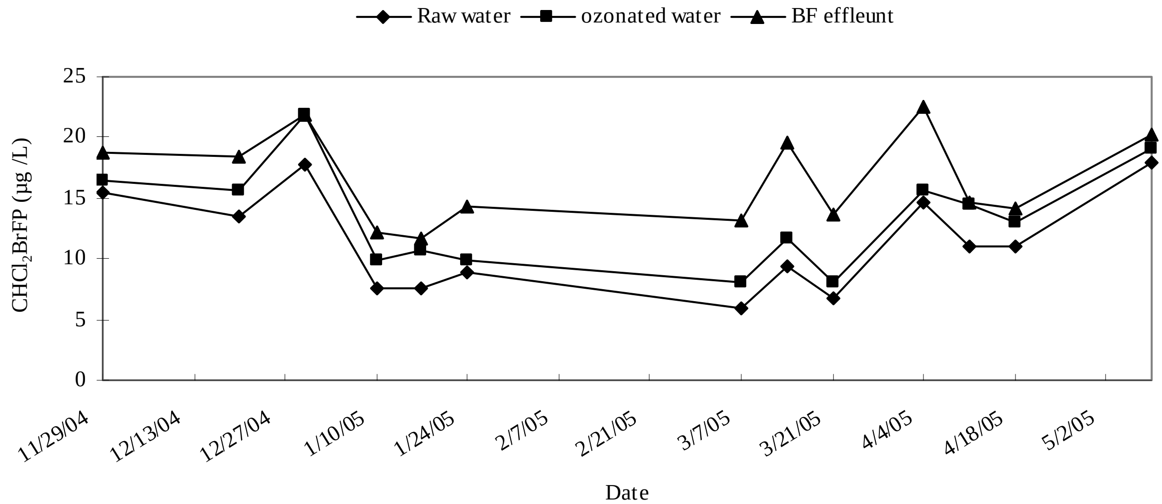

Figure 6. Change of CHCl2BrFP in the combined pre-ozonation and biofiltration.

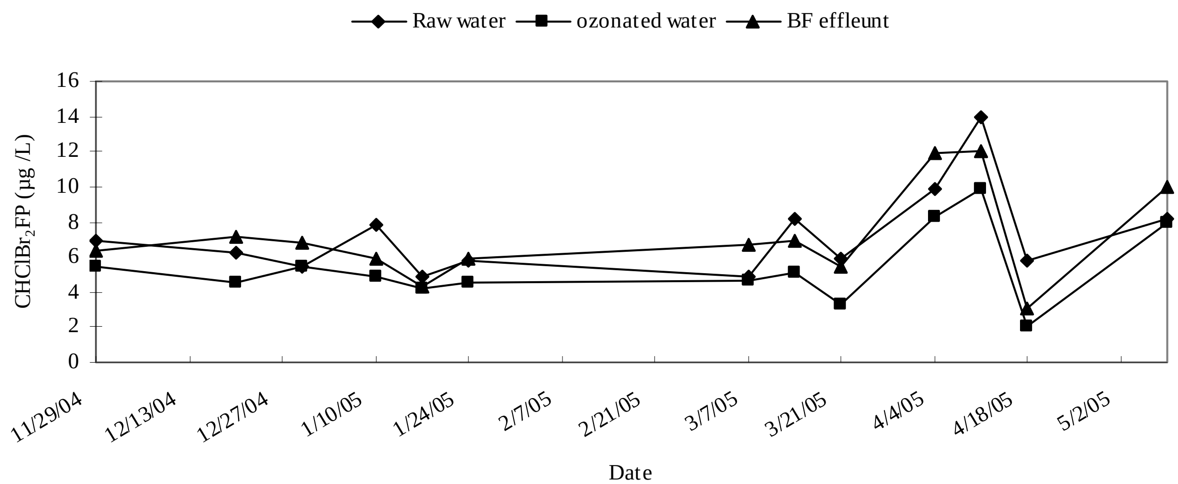

Figure 7. Change of $CHClBr_2FP$ in the combined pre-ozonation and biofiltration.

However, the $CHClBr_2FP$ in waters was reduced in pre-ozonation but then increased in biofiltration, so the reduction in the combined pre-ozonation and biofiltration was very limited and sometimes even a rise of $CHClBr_2FP$ in water was observed (Figure 7). Therefore, the combined pre-ozonation and biofiltration could not effectively reduce the THMFP and sometimes may result in a rise of the THMFP in waters. Moreover, due to the complicated changes both in pre-ozonation and in biofiltration, UV_{254} was not a suitable surrogate parameter of THMFP in this study, in part presumably due to the role of algae on THMFP. Moreover, for the same reason there was no obvious relationship between the change of COD_{Mn} and that of THMFP in the combined pre-ozonation and biofiltration.

The changes of DCAAFP and TCAAFP in the combined pre-ozonation and biofiltration are shown in Figure 8 and 9, respectively. The DCAAFP in raw waters fluctuated slightly, from 3.5 to 5.3 µg/L, and the reduction of the DCAAFP was always observed in pre-ozonation; however, the rise of the DCAAFP was usually observed in biofiltration (Figure 8). Therefore, a limited reduction of the DCAAFP in the combined pre-ozonation and biofiltration was observed in this study.

The TCAAFP in raw waters fluctuated greatly, from 1.8 to 34 μg/L, but the reductions of TCAAFP were observed both in the pre-ozonation and biofiltration. When the TCAAFP in raw water was high (34 μg/L), it could be effectively reduced in the combined pre-ozonation and biofiltration, with reduction rates of 54% and 22% in the pre-ozonation and biofiltration, respectively.

Changes of ammonia and nitrite

The changes of ammonia and nitrite in the combined pre-ozonation and biofiltration are shown in Figures 10 and 11, respectively. The pre-ozonation had poor or even no reduction of ammonia, but the biofiltration performed well for reducing ammonia (Figure 10). The total reduction rate of ammonia in the combined pre-ozonation and biofiltration was 32.1 ~ 100 % (average 67.6 %).

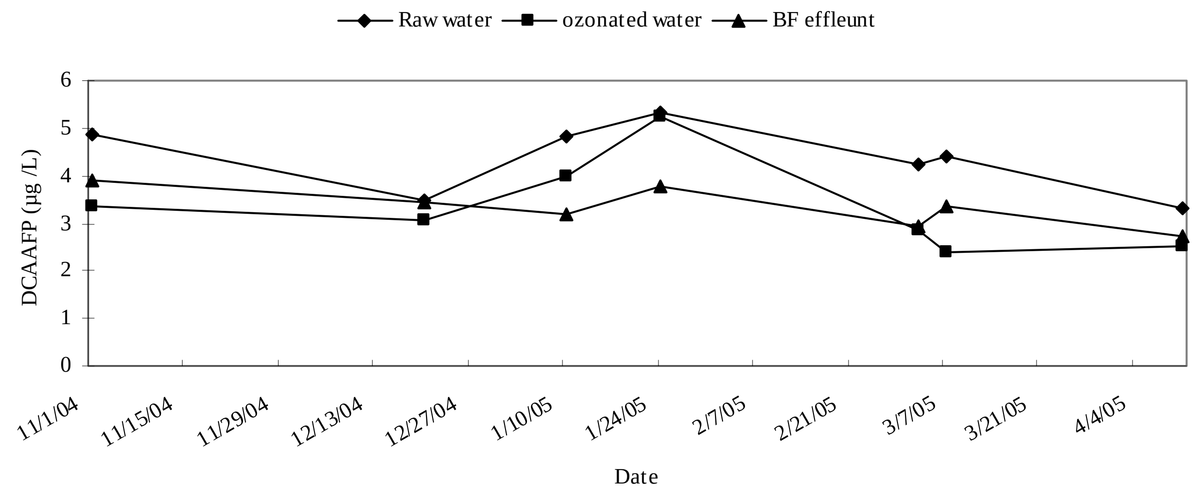

Figure 8. Change of DCAAFP in the combined pre-ozonation and biofiltration.

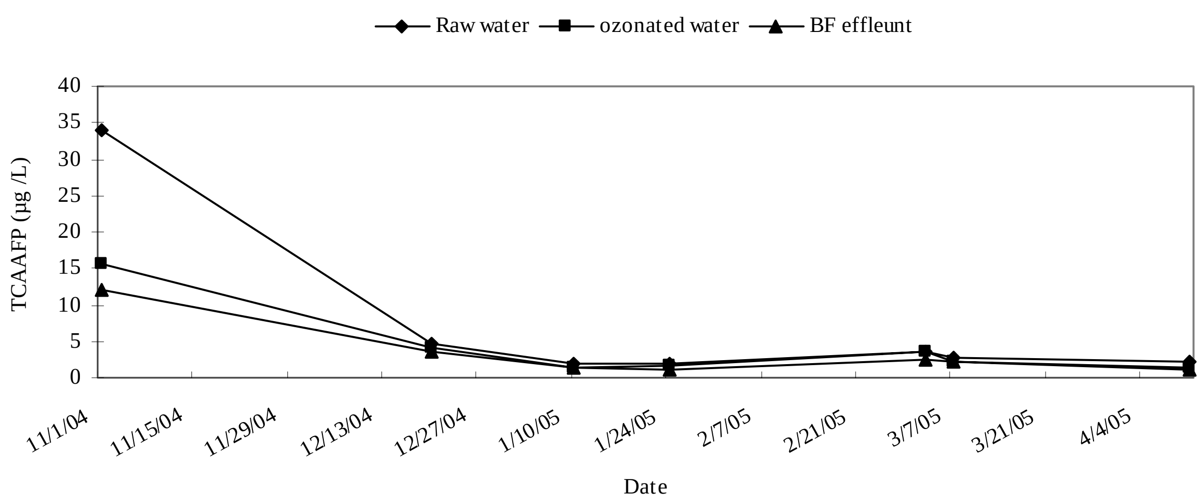

Figure 9. Change of TCAAFP in the combined pre-ozonation and biofiltration.

However, the effect of temperature on reducing ammonia was observed in this study. During fall temperatures, the combined pre-ozonation and biofiltration performed well in reduction of ammonia, with a total reduction of 55~100%, even at temperatures below 5^{o}C (with reference to Figure 2 and 10). However, in winter, due to a sudden rise of the concentration of ammonia in raw water and low temperature effect on nitrifying activity in the BF, the reduction rate of ammonia in the combined pre-ozonation and biofiltration significantly declined (32~50%) although the total amount of ammonia reduced did not obviously decline. Generally, the rise of temperature has many positive effects on nitrification: the increase of specific substrate utilization, specific growth rate, and higher affinity of

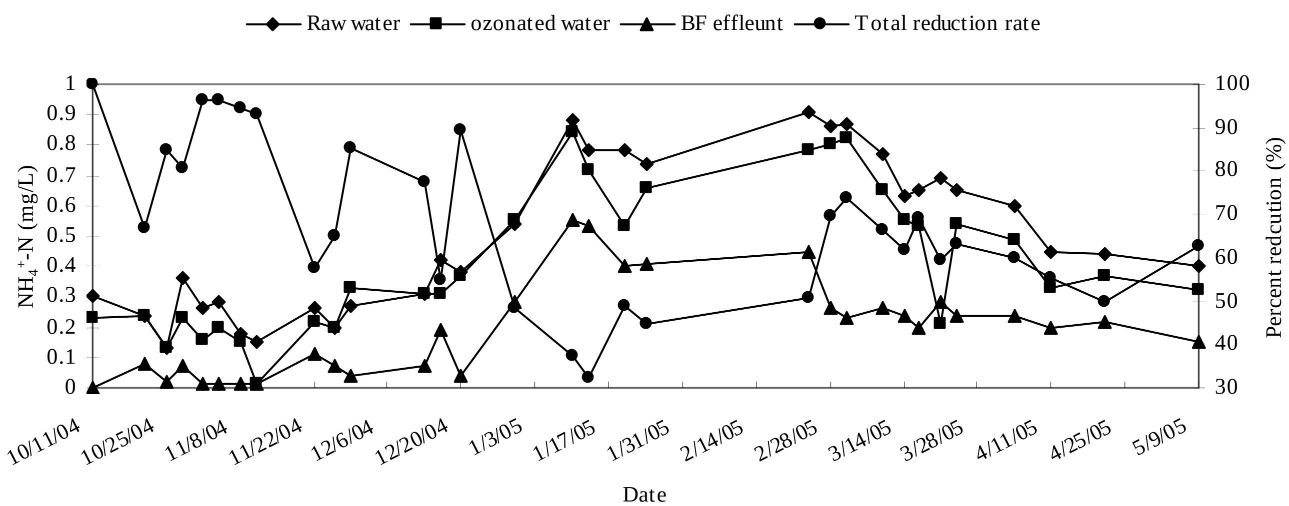

Figure 10. Change of ammonia in the combined pre-ozonation and biofiltration.

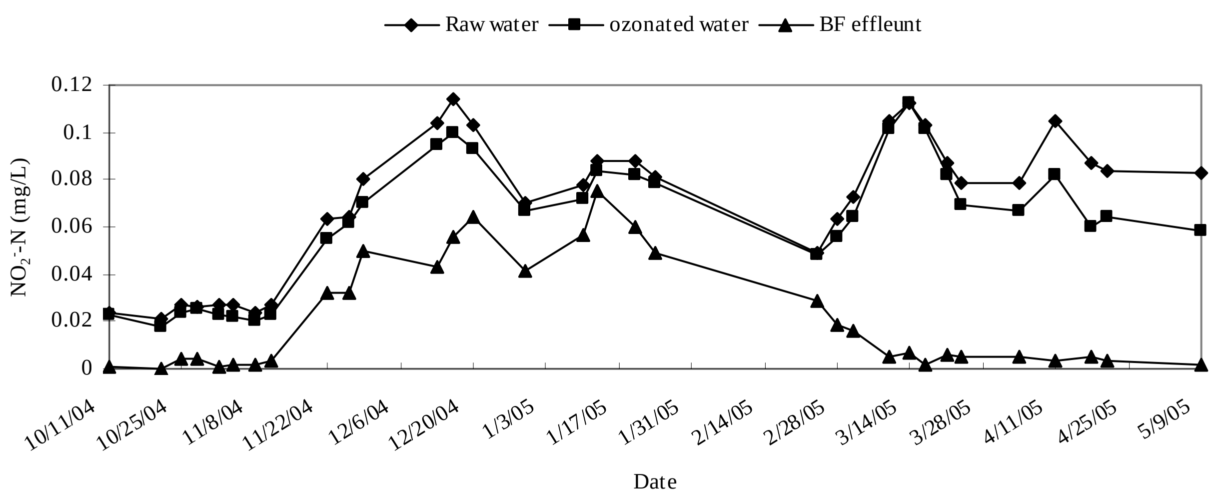

Figure 11. Change of nitrite in the combined pre-ozonation and biofiltration.

nitrifiers for substrates due to softening of the lipids of the membrane (13). In spring, when the water temperatures were above 5°C, the reduction of ammonia in the combined pre-ozonation and biofiltration was obviously improved even though the concentration of ammonia in raw water was still high (above 0.75 mg/L). However, the percent reduction of ammonia did not continuously increase with the rise of water temperature. One possible reason was that the growth of nitrifying biomass as the result of temperature rise was limited by hydraulic disturbance, competition of heterotrophic biomass and/or other factors.

Though the pre-ozonation only had a minor reduction of nitrite, the biofiltration significantly reduced nitrite (Figure 11). 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*. In winter, due to the rise of the concentrations of ammonia and nitrite (with reference to Figure 2, 10 and 11) and the low temperature effect on nitrifying activity in the BF, the nitrite in the BF effluent was relatively higher. However, in spring, when the water temperatures were above 5°C, the nitrite in the BF effluent significantly declined even though the concentrations of ammonia and nitrite in raw water were still high. Therefore, the temperature of 5°C was critical for the reduction of ammonia and nitrite (nitrification).

Conclusions

The combined pre-ozonation and biofiltration using a BF was first introduced to investigate the feasibility of reducing ammonia, THMFP and HAAFP in Yellow River water. The reduction of COD_{Mn} was very poor and sometimes even absent in the pre-ozonation, but it was significant in the biofiltration. Both pre-ozonation and biofiltration played an obvious role in reduction of UV_{254}. The changes of $CHCl_3$FP, $CHCl_2Br$FP and $CHClBr_2$FP in the combined pre-ozonation and biofiltration were much different and UV_{254} was not a suitable surrogate parameter of THMFP in this study. The combined pre-ozonation and biofiltration could not effectively reduce the THMFP and sometimes may result in an increase of THMFP in waters. The changes of DCAAFP and TCAAFP in the combined pre-ozonation and biofiltration were also different. The reduction of the DCAAFP in the combined pre-ozonation and biofiltration was limited; however, TCAAFP could still be effectively reduced in the combined pre-ozonation and biofiltration when it was high in raw water. Moreover, there was no obvious relationship between the change of COD_{Mn} and that of THMFP or HAAFP in the combined pre-ozonation and biofiltration. Since the quality of the raw water varied greatly, especially the DCAAFP and TCAAFP, and the change of formation potential of each THM and HAA specie both in pre-ozonation and biofiltration was very complicated, much effort was still necessary in order to fully and objectively evaluate the feasibility of reducing THMFP and HAAFP in Yellow River water using the combined pre-ozonation and biofiltration.

The pre-ozonation had poor or even no reduction of ammonia and nitrite, but the biofiltration performed well at reducing ammonia and nitrite. In winter, the reduction of ammonia and nitrite in the biofiltration was obviously lower but still significant. In spring, when the water temperatures were above 5°C, nitrification in the BF was obviously improved even though the concentrations of ammonia and nitrite in raw water were still high. Therefore, the combined pre-ozonation and biofiltration was suitable for the reduction of ammonia and nitrite even at low temperatures.

Acknowledgements

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