

# Experimental study on the removal of organic pollutants and NH<sub>3</sub>-N from surface water via an integrated copolymerization air flotation-carbon sand filtration process

Yong Lei Wang, Xuexin Xu, Ruibao Jia, Baozhen Liu, Wuchang Song and Junqi Jia

## ABSTRACT

Micro-polluted surface water sources contain organic pollutants and NH<sub>3</sub>-N contents that exceed the limits, and the effluent from conventional water plant operations poses a threat to water supply safety. In this paper, countercurrent-cocurrent dissolved air flotation (CCDAF) and carbon sand double-layer filtration were integrated to produce a copolymerization air flotation-carbon sand filtration process. The results of the pilot studies show that the average removal percentage for COD<sub>Mn</sub> and UV<sub>254</sub> reached 47.86% and 58.80%, respectively, and the removal efficiency of UV<sub>254</sub> was better than that of COD<sub>Mn</sub> using the air flotation unit. The removal of COD<sub>Mn</sub> was also better than the removal of UV<sub>254</sub> using the filtration unit, and the organic matter removal primarily occurred in the activated carbon layer. The total removal percentage of trihalomethane formation potential (THMFP) was 24.43%. The average removal percentage of NH<sub>3</sub>-N was 27.50%, and the removal percentage of the filter unit for total nitrogen (TN) and NH<sub>3</sub>-N was 15.00% and 54.00%, respectively. The sufficient dissolved oxygen content in the floating filter enhanced the removal of the organic matter and nitrogen, and the advantages of the direct filtration process were obvious as the influent pollutant load increased.

**Key words** | ammonia, carbon sand double layer filtration, CCDAF, nitrogenous compounds, organic

**Yong Lei Wang** (corresponding author)  
**Xuexin Xu**  
**Baozhen Liu**  
**Junqi Jia**  
College of Environmental and Municipal  
Engineering,  
Shandong Jianzhu University,  
250101, Jinan,  
China  
E-mail: wyl1016@sina.com

**Yong Lei Wang**  
**Ruibao Jia**  
**Wuchang Song**  
Shandong Province City Water Supply and  
Drainage Water Quality Monitoring Center,  
250021, Jinan,  
China

**Yong Lei Wang**  
Co-Innovation Center of Green Building,  
250101, Jinan,  
China

## INTRODUCTION

Currently, reservoir water pollution problems are becoming increasingly prominent, especially organic pollution, and the levels of nitrogen and phosphorus exceed the standards for drinking water quality (Ministry of Health PRC 2006). The eutrophication degree of water sources is increasing annually, but the conventional water plant processes have limited removal abilities for organic matter and NH<sub>3</sub>-N (Yue *et al.* 2005; Luo *et al.* 2015). In addition, a large amount of natural organic matter (NOM) in micro-polluted water sources is often the main precursor of chlorinated disinfection by-products. These substances pose a threat to the operation of water plants and the safety of the water supply

(Henderson *et al.* 2008; Jiuhui 2011; Coleman *et al.* 2012). Air-floating filter technology is a combination of air flotation and filtration methods, and their integration can remove algae turbidity, reduce the pollution load of the filter pool, and prolong the filtration period (Coleman *et al.* 2012; Zhang *et al.* 2013). The filter unit uses carbon sand filtration, which can degrade adsorbed organic matter, odours and trihalomethane formation potential (THMFP) simultaneously when the particles are trapped (Cook *et al.* 2001; Tuovinen *et al.* 2005; Luo *et al.* 2014). In addition, the dissolved micro-bubbles of the air flotation unit provide sufficient dissolved oxygen conditions for the biological action of

activated carbon, which can promote the organic matter and ammonia-nitrogen degradation in the micro-polluted water source; therefore, the gas flotation-filtration combined process has a synergistic pollution removal efficiency. Domestic and foreign experts and scholars have performed research on the air flotation-filtration process. Prof. Zhang Xiaojian (Xie *et al.* 2004; Yang *et al.* 2004; Kong *et al.* 2007) of Tsinghua University used a developed deep bed floating filter with activated carbon to treat a water source with a high concentration of organics and algae in Miyun Shuiku and obtained good results. Eades & Brignall (1995) studied countercurrent dissolved air flotation (DAF) and filtration combined processes and overcame the seasonal algae propagation problem in raw water. In recent years, this research group used a DAF-sand dual media filter technology on Yellow River reservoir water. The algae removal efficiency increased significantly, and all the indexes showed a good treatment effect (Wang *et al.* 2016a, 2016b). In this paper, the original flotation – carbon sand two-layer filter (floating filter) technology was combined with the self-developed countercurrent-cocurrent dissolved air flotation process (CCDAF) (Wang *et al.* 2010, 2018). In the floating filter process, dissolved gas was injected into the water two times. The dissolved gas was directly injected into the water in the flocculation tank, and the micro-bubbles were directly involved in the condensation process and the floc was formed. Then, ‘copolymerization gas flotation’ occurred with the large flocs, and the dissolved gas was used to bubble the floc adhesion in the water. The filter media is composed of double-layer filtration material made of activated carbon and quartz sand. The copolymerization air flotation was combined with the carbon sand filtration to construct the copolymerization air flotation-carbon sand filtration integration process (Figure 1(a)) and to perform a pilot test study. The characteristics of the synergistic removal of organic matter and nitrogen by copolymerization gas flotation and carbon sand filtration were investigated, and some key techniques of the effects of air flotation, pollution removal and dissolved oxygen on the removal of nitrogen and organic compounds in the filter bed were studied. This study provides technical support for engineering applications of the copolymerization air flotation filter technology.

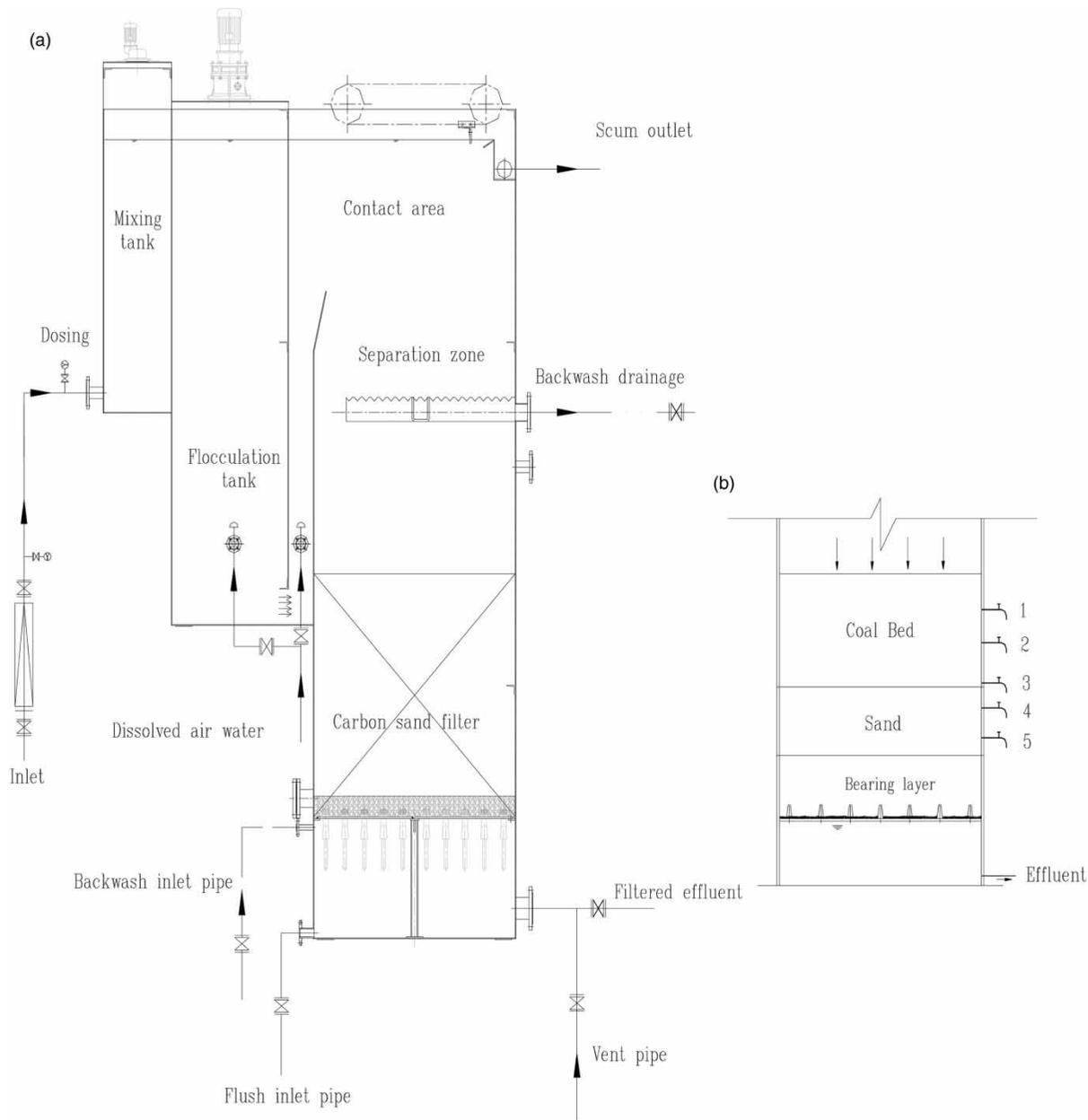
## PILOT PLANT AND TEST METHOD

### Pilot plant

The copolymerization air flotation-carbon sand filtration setup is shown in Figure 1(a). The pilot plant installed in Jinan Quehua water plant, has been in stable operation for ten years. The device combines the copolymerization air flotation with the carbon double sand layer filtration and forms an integration, which consists of the mixing tank, the copolymerization flocculation tank, the contact zone, the separation area and the carbon sand filter. The upper part of the setup is a mixed pool with a flocculation pool and a flotation tank, and the lower part is a carbon sand filtration zone. The design processing capacity was 5.0 m<sup>3</sup>/h, and the size of the air flotation filter was 2.6 m × 0.8 m × 4.3 m (length × width × height) with a filtration area of 0.96 m<sup>2</sup>. The upper part of the filter layer is the active carbon layer, which measures 600 mm, the lower part is the quartz sand layer, which measures 300 mm, and the bottom pebbles are the supporting layer, which measures 400 mm. Process operation is as follows. The reservoir water is mixed into the flocculation tank after adding chemicals. Partially dissolved gas water enters the flocculation tank. The copolymerization of the bubbles with the flocs results in larger flocs, and the bubbles and flocs enter the air flotation contact chamber. In this chamber, the micro-bubbles and the flocs are in contact, and the separation zone is used to remove the flocs. After the air flotation process is complete, the water enters the carbon sand filter layer under the filter.

The device dissolved gas water comes from dissolved gas and gas release system. Dissolved gas system consists of air compressor, high pressure pump and dissolved gas tank. Pressurized water adopts the filtered effluent and gas comes from air. After releasing the dissolved gas water through the diverter valve, the gas release system uses the TS release device to separate the dissolved air water into the flocculation tank and the air flotation contact zone.

The following test conditions were used: coagulant adopts PAFC, dosage [Al<sup>3+</sup>] is 5.0 mg/L; dissolved gas pressure, 0.40 MPa; dissolved water total reflux ratio, 12% (R1: back to the copolymerization flocculation



**Figure 1** | Schematic of the copolymerization air flotation-carbon sand filtration device (a) and depth sampling positions of the dual-media filter (b).

pool 4%, R2: back to the flotation contact chamber 8%); R1/R2 value,  $\frac{1}{2}$ ; and filtration rate, 5.2 m/h.

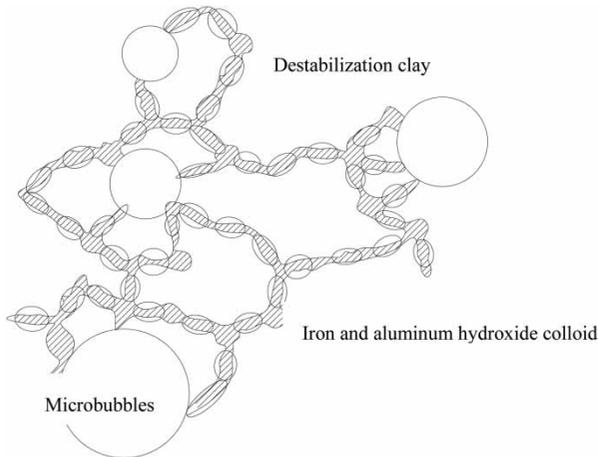
### Process characteristics

The floating filter process combines a reverse-synchronous flow flotation process with carbon sand double layer filter media to achieve integration. The removal of high levels of

algae, organic matter and  $\text{NH}_3\text{-N}$  in micro-polluted water sources is advantageous.

In the process of reverse-synchronous flow flotation process, the micro-bubbles of dissolved gas and water are directly involved in coagulation, the air bubbles are trapped between the flocs to form a 'copolymerization air flotation' (Figure 2).

The sufficient dissolved oxygen concentration of the air flotation unit promotes the biological functions of the



**Figure 2** | Copolymerization of micro-bubbles with flocs.

activated carbon layer. In the early stage of operation, activated carbon is mainly used for filtering and adsorption of organic matter. After a long period of operation, pollutants are gradually biodegraded by biofilms, which are formed around the activated carbon, with the air flotation unit providing the biological metabolism processes of the required dissolved oxygen conditions, which enhances the removal of organics and organic nitrogen.

### Raw water quality

The Jinan Quehua reservoir was used as the raw water source. During the two-month test period, the raw water had the following properties: water temperature: 10–20 °C, turbidity: 20.0–27.0 NTU, pH: 8.10–8.40, COD<sub>Mn</sub>: 4.0–5.5 mg/L, UV<sub>254</sub>: 0.135–0.15 cm<sup>-1</sup>, and algae count: 3.56–5.12 million cells/L.

### Analysis method

The monitoring methods, instruments and routine indexes are shown in Table 1. The routine indexes were detected using the Water and Wastewater test method (Editorial Board of the State Environmental Protection Administration 2002). Test sampling frequency of testing was once a day, and three parallel tests were performed under the same influent conditions for each monitoring.

## RESULTS AND DISCUSSION

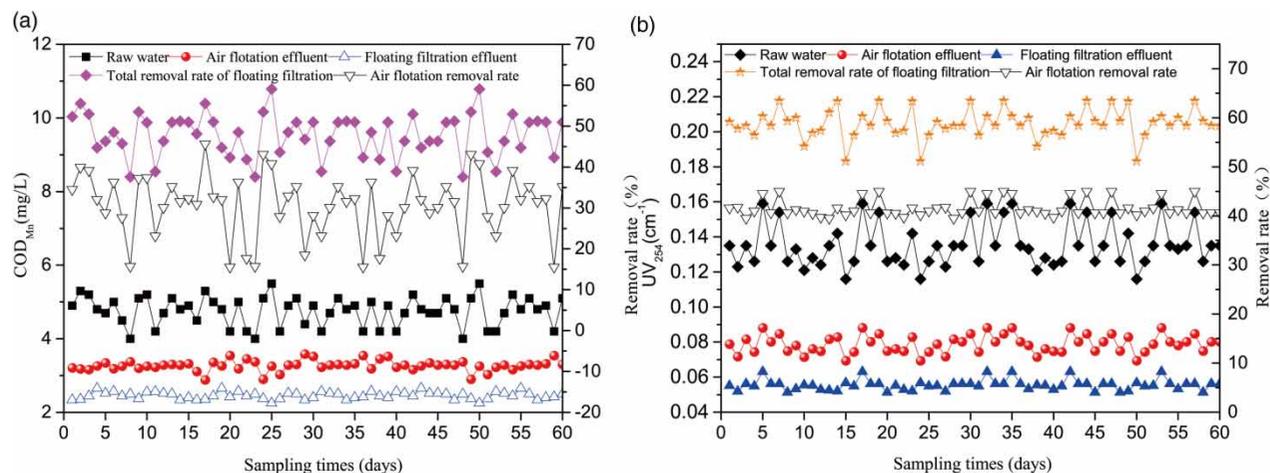
### Organic matter removal efficiency

COD<sub>Mn</sub> is a type of suspended organic matter that is a component of organic compounds in water, and it can be easily neutralized by electricity. COD<sub>Mn</sub> forms flocs in the coagulation stage, and the flocs are floated and removed in the air flotation stage. During the continuous operation of the process, the influent COD<sub>Mn</sub> ranged from 4 to 5.5 mg/L, and the flotation effluent COD<sub>Mn</sub> was maintained at 2.88–3.58 mg/L. The removal percentage (the ratio of the amount of material removed to the total amount of material) was 15.7–40.8% with an average rate of 30.60%, and after filtration, the total removal percentage of COD<sub>Mn</sub> was 37.6–59% with an average of 47.86%. The final effluent COD<sub>Mn</sub> ranged from 2.25 to 2.65 mg/L with an average of 2.46 mg/L (Figure 3).

The UV<sub>254</sub> values reflect the humic compounds, macromolecules, and aromatic compounds that contain C = O and C = C double bonds present in natural water; the polarity of

**Table 1** | Analytical method and instruments

Monitored parameter	Analytical method	Monitored parameter	Analytical method
pH	Determination of pH TESTER	THMFP	Gas chromatography, Agilent 6890 N
COD <sub>Mn</sub>	Potassium permanganate method	NH <sub>3</sub> -N	Nashi Reagent Photometry
UV <sub>254</sub>	Ultraviolet-visible light photometer (TU-1810)	Nitrite nitrogen	N-(1-naphthyl) ethylenediamine dihydrochloride spectrophotometric method
Fluorescence characteristics	Fluorescence photometric method (F-7000)	Nitrate nitrogen	Phenol-2-sulfonic acid spectrophotometry
Microbial biomass	Lipid phosphorus method		



**Figure 3** | COD<sub>Mn</sub> (a) and UV<sub>254</sub> (b) removal effect of the combined process.

these molecules is small, and they can be easily adsorbed. During the continuous operation of the process, the influent UV<sub>254</sub> range was 0.135 to 0.15 cm<sup>-1</sup>, and the air flotation effluent UV<sub>254</sub> was approximately 0.08 cm<sup>-1</sup> with a removal percentage ranging from 40% to 45%. The final removal percentage of the filter unit UV<sub>254</sub> was 51% to 63% with an average value of 58.8%. The final effluent UV<sub>254</sub> value was below 0.06 cm<sup>-1</sup>.

The removal of COD<sub>Mn</sub> and UV<sub>254</sub> via the floating filter shows that the air flotation and filtration unit have a good effect on the removal of organic matter, and the removal of UV<sub>254</sub> in the air flotation unit is better than that of the COD<sub>Mn</sub>. The filtration unit COD<sub>Mn</sub> values were better than the UV<sub>254</sub> value because UV<sub>254</sub> represents aromatic or hydrocarbon organic compounds that contain benzene or conjugated double bonds, i.e., macromolecules and hydrophobic organic compounds, and in the process of coagulation and flotation, some of the macromolecular aromatic compounds adhere to the surface of the particles, flocs and bubbles. The organic particles that adhere to the colloidal particles can become unstable at the coagulation stage, resulting in condensation, polymerization, and adsorption on the surface of the alum and floating removal of the particles under the adhesion of micro-bubbles. The activated carbon filter unit primarily adsorbs low and medium molecular weight hydrophobic organic matter from water, and after many runs, the adsorption performance of activated carbon is relatively weak, primarily because of biodegradation (He *et al.* 2003; Peng & Hai-lu

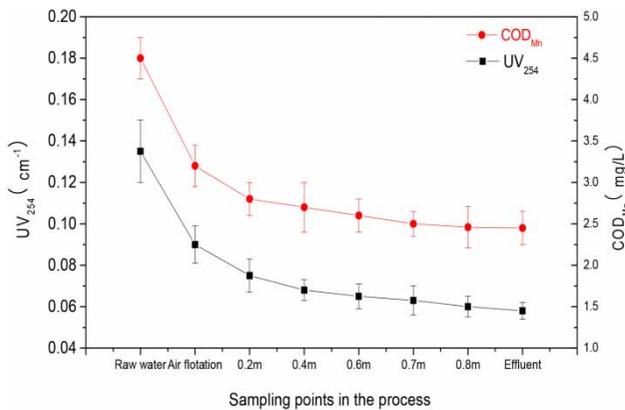
2003). The UV<sub>254</sub> values are representative of the difficult degradation of aromatic organic compounds, and because the filter layer residence time is short, the biodegradation function is limited (Shao-jie & Zong-yuan 2002).

### Organic matter removal over depth

To study the depth degradation and transformation of organic matter in the filtration layer, five sampling ports from the top to the bottom were used, and the organic matter was studied as the process continued. The eight samples were raw water, air flotation water, carbon filter effluent (points 1, 2, 3, 4, and 5), and the final filtered water (Figure 1(b)). Three parallel tests were performed under the same water conditions. The level of organic matter adsorption and degradation was primarily tested during the air flotation-filtration process, and the detection indices were COD<sub>Mn</sub> and UV<sub>254</sub>. The biomass of each carbon layer and sand layer was analyzed correspondingly.

The filter bed surface was point 0. Along the direction of the flow, i.e., 0.2 m, 0.4 m, 0.6 m, 0.7 m and 0.8 m from the water intake, the water intake numbers were 1, 2, 3, 4, and 5, respectively. The sample points 1, 2 and 3 take water from the carbon layer, and points 4 and 5 take water from the sand layer. The effluent test indices for the eight sampling points are COD<sub>Mn</sub> and UV<sub>254</sub>, as shown in Figure 4.

As shown in Figure 4, the air flotation unit has a removal effect on the COD<sub>Mn</sub> value, and the overall effect is similar to that of the CCDAF process. The COD<sub>Mn</sub> removal by the filter

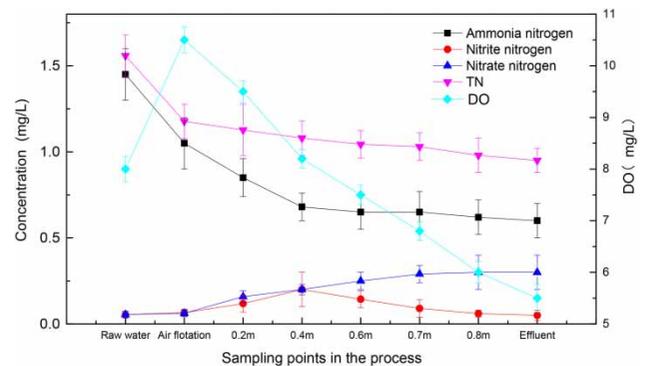


**Figure 4** | Variation trends in COD<sub>Mn</sub> and UV<sub>254</sub> at different sampling points in the combined process.

unit shows a marked change in the 600-mm carbon layer, and the removal of 0.6 mg/L COD<sub>Mn</sub> in the carbon layer accounts for 29% of the total removal. The 300-mm sand layer removes 0.15 mg/L COD<sub>Mn</sub>, which accounts for 7.3% of the total removal. The carbon layer removed 0.025 cm<sup>-1</sup> of the UV<sub>254</sub>, accounting for 32% of the total removal, and the sand layer removed 0.007 cm<sup>-1</sup> of UV<sub>254</sub>, accounting for 9.1% of the total removal. From the above data analysis, most of the organic matter removal in the filter layer occurs in the carbon layer, and the sand layer removal contribution is relatively small. The organic matter removal in the carbon layer was primarily concentrated above a depth of 0.2 m, revealing that the biodegradation in the carbon layer is stronger than that in the sand layer, and the removal percentage in the carbon layer is not balanced. Therefore, the biodegradability of the carbon layer is stronger.

### Distribution characteristics of biomass in the carbon sand filtration layer

After a long period of stable operation, the microorganisms adsorbed on the filter layer will reproduce due to a sufficient amount of dissolved oxygen from the air flotation; dissolved oxygen in the activated carbon layer has remained above 7.0 mg/L (in Figure 5). Some pollutants in the water, such as organic matter and NH<sub>3</sub>-N, are nutrients for these microorganisms. Therefore, the pollutants are degraded via microbial metabolism processes. The lower layer of quartz sand provides an effective barrier to the biofilm to ensure effluent quality.



**Figure 5** | Removal and transformation of nitrogen and changes in the concentration of dissolved oxygen during the combined process.

As shown in Table 2, most of the microorganisms were found in the upper layer of the activated carbon filter material, and the highest value was 50.2 nmol p/g, which was 16.7 times higher than the p/g value (3.0 nmol). This finding is related to the physical and chemical characteristics of the filter materials, such as the specific surface area, specific gravity, and porosity, because these indicators directly affect the biological attachment growth; however, activated carbon in the production process was due to oxidation and activation of the formation of a complex pore structure (Li *et al.* 2005; Qiang *et al.* 2005). Functional groups and complex hydrocarbons, including carboxyl, phenolic hydroxyl, ether, ester and cyclic peroxide groups, can also form on the surface of activated carbon. The formation of functional groups and oxides, as well as the physical properties of activated carbon with porosity, light weight and large specific surface area, enhance the adsorption capacity of the filter material (Guanhua *et al.* 2007). As the concentration gradient of the substance increases, the film thickness is reduced, resulting in a stronger adsorption capacity.

The adsorption occurs via Van der Waals forces, double electrostatic repulsion, and hydrophobic interactions. The

**Table 2** | The variation of biomass in different depths of carbon sand filter

Sampling point	Biomass (nmol p/g)
1#	36.71 ± 0.61
2#	50.16 ± 1.21
3#	40.23 ± 0.90
4#	16.8 ± 0.29
5#	3.01 ± 0.03

suspended biomass is easy to wash off, and when the backwash strength is greater than the adsorption strength, the attached biomass can be washed out.

### Removal and transformation characteristics of nitrogen

The concentration of  $\text{NH}_3\text{-N}$  in the Queshan reservoir was only 0.45–0.55 mg/L. The  $\text{NH}_3\text{-N}$  degradation and transformation with the depth of the filter layer changes of the process was investigated by adding a small amount of  $\text{NH}_4\text{Cl}$  to the influent. To investigate the degradation and transformation of  $\text{NH}_3\text{-N}$  along the filter layer, an experimental study on the nitrogen containing organic matter was performed. The sampling points are shown in Figure 1(b), and the test primarily detected the removal efficiency of nitrogen by the air flotation-filtration process and studied the migration and transformation of the carbon sand filter layer during the  $\text{NH}_3\text{-N}$  removal under the air flotation conditions.

The test indices of eight sampling points are  $\text{NH}_3\text{-N}$ , nitrate nitrogen ( $\text{NO}_3\text{-N}$ ), nitrite nitrogen ( $\text{NO}_2\text{-N}$ ) and TN. The test results are shown in Table 2.

The raw water primarily contains  $\text{NH}_3\text{-N}$ , which accounts for approximately 80% to 85% of the TN. Figure 5 shows the raw water during flotation, and the TN and nitrogen concentrations change slightly. The  $\text{NH}_3\text{-N}$  and TN concentrations decreased, and the  $\text{NO}_2\text{-N}$  and  $\text{NO}_3\text{-N}$  concentrations increased slightly. The content of  $\text{NH}_3\text{-N}$  in the flotation water is the main factor, and the average flotation removal percentage of  $\text{NH}_3\text{-N}$  is 27.5%. There are three main removal pathways for  $\text{NH}_3\text{-N}$ : condensation adsorption, volatilization and nitrogen oxidation-reduction transformation (Qingliang & Xiangzhong 1999; Jian *et al.* 2002). The flotation process uses three methods to remove ammonia. Nitrogen oxide reduction plays a small role in lowering the amount of nitrifying bacteria, and the adequate dissolved oxygen conditions in the air flotation unit play an even smaller role. In the biological flotation effluent,  $\text{NO}_3\text{-N}$  and  $\text{NO}_2\text{-N}$  concentrations show no increase, which can explain this point. Condensation, volatilization and escape are the primary pathways to remove  $\text{NH}_3\text{-N}$  during the air flotation process, and the adsorbed  $\text{NH}_3\text{-N}$  is discharged via the scum overflow.

After the carbon sand filtration, the  $\text{NH}_3\text{-N}$  and TN concentrations decreased, the  $\text{NO}_3\text{-N}$  concentration slightly

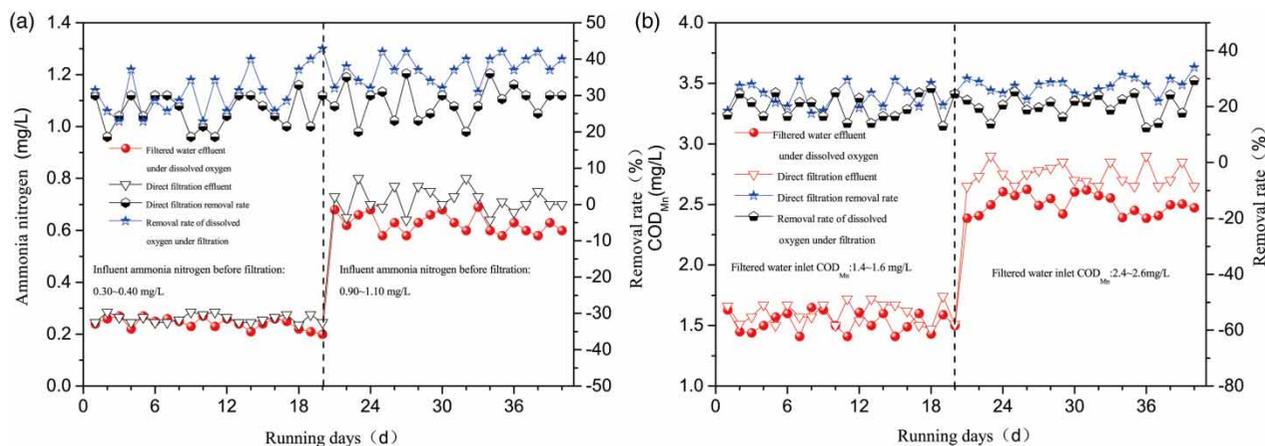
increased, and the  $\text{NO}_2\text{-N}$  concentration increased and then decreased in the filtration layer. The TN and  $\text{NH}_3\text{-N}$  removal percentage in the filtering unit were 15% and 54%, respectively, and the removal percentage of  $\text{NH}_3\text{-N}$  was higher than the removal percentage of TN and  $\text{NH}_3\text{-N}$  due to the three removal mechanisms. The mechanisms are transformation into  $\text{NO}_2\text{-N}$ ,  $\text{NO}_3\text{-N}$ , the second is the synthesis of cell material, and the third is active carbon adsorption. The activated carbon in the pilot plant has been running for about two years. The filter water with a high concentration of ammonia provides a sufficient substrate for the growth and reproduction of slow nitrifying bacteria, and flotation provides conditions for nitrification with a sufficient amount of dissolved oxygen, which is conducive to the formation of ammonifying bacteria and nitrifying bacteria layers on the activated carbon.

The removal percentage of the TN in the filtration unit was only 15%, primarily because the TN amounts were accounted for by the synthesis of cells and the adsorption by activated carbon.  $\text{NO}_2\text{-N}$  showed a slight accumulation in the filter layer and accumulated mainly in the upper part of the carbon layer (but the amount was not large). As the water flowed into the lower carbon layer, the concentration of  $\text{NO}_2\text{-N}$  in the water dropped below 0.10 mg/L. The accumulation of  $\text{NO}_2\text{-N}$  in the filter layer was primarily due to the high concentration of  $\text{NH}_3\text{-N}$  in the influent, the low C/N, an insufficient carbon source and the low denitrification efficiency. The concentration of  $\text{NH}_3\text{-N}$ ,  $\text{NO}_2\text{-N}$  in the effluent were below 0.5 mg/L.

### Effect of the dissolved oxygen concentration on the organic matter removal and denitrification performance in the filter layer

To investigate the effect of the dissolved oxygen concentration on the carbon layer degradation of the organic matter, different concentrations of raw water were studied, and the effects of the air flotation-filtration and carbon sand direct filtration on the removal of the organic matter and  $\text{NH}_3\text{-N}$  were compared. To match the two process conditions, raw water before the filtration was used as the process water.

Figure 6 shows that for the air flotation-filtration, regardless of the concentration of the organic matter in



**Figure 6** | Influence of the dissolved oxygen concentration on the NH<sub>3</sub>-N (a) and COD<sub>Mn</sub> (b) removal in the filter.

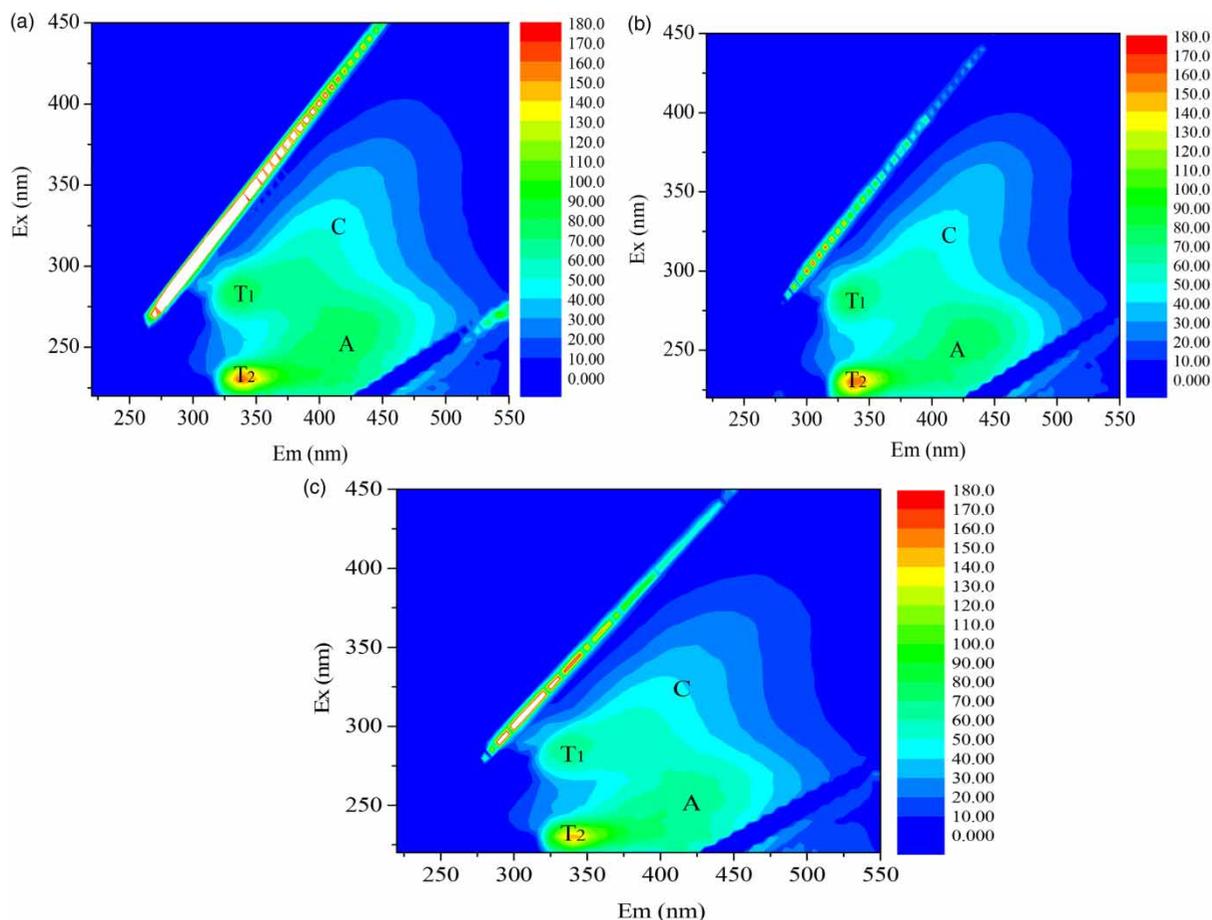
the water before the filtration, the effluent quality is better than that from the direct filtration. However, the figure shows that the advantages of air flotation-filtration are more obvious than those of direct filtration, and there is a certain difference based on the influent pollutant load. For a low load (ammonia: 0.30–0.40 mg/L, COD<sub>Mn</sub>: 1.4–1.6 mg/L), the filtered water and floating direct filtration effluents were only slightly different, and the air filtration effluent quality was slightly better than the effluent quality from direct filtration. The average removal percentage of COD<sub>Mn</sub> and ammonia increased by 5.14% and 3.8%, respectively. With the increase in the influent load, the advantage of the floating filtration process was gradually enhanced. Under high load conditions (ammonia: 0.9–1.1 mg/L, COD<sub>Mn</sub>: 2.4–2.6 mg/L), the float filtration and direct filtration removal of NH<sub>3</sub>-N was 0.63 mg/L and 0.72 mg/L, respectively, and the average effluent COD<sub>Mn</sub> values were 2.50 and 2.75 mg/L, respectively. The average removal percentage of NH<sub>3</sub>-N and COD<sub>Mn</sub> increased by 8.95% and 7%, respectively. Thus, the dissolved oxygen concentration enhanced the removal of organic matter and NH<sub>3</sub>-N because after the air flotation, sufficient dissolved oxygen conditions existed for the ammonifying bacteria and nitrifying bacteria. Under lower load conditions, i.e., a low concentration of organic matter, less oxygen is needed, and the advantage is not as obvious. However, as the influent organic load increases, the dissolved oxygen condition ensures the oxygen needed for microbial degradation, and the biodegradation in the

carbon sand filter layer strengthened, resulting in a significant reduction in the organic content of the effluent.

#### Fluorescence characteristics of DOM removal

Dissolved organic matter (DOM) is a soluble organic substance that can permeate a 0.45 mm pore membrane. The main components of DOM in water are polysaccharides, amino acids and humic acids. In three-dimensional excitation and emission matrix (3D-EEM) fluorescence spectra, the A peak indicates that the soluble organic matter in water is composed of humic substances with a high molecular weight, e.g., hydrophobic humic acid and fulvic acid. The T peaks indicate that the soluble organic matter in water is a type of protein with a low molecular weight, e.g., hydrophilic amino acid proteins.

Figure 7 shows the 3D-EEM fluorescence spectra, revealing that the DOM in the water is mainly composed of soluble proteins and humic substances. Figure 7(a) and 7(b) show the before and after air flotation water peaks for A (80.62 reduced to 70.61), T<sub>1</sub> (81.63 reduced to 76.66), and T<sub>2</sub> (162.24 reduced to 160.05) had different degrees of reduction, indicating that the DOM was partially removed, but the removal effect was limited. The reduction in the A peak was relatively large, which indicated that the air flotation removal effect is better for high molecular weight and high hydrophobicity molecules, e.g., humic acid and fulvic acid. As shown in Figure 7(b) and 7(c), the A (70.61 to 68.63), T<sub>1</sub> (76.66 to 65.19) and T<sub>2</sub> (160.05 to 147.84)



**Figure 7** | Fluorescence spectra of DOM in raw water (a), flotation effluent (b) and filtration effluent (c).

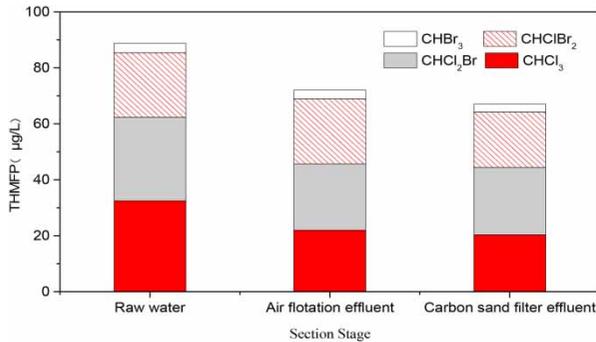
peaks were reduced by varying degrees before and after the filtration. Compared with the peaks of T<sub>1</sub> and T<sub>2</sub>, the A peak has a large T peak reduction, which indicates that the removal is better for the amino acids with a low molecular weight and hydrophilic aromatic ring structure. 3D-EEM shows that the air flotation-filtration process has a certain selectivity for DOM removal in water, and the removal of high molecular weight and hydrophobic humic and fulvic acids was superior to that in the carbon sand filtration. For low molecular weight and hydrophilic amino acid proteins with aromatic ring structures, the carbon sand filtration is better than air flotation for removal.

#### THMFP removal efficiency

Trihalomethanes (THMs), including chloroform (CHCl<sub>3</sub>), dichlorobromomethane (CHCl<sub>2</sub>Br), dibromochloromethane

(CHClBr<sub>2</sub>) and bromoform (CHBr<sub>3</sub>), have obvious mutagenic and carcinogenic effects, and their precursors are mainly natural organic compounds in water (Xiaohong *et al.* 1998; Zhongchen *et al.* 2012). The THMFP is a natural organic compound that reacts with chlorine to produce THMs in water. If the THMFP is removed before chlorination, the production of THMs can be effectively controlled.

Figure 8 shows the THMFP content of each unit during the test, revealing that the main composition of the raw water THMFP is CHCl<sub>3</sub> and CHCl<sub>2</sub>Br, which accounted for approximately 70% of the total. Because the content of THMFP in raw water is relatively low, the removal efficiency of the whole process is not obvious. The total influent THMFP was 88.8 g/L, and the total effluent THMFP was 67.1 g/L. The total removal percentage was 24.43%. In the air flotation process, the agitation and desorption of the bubbles removed the THMFP. The activated carbon



**Figure 8** | The THMFP composition in each unit of the combination process.

adsorption is divided into two stages. In the first stage, the small molecular mass organic matter is quickly adsorbed, and in the second stage, the larger molecular mass organic matter is slowly adsorbed. The performance of the active carbon for adsorbing organic matter is related to the molecular weight of the organic matter and the nature of the organic matter itself. Because the contact time between the carbon sand filter and raw water is short, it is difficult for the activated carbon to absorb the THMFP. Compared with the CCDAF process, the THMFP removal efficiency of the copolymerization air flotation filter is low.

## CONCLUSIONS

1. Combination process to suggest the optimum parameters: coagulant, PAFC;  $[Al^{3+}] = 5.0$  mg/L; dissolved gas pressure, 0.40 MPa; reflux ratio, 12% (back to the copolymerization flocculation pool 4%, back to the flotation contact chamber 8%); R1/R2 value,  $\frac{1}{2}$ ; and filtration rate, 5.2 m/h. The average removal percentage of  $COD_{Mn}$  and  $UV_{254}$  reached 47.86% and 58.8%, respectively, in the combined treatment process. The removal efficiency of  $UV_{254}$  was better than that of  $COD_{Mn}$  due to the removal by the air flotation unit, and the removal of  $COD_{Mn}$  by the filtration unit was better than that of  $UV_{254}$ . Most of the removal of the organic matter in the filter layer occurs in the upper half of the carbon layer. For the humic and fulvic acids, air flotation performs better than the carbon sand filtration. For proteins, carbon sand filtration performs better than air flotation. The total removal percentage of the THMFP was 24.43%.

2. The average removal percentage of  $NH_3-N$  via air flotation was 27.5%, and the removal percentage of TN and  $NH_3-N$  via filtration unit was 15% and 54%, respectively.  $NH_3-N$  showed a distinct decrease, from 1.45 mg/L to 0.60 mg/L, in the dual-media filter, but the decrease in the amplitude of TN was slow. The  $NO_3-N$  nitrogen in the filter layer increased slightly, and  $NO_2-N$  appeared first and then decreased in the filter layer.
3. The concentration of dissolved oxygen promotes the removal performance for organic matter and nitrogen in the floating filtration process, and the water quality in the floating filter process is superior to the water quality in the direct filtration process. With the increase in the influent pollutant load, the advantage of the floating filtration process was gradually enhanced. Under a high influent load, the removal percentage for  $NH_3-N$  and  $COD_{Mn}$  increased by 9% and 7%, respectively.

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