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Experimental study on the treatment of algae-polluted reservoir water by the co-coagulation- dissolved air flotation (DAF) and carbon-sand filtration process

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ABSTRACT

By examining the water quality characteristics of Jinan Yellow River reservoir water, which was high algae and high organic matter content in summer and low temperature and low turbidity in winter, this study described a co-coagulation-dissolved air flotation (CCDAF)-carbon sand filtration process. The combining system was constructed to investigate its synergistic effect on turbidity removal, algae removal and operation characteristics of algae metabolites. Taking the water from the Queshan Yellow River Reservoir in Jinan as the water source, the experimental results showed that the combined process was stable and reliable, and the total removal rates of turbidity, COD_{Mn}, UV_{254} and THMFP were 98.84%, 47.86%, 58.8% and 24.43%, respectively. The effect of algae removal by the copolymerization flotation was 97.0%, the total removal rate after filtration reached 99.57%. Though the removal of MC-LR by the process was limited, the removal of 2-MIB was satisfactory with a removal rate of 95.88%. The flotation unit dissolved adequately oxygen to strengthen the filter unit for organic removal. The integrated floating filtration process was better than directly filtration; as the influent pollutant load increases, the advantage of the flotation process was gradually enhanced. The CCDAF-carbon sand filtration process improved algae removal efficiency by 6.41% compared with the traditional air floating filter, although the filtration period was significantly longer.

Keywords: High algae reservoir water; Copolymerization flotation; Carbon sand filtration

1. Introduction

In recent years, eutrophication of nature water bodies has posed a great threat to human health and aquatic ecosystem [1,2]. Eutrophication of water causes a large number of algal blooms. The traditional process like coagulation-sedimentation-filtration is challenged to remove algae effectively, owing to the high stability of algae [3]. Algae could causes filter blockage, flat knots, frequent backwashing and increasing water consumption, and it may even lead to permanent damage of water plants [3]. Furthermore, some algae excrete algal toxins under certain circumstances, adversely influencing water supply safety [3].

Flotation technology to remove algae has a unique advantage, and plenty studies has been conducted to strengthen the flotation effect in recent years on parallel-flow flotation, counter-flow flotation, copolymerization flotation, etc [4–7]. In the copolymerization flotation, microbubbles are involved in the flocculation reaction process, forming copolymer flocs which are stable and

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cannot be easily desorbed, the flocculation efficiency is significantly increased, and the application prospect is broad [8–10]. Recently, the flotation technology and other processes have been combined organically to form a combination process of floating filter and floating sedimentation tank, which has shown good synergistic effect on water purification. Floating filter technology is the combination of flotation technology and filtration technology, flotation and filtration integration. Air flotation can effectively remove turbidity and algae, reducing the pollution load for the filter and extend the filtration cycle, while filtration can further improve the quality of the effluent. Domestic and foreign experts and scholars have extensively researched the float filter and achieved some results [11–17]. Zhang et al., used the activated carbon deep-bed filter flotation unit to handle the water from Miyun Reservoir with high-algae and high organic matter levels, and achieved good results [18,19]. Eades studied the combined process of counter current dissolved air flocculation (DAF) and filtration to overcome the problem of seasonal algal blooms in raw water [20]. Our research group used air flotation–double charcoal filter to treat the water from Yellow River reservoir found that the removal of algae was significant [21,22]. Liu et al. found that the floating filter was more suitable for surface water with low turbidity and high algae, the coagulation effect was good and the effluent was more stable [23]. Zhang et al. found the DAF process applied to high-algae, micro-polluted water and low-temperature and low-turbidity water had good results [24,25]. Martinez and Hu show that the flotation process is suitable for the treatment of micro-polluted raw water with low temperature and low turbidity and algae and is generally adaptable to reservoir water treatment with a turbidity of less than 100 NTU [26,27].

The traditional floating filter process is the combination of air flotation technology and filtration technology, by placing the flotation tank on the top of the filter tank. The two pools are superposed to form an floatation filter. The traditional cocurrent DAF process is used in the DAF process, and the adhesion process of the floc is co-rotating flow. This paper describes an integrated process of CCDAF-carbon sand filtration. The process comprises a floating filter introducing the dissolved air water twice. The initially dissolved air water directly passed into the flocculation tank, and then the micro-bubbles directly participate in the process of aggregation and co-polymerize with flocs to form "copolymerization flotation". The copolymer air flotation and carbon sand double filtration organic combination with granular activated carbon (GAC) could effectively remove organic matter, odor and other substances [28], and at the same time as particulate matter was intercepted, the organics, order and THMFP were degraded and absorbed. A pilot study was conducted to investigate the effect of synergistic removal of turbidity and organic matter, denitrification, algae and algal metabolites (microcystotomin-LR (MC-LR), GSM, 2-MIB) by CCDAF and GAC-sand filtration. The focus was on investigating the fouling removal efficiency of copolymerization flotation, while comparing the decontamination efficiency and operating conditions of copolymerization flotation filter with a traditional flotation filter. The results will assist in providing technical support for the application of the flotation filter process technology.

2. Materials and methods

2.1. Experimental equipment and operation

The experimental setup for testing was the CCDAF-carbon sand filter process pilot plant (Fig. 1) included a 2.6 m × 0.8 m × 4.3 m flotation filter, with filter area of 0.96 m^2 (L*B = 1.2*0.8). The technology combined CCDAF with carbon-sand double filter, it included mixing, flocculation, copolymerization flotation, carbon-sand filtration and other processes, and achieve integration. The upper part of the device contained a mixing pool, a flocculation tank and a flotation tank, while the lower part was a carbon-sand filtration zone. The upper filter layer was 600 mm depth of granular activated carbon layer (mesh number of 8*30), and the middle layer was 300 mm depth of homogeneous quartz sand (diameter of 0.9–1.2 mm), and the lowest part was pebble support layer was 400 mm.

Based on the traditional carbon sand double-layer filter flotation filter, the device combines the CCDAF with the double-layer carbon-sand filter. It has outstanding advantages in dealing with the water quality of high-algae and low-turbidity reservoirs: 1) integrated process operation, response to high algae, low turbidity and other reservoir water and reduced area; 2) microbubbles join the flocculation zone, participate in the flocculation process, strengthen the flocculation process and the effect, and reduce required dosages of cleaning agents. The air flotation effect was significantly enhanced, reducing the car-

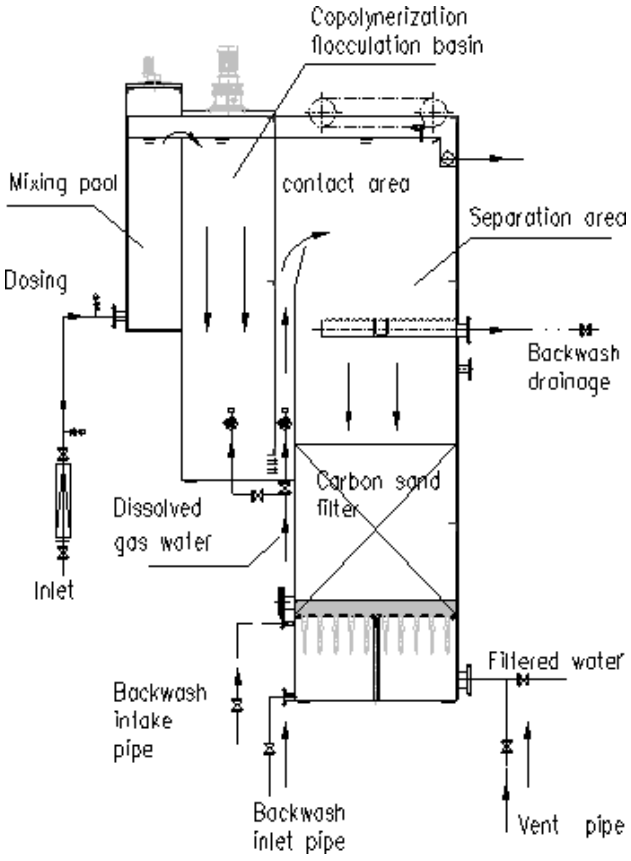

Fig. 1. Sketch map of CCDAF-carbon sand filter device.

bon sand filter load and extending the filtration cycle; 3) the flotation run side is flexible and can effectively address changes in water quality; 4) air flotation units can increase dissolved oxygen in water, and biofilms can easily grow on the surface of activated carbon, which enhances the biological treatment ability of organic matter and organic nitrogen.

The coagulant was PAFC, the dosage (by Al^{3+}) was 5.0 mg/L, the dissolved gas pressure was 0.40 MPa, the total reflux ratio was 12%, the flocculation pool reflux ratio was 4%, the contact chamber reflux ratio was 8%, and the filtration rate was 5.2 m/h.

2.2. Raw water quality

Raw water was sampled from the Jinan Queshan Yellow River reservoir, during the 2 month experiment, the quality of raw water is shown in Table 1.

2.3. Test methods

Trihalomethanes (THMs) were determined by head-space-gas chromatography (6890N gas chromatograph (Agilent)). The samples were stored in an incubator at (25 + 2)°C and tested after 5 d.

Before and after of flotation and filtration, the morphology of algal cells was observed using Hitachi H-8010 scanning electron microscope (SEM). The SEM image production procedure of algal morphological cells before and after of air flotation and filtration was as follows: 1) Sample fixation method: the samples were fixed with rouge iodine solution (1%), paraformaldehyde (1%), formalin (4%) and glutaraldehyde (2.5%) respectively; 2) Sample dewatering procedure: about 200 mL fixed cells were centrifuged at 2000 rpm. Meanwhile, 15%~70% ethanol was added to the collected algae for gradient dehydration every 10 min. Then 70% ethanol was dehydrated, and then 95% and 100% ethanol were dehydrated for twice after overnight. During the experiment, the cell density and dehydration effect were observed by microscope. Finally, it was replaced twice with 100% isopentyl acetate, and the collected algal cells were preserved in 100% isopentyl acetate.

Algae toxins (only extracellular MC-LR was tested) were determined using an online solid phase extraction–liquid phase meter (the United States Diane, ULTIMAT-E3000DGLC). Algal toxin is one of the metabolites of algae, the most common of which is microcystotoxin–LR (Mc-lr), and there's MC-RR MC-YR and so on. Only extracellular Mc-lr was detected in this experiment

Table 1
Water quality information of raw water

Temperature (°C)	10~20
Turbidity (NTU)	20.0~27.0
pH	8.10~8.40
CODMn (mg/L)	4.0~5.5
UV_{254} (cm^{-1})	0.135~0.15
Alkalinity (mg/L)	90~110
TOC (mg/L)	2.9~3.25
Number of algae (million cells/L)	3.56~5.12

Fluorescence characteristics were measured using an F-7000 fluorophotometer. The measurement process is as follows: 1) 100 mL filtrate (passing 0.45 μm membrane) was shaked and put in quartz colorimeter utensil to detect; 2) Under the same conditions, ultra-pure water was used as a blank to eliminate Raman scattering and background noise.

The chlorophyll a (Chla) was measured by a UV/visible spectrophotometer (UV2550, SHIMADZU), and the concentration of Chla was calculated using a formula. The measurement process was as follows: Chla was extracted with 90% acetone after water samples were collected and filtered; after centrifugation and constant volume, the absorbance value of the extraction solution after acidification was measured at the wavelength of 665 nm and 750 nm by UV/VIS spectrophotometer. Finally, the concentration of Chla was calculated according to the formula

The number of particles was determined by a particle counting instrument (Hangzhou green GREAN IBR Versa Count). Other parameters were measured according to "water and wastewater detection and analysis methods" (fourth edition supplement). The test sampling frequency was 1 times per day, and 3 parallel tests were done under the same influent condition.

3. Results and discussion

3.1. Process synergistic turbidity removal characteristics

3.1.1. Turbidity removal efficiency

As shown in Fig. 2, during 60-d experiment, the turbidity of influent fluctuated between 20.6 NTU and 27.2 NTU. The turbidity of the air flotation effluent stabilized at 1.5~2.0 NTU with the removal rate of 90%~94%. After air flotation filtration, the turbidity was at 0.1 NTU~0.3 NTU with the average removal rate of 98.84%, and the operation of each unit was stable (Details seen Supplementary Information 1). The activated carbon deep-bed floating filter was constructed by Zhang [29], and the original water of different water quality was tested. The test results showed that

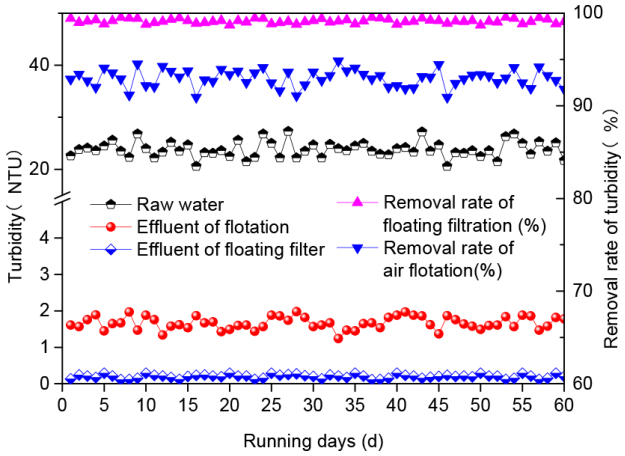

Fig. 2. Turbidity removal rate of combined process

for better water quality, highly algae-laden water and low temperature and low turbidity water, the removal rates of turbidity after filtration were 88%, 93.9% and 82.4, respectively. Under the condition of highly algae-laden water, the removal rate of turbidity after flotation was approximately 90%. Jia used the hierarchical copolymerization flotation to treat Yellow River Reservoir water, and the test results showed that the turbidity of the flotation effluent water of the graded copolymerization was 0.565~1.08 NTU, and the average removal rate was 95.2% [30].

3.1.2. Particle removal characteristics

The influent turbidity was in the range of 20.0–25.0 NTU, and Table 2 presents the size distribution of particles in air flotation and filtration effluent.

As shown in Table 2, the distribution of particles in the effluent of air flotation and filtration was similar to the raw water. The effect of air flotation and filtration on the removal of particles was significant with the removal rate more than 93%. In terms of removal efficiency, the removal efficiencies of the air flotation on particles in the range of 5~7 μm, 7~10 μm, 10~15 μm and 15~20 μm were more significant than those of the 2~3 μm and 3~5 μm, the removal rates of both in air flotation units were 95.95~99.06% and 92.93~94.86% respectively. For filtration, removal rates of 2~3 μm and 3~5 μm were 99.22~99.65%, higher than others. For a high range of water turbidity fluctuations, the total number of particulates through air flotation and filtration was maintained at an average of 500 particles/mL, ensuring the quality of the effluent.

3.2. Characteristics of process synergistic algae removal

3.2.1. Algae removal efficiency and algal morphological characteristics

During the test, the water temperature at 10~20°C and the pH value was 8.10 ~ 8.40. As shown in Tables 3 and 4, the raw water algae ranged from 3.56 to 5.12 million cells/L, and the concentrations of Chla were 8.12~11.70 μg/L. During the high algae period of operation, the algae content and Chla in effluent of each unit were measured and show in Tables 3 and 4.

The influent algae content was 3.56~5.12 million cells/L, and the flotation unit reduced algae by 1 to 2 orders of magnitude with an average removal rate of 97.0%. After filtration, the final number of algae in effluent was 8.5~35.8

Table 2
Particle distribution rule of combined process in the effluent

Particle size range (μm)	Raw water (cnt/ml)	Flotation effluent water (cnt/ml)	Filtered water (cnt/ml)	Flotation removal rate (%)	Total removal rate (%)
2~3	47306~56190	3313~3428	253~367	93.00~93.90	99.22~99.55
3~5	34387~39492	2031~2431	139~249	92.93~94.86	99.28~99.65
5~7	24960~25386	572~1012	65~109	95.95~97.75	99.56~99.74
7~10	19004~23046	341~550	46~72	97.11~98.52	99.62~99.80
10~15	8404~9148	107~160	29~41	98.10~98.83	99.51~99.68
15~20	1237~1920	18~35	10~19	97.17~99.06	98.46~99.48
20~25	232~300	5~9	2~7	96.12~98.33	96.98~99.33
25~	102~120	2~4	1~3	96.08~98.33	97.06~99.17

Table 3
Algae removal of combined process

	Raw water	Flotation effluent water	Filtered water	Flotation removal rate	Total removal rate
The total number of algae (Ten thousand cells/L)	351	8.3	0.85	97.64%	99.75%
	467	20	3.58	95.70%	99.23%
	512	12	1.31	97.66%	99.74%

Table 4
Chla removal of combined process

	Raw water	Flotation effluent water	Filtered water	Flotation removal rate	Total removal rate
Chla (μg/L)	8.12	1.73	0.93	78.69%	88.55%
	9.32	2.11	1.16	77.36%	87.55%
	11.70	2.32	1.45	80.17%	87.60%

thousand cells/L, and the total average removal rate was 99.57%, indicating that the effluent algae content was significantly reduced.

The average Chla concentration in the influent was 9.71 μg/L, the average Chla concentration in the effluent of the air flotation was 2.05 μg/L, with the average removal rate was 78.74%. After filtration, the average Chla concentration in the effluent was 1.18 μg/L, and the total average removal rate of the process for Chla was 87.90%.

The CCDAF–carbon sand filtration process had better removal capacity for algae. Due to the participation of micro bubbles in floc condensation reaction, the floc copolymers formed are stable and difficult to desorb, which significantly improves the adhesion efficiency of flocs. Most of the algae were removed in the air flotation, and the contribution of the filtration unit to the removal of algae was relatively small. SEM images of algae before and after air flotation and filtration (Supplemental information S1) also showed that the number of algae decreased significantly after air flotation. However, the cells wall of alga before and after air flotation was smooth, the algae body was full, and the morphology of the algal cells remains intact without deforming. After filtering, some algae cells no longer appear smooth and no longer have a full outer wall shape like algae cells before flotation, they wilted and damaged. This appearance indicates that some algal cells in the filter layer were damaged or dead owing to wear, extrusion and deposition and other reasons, resulting in the escape of intracellular protoplasm, organic matter and other substances into the effluent.

3.2.2. Removal characteristics of alga toxin

Algae cells release some substances of the body during the process of growth or death. These substances are made up of extracellular organic matter (EOM) and intracellular organics (IOM) [31]. These substances are released into water during the growth or death of algal cells. As shown in MC-LR removal map (Supplementary Fig. S2), MC-LR appeared to decrease firstly and then increased in the combined process. As a whole, the process had limited ability to remove MC-LR. The combined process had undergone two stages: air flotation and filtration. After the flotation, microbubbles were physically adhered to the alga and float up to removal it, and MC-LR was partly removed.

The intracellular MC-LR is one of the IOM substances. Studies have shown that in the process of death or breakage of algae cells, intracellular MC-LR will be released to the surrounding environment [32,33]. In the filtration stage of carbon sand, the algae cells were stuck in the filter layer, resulting in the release of IOM once it damaged or dead [34]. This leaded to the increase of extracellular MC-LR, such that the MC-LR increases in the filtered water, and the effluent rose from 0.15 μg/L after air flotation to 0.25 μg/L.

3.2.3. Odor removal characteristics

At present, frequent odor problems caused by algae occur with increasing eutrophication of water source. Biological metabolites are the main causes of the smell, of which the GSM and 2-MIB secreted by algae during metabolism are the main hetero olfactory substances [35].

As shown in Fig. 3, the content of GSM in the influent was lower than that of the standard limit (<10 ng/L). After air flotation, the GSM value decreased greatly (from 0.96 ng/L to 0.10 ng/L). The GSM value of the filtered water increased greatly, and the GSM value in the effluent reached 1.35 ng/L. Because GSM is a product of the combination of algae and actinomycetes, during the process of coagulation, the increase in GSM could be the result of damaged algae in the coagulation. In the filtration, GSM increased greatly, because most of the odorous substances produced by microcystis were stored in cells which were deposited in the filter layer. After decomposition, the smelly substances entered water bodies, resulting in the increase of GSM. However, the GSM in the effluent was lower than the detection limit (the drinking water standard). Cook, Chestnutt and other researchers reported that GSM was more easily adsorbed by PAC and GAC than 2-MIB [36,37]; however, because of the long operation time of the carbon sand filter, the adsorption point was less, and the adsorption was weak, leading to poor performance of the activated carbon in removing the GSM. Ndreadakis and others used advanced oxidation processes to study the removal efficiency of GSM and MIB in water sources of different water quality. The results showed that the odor

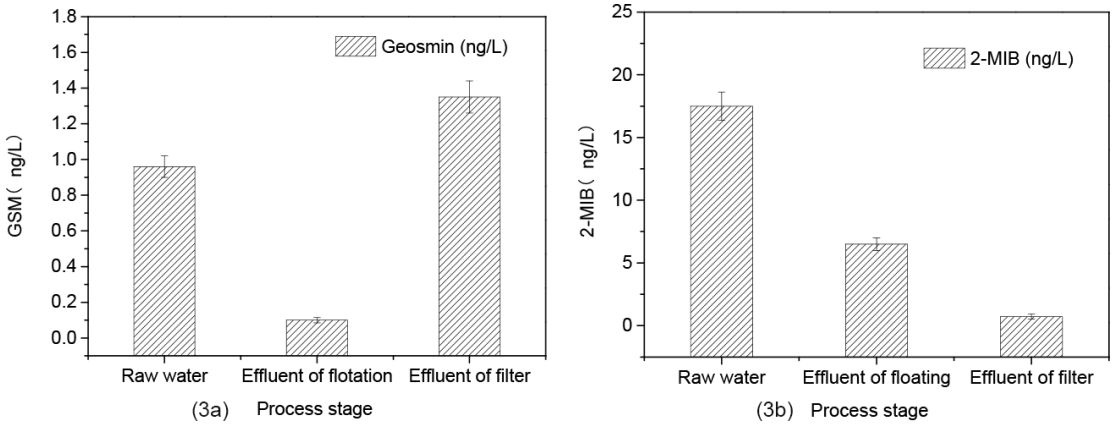

Fig. 3. Removal rule of GSM and 2-MIB in combined process each unit.

and odorous substances in the effluent merely reached the human olfactory threshold (10 ng/L) [38].

As seen from Fig. 3, 2-MIB had a high influent content of 17.50 ng/L, indicating that most of the odorous substances in the raw water were caused by 2-MIB, which was produced by the metabolism of algae and actinomycetes or by a mixture of some organic substances and disinfectants. After the air flotation, the 2-MIB further decreased. The 2-MIB content in the air flotation water was 6.50 ng/L, and the removal rate was 60.24%. The concentration of 2-MIB decreased substantially after filtration, due to the adsorption and biological degradation of activated carbon. The average content of 2-MIB in the effluence of filter was 0.72 ng/L. In the final effluent, the average removal rate of 2-MIB reached 95.88%, and the removal effect was good. Research by Terauchi et al. showed that the removal rate of 2-MIB by a bio-filter was up to 63.6% [39]. The research of Jiao showed that the removal rate of 2-MIB could reach 69% (and even up to 88%) if adding powdered activated carbon before precipitation. The removal rate of 2-MIB could reach more than 98% after a subsequent ozone biologically activated carbon advanced treatment. However, when the content of 2-MIB was high, the cost of adding PAC was higher [40]. It can be seen from the comprehensive comparison that the overall removal effect of the CCDAF-carbon sand filtration process on olfactory substances was better, and it can guarantee improved drinking water quality.

3.3. Processing synergistic properties of organic compounds

3.3.1. Removing organic compounds and performance of techniques

COD_{Mn} reflects suspended organic matter that is easy to be neutralized using electricity in the water. This part of organic matter forms flocs through the coagulation stage which are removed in the air flotation stage. During the continuous operation, the range of influent COD_{Mn} was 4~5.5 mg/L, the COD_{Mn} in the effluent of air flotation was between 2.88 and 3.58 mg/L, and the average removal rate was 30.60%. The average removal rate of COD_{Mn} after filtration was 47.86%, and the final effluent COD_{Mn} remained between 2.25 and 2.65 mg/L, with an average of 2.46 mg/L.

UV_{254} reflects the presence of humic organic macromolecules and aromatic compounds with C=O bonds and C=C bonds in natural water. During continuous operation, the range of influent UV_{254} was 0.135 ~ 0.15 cm^{-1}, the UV_{254} of air flotation effluent was 0.08 cm^{-1}, and the removal rate was 40% ~ 45%. After the filtration unit, the final removal rate of UV_{254} was 58.8%, and the final effluent UV_{254} was less than 0.06 cm^{-1}. Generally, the removal rate of UV_{254} was less than that of COD_{Mn}, and the removal rate of the filter unit was only 17.2%. UV_{254} was a macromolecular aromatic refractory organic compound, and compared with benzene or conjugated double bond aromatic or hydrocarbon organic compounds, such molecules have weak polarity and are easy to be adsorb. However, due to the longer operation time of the filter, the adsorption point of activated carbon was decreased, and the adsorption effect was weakened. Although the biological degradation in the filter layer gradually played a role, the final biological action has little contribution to the removal of UV_{254}.

Zhang et al. used an activated carbon deep bed filter to treat high-algae water, and the results showed that the removal rates of air flotation effluent for UV_{254} and COD_{Mn} were 30% and 37%, respectively; the total removal rates of UV_{254} and COD in the effluent after filtration were 50% and 53%, respectively [29]. The removal efficiency of COD_{Mn} was better than that of UV_{254}. Liu used an activated carbon deep bed floating filter to treat Miyun reservoir water. The research showed that under high alga and good raw water quality, the total removal rate of UV_{254} and COD_{Mn} was 51.5% and 55.5% respectively [41].

3.3.2. Effect of dissolved oxygen on the removal of organic matter by filter layer

To investigate the effect of dissolved oxygen on the degradation of organic matter by a carbon layer after flotation, different concentrations of raw water were prepared, and the removal efficiency of organic matter by air flotation filtration and carbon sand direct filtration was compared. To make the conditions of the two processes consistent, the water prior to filtration was used as process water. The test results are shown in Fig. 5.

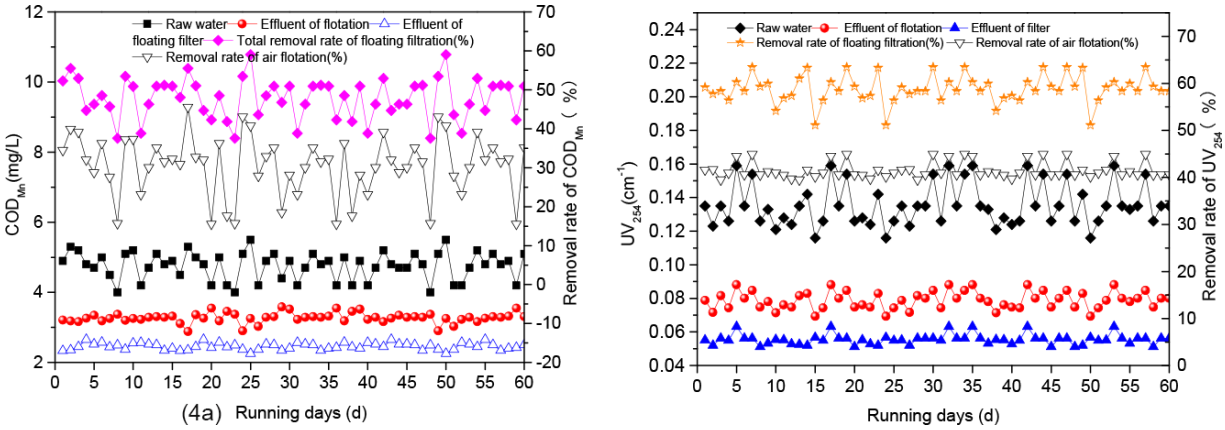

Fig. 4. (a) COD_{Mn} removal effect of combined process. (b) UV_{254} removal effect of combined process.

As shown in Fig. 5, for air flotation filtration, because dissolved oxygen exists after air flotation, no matter the concentration of organic matter in the water before filtration, its effluent was better than that of direct filtration, the average removal rate of COD_{Mn} by air flotation filtration and direct filtration was 26.13% and 20.07 respectively. However, it can be seen from the figure that the advantages of flotation filtration over direct filtration had a certain relationship with the load of pollutants in the raw water. Under lower load conditions (COD_{Mn}: 1.4~1.6 mg/L), little difference was found between the floating filter effluent and direct filtration effluent. Flotation effluent was slightly better than direct filtration, and the COD_{Mn} removal rate was increased by 3.8%. With the increase of the influent load, the advantages of the floating filtration process were gradually enhanced. Under the condition of high load (COD_{Mn}: 2.4~2.6 mg/L), the average value of COD_{Mn} in the water after floating filter and directly filtered was 2.50 and 2.75 mg/L, respectively, and the removal rate of COD_{Mn} was increased by 7%. It can be concleded that the dissolved oxygen condition enhanced the removal of organic matter. The reason was that dissolved oxygen after air flotation provided sufficient dissolved oxygen for the biological effects of ammonifying bacteria and nitrifying bacteria. Under the condition of lower influent load, the concentration of organic matter was lower, and the required dissolved oxygen was less, and the advantage of dissolved oxygen was not obvious. However, with the increase of influent organic load, the dissolved oxygen conditions ensure the oxygen needed for microbial degradation and strengthening the biodegradation of charcoal within the filter layer, resulting in a significant improvement of the floating filer than direct filter.

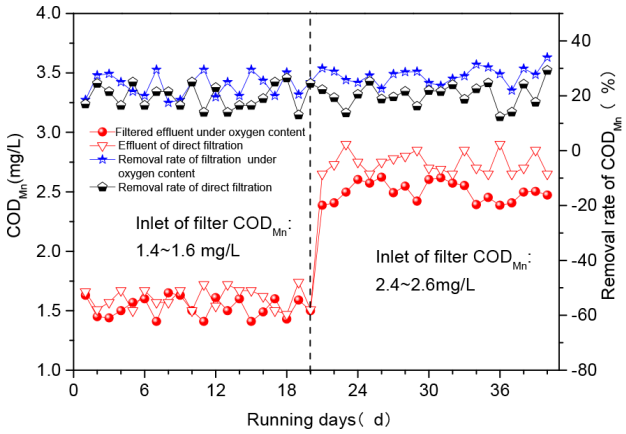

Fig. 5. Influence of dissolved oxygen on COD_{Mn} removal in the filter.

3.3.3. Fluorescence characteristics of DOM removal

Dissolved organic matters (DOM) can pass through a 0.45 μm membrane and the main components in water are polysaccharides, amino acids and humic acids and protein [42]. From the 3D-EEM fluorescence spectrum in Fig. 6, it can be seen that the dissolved organic matters in water were mainly organic matter of dissolved protein and humic acids. Figs. 6a and 6b show that, before and after air flotation, the A peak value dropped from 80.62 to 70.61, the T1 peak value dropped from 81.63 to 76.66, and the T2 peak value dropped from 162.24 to 160.05, indicating that DOM was partially removed; however, the removal rate of protein removal was limited. The reduction of the A peak was slightly larger than that of the T peak, indicating that the removal of high-weight molecular and hydrophobic humic acid and fulvic acid by air flotation was higher. Fig. 6b and 6c showed that before and after filtration, the A peak value decreased from 70.61 to 68.63, the T1 peak value decreased from 76.66 to 65.19, and the T2 peak value decreased from 160.05 to 147.84. The A peak was compared with the T1 and the T2 peaks. The reduction of the T peak was slightly larger than that of the A peak, indicating that the filtering method was better for the removal of amino acid proteins with an aromatic rings low molecular weight and hydrophilicity.

It is known from the three-dimensional EEM fluorescence spectrum that the air flotation filtration process had a certain selectivity to removal DOM from water. For humic acid and fulvic acid substances (high molecular weight and hydrophobic organics), flotation was better than carbon sand filtration. For low molecular weight and hydrophilic amino acid proteins with an aromatic ring structure, carbon sand filtration was better than air flotation.

3.3.4. Removal efficiency of THMFP

Trihalomethanes (THMs) are the general term for four kinds of haloalkanes, such as $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$, which are mutagenic and carcinogenic. Their precursors are mainly natural organic matter in water. Three halogenated methane generating potential (THMFP) is the natural organic matter that can react with chlorine to pro-

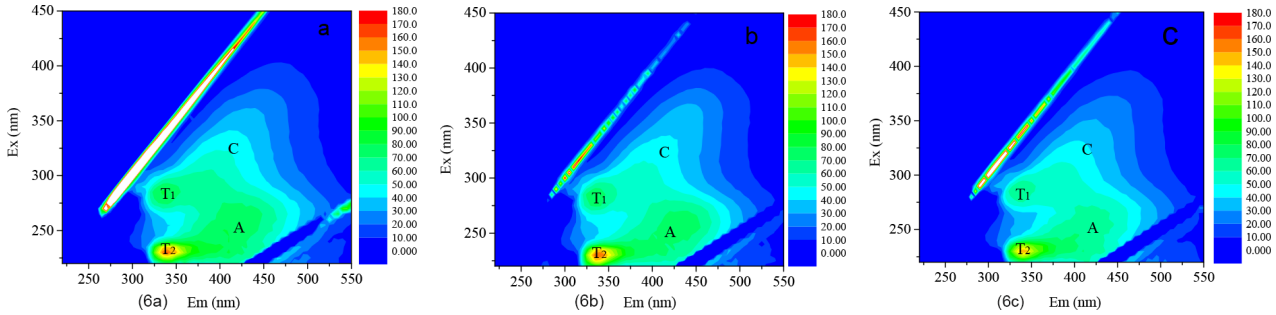

Fig. 6. Fluorescence spectra of DOM in raw water (a), flotation effluent (b) and filtration effluent (c).

duce THMs in water. If the THMFP is removed before chlorination, it can control the amount of THMs effectively.

The THMFP content of each unit during the test was shown in Table 5. Because the content of THMFP in the original water was relatively low, the removal efficiency of the whole process was not obvious. The total amount of THMFP in the water was 88.8 μg/L, the total amount of THMEP in the final effluent was 67.1 μg/L, and the total removal rate was 24.43%.

In the process of air flotation, the removal of THMFP mainly depends on the stirring and blowing off of the bubbles. The removal of THMFP by activated carbon adsorption consisted of two stages. The first one was the rapid adsorption of the organic matter with small molecular weight, and the second one was the slower adsorption of the organic matter with larger molecular weight. Because of the shorter retention time between the carbon sand filter and the original water, it was difficult for activated carbon to adsorb THMFP; thus, the removal capacity of THMFP was not improved by the activated carbon filter.

4. Comparison between copolymer floating filter and conventional floating filter efficiency

The emergence of the integration of flotation filtration technology originated from the patented integrated flotation and quartz sand filter developed by Sweden in the 1960s [43]. In this experiment, the CCDAF-carbon sand filtration process was adopted. The dissolved air of the flotation section was added twice. The earlier dissolved air water micro bubbles were directly involved in the process of agglomeration and co-polymerized by the flocs to form "copolymer flotation." In the conventional air floating filter process, the dissolved air water in the air flotation section was added only once, and the clash of the floc was completed in the air flotation contacting tank. The conventional air floating filter operating process parameters were as follows: dissolved gas pressure of 0.40 MPa, reflux ratio of 12%, and filtration rate of 5.2 m/h.

4.1. Comparison of turbidity removal efficiency

As shown in Fig. 7, the turbidity of raw water was 20–27 NTU, the turbidity of copolymerization flotation effluent was within the range of 1.34~1.97 NTU, with an average of 1.67 NTU. The turbidity of the air floating effluent in the traditional floating filter was within the range of 1.51~2.47 NTU, with an average of 2.01 NTU. The results show that the copolymer flotation was better than traditional flotation, and the removal efficiency of turbidity in the effluent water of the copolymer flotation was improved by an average of 0.34 NTU than tradition flotation. It can be seen that the introduction of some dissolved air water in the flocculation stage resulted in micro bubbles that were directly involved in flocculation and copolymerized with the flocs, thereby greatly enhancing the effect of copolymerization. The flocs acted as the "nucleus" of microbubbles and formed a floc-micro bubble-particle polymer, which was stable and not easy to desorb. Micro bubbles play an important role of copolymerization and carrier gas uplift.

In a filtration period, the turbidity in effluent of the copolymerization floating filter process was 0.09 NTU lower than that of the conventional floating filter, and the turbidity of the co-floating filter effluent was stable within 0.3 NTU. With conventional air floating filters, the filtered water turbidity reached below 0.3 NTU within the first 48 h, but for more than 48 hours, the effluent turbidity increased rapidly, and the effluent turbidity reached 0.5 NTU at 50–60 h,. Therefore, for one filtration cycle, the effluent from the copolymerization floating filter was more stable.

Table 5
The THMFP composition in each unit of combination process

	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
	μg/L			
Raw water	32.5	29.8	23.1	3.4
Effluent of flotation	22	23.7	23.2	3.2
Effluent from carbon sand filter	20.3	24.1	19.8	2.9

4.2. Comparison of algae removal efficiency

It is shown in Table 6 that the number of algae in the original water was 3.51 ~ 6.56 million cells/L, and the removal rate of the algae by the copolymerization air flotation was above 95%. The removal rate of algae by traditional air flotation was just over 90%. The removal rate of the copolymerization air flotation on the algae was 6.41% higher than that of the traditional air flotation.

4.3. Filter cycle comparison

For the head-loss of filtering, the performance of the combined process was better than that of the conventional air floating filter, and the filtration cycle of the copolymerization floating filter was much longer than that of the conventional floating filter. As shown in Fig. 8, the increase of head-loss of the two processes was relatively slow in the first 24 h, and the difference was not very large. However,

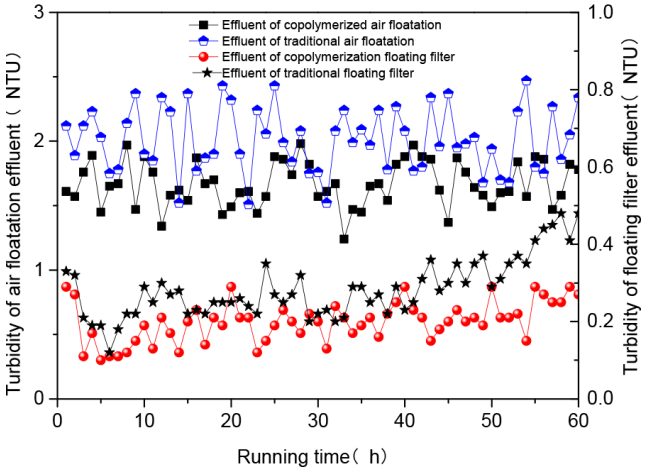

Fig. 7. Turbidity removal effect comparison of co-coagulation floating filter with traditional floating filter.

Table 6
Algae removal effect comparison of co-coagulation floating filter with traditional floating filter

	Raw water (million cells/L)	Effluent of flotation (million cells/L)	Effluent of filtered (million cells/L)	Removal rate of air flotation (%)	Total removal rate (%)
Copolymerization floating filter process	3.51	0.083	0.0085	97.64	99.75
	4.67	0.20	0.0358	95.70	99.23
	5.12	0.12	0.0131	97.66	99.74
Conventional air flotation filter	5.37	0.534	0.0565	90.06	98.94
	5.73	0.538	0.0678	90.61	98.82
	6.56	0.584	0.0762	91.10	98.84

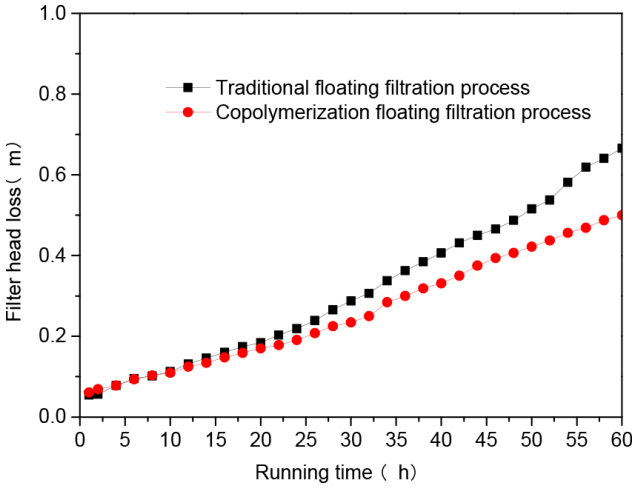

Fig. 8 Head loss comparison of co-coagulation floating filter with traditional floating filter.

after 24 h, the head-loss of the two processes increased rapidly, and the difference of head-loss between the two processes was obvious. With controlled to 0.5 m of total water head-loss, the head-loss of the conventional air floating filter reached 0.49 m at 48 h, and the filter water head-loss of the copolymerization floating filter was only 0.40 m. With an operating duration of 56 h, the water head loss of the copolymerization floating filter reached 0.47 m. If the water head-loss was controlled to 0.5 m, the filter period of the copolymerization floating filter was more than 8 h longer than that of the conventional air filter.

4 Conclusion

(1) The integrated process of the CCDAF-carbon sand double filtration was stable and reliable. The turbidity of the filtered water was stable at 0.1 NTU ~ 0.3 NTU, and the total removal rate was 98.84%. The removal effect of air flotation on particles within the range of 5~20 μm was higher than for those within 2~5 μm. Filtration was more effective for removing particles in the range of 2~5 μm. The effect of the air flotation unit removing the UV_{254} was a slight better than the removal of COD_{Mn}, while more COD_{Mn} was removed by a filter unit than UV_{254}.

(2) The dissolved oxygen enhanced the performance of the flotation process to remove organic matter. The effluent from the floating filtration process was better than the effluent from the direct filtration. With an increase of inlet water pollutant load, the advantage of the floating filtration technology was more obvious.

(3) Algae were removed mainly in the air flotation unit, and the total removal rate after filtration was 99.57%. The combined process had a limited ability to remove MC-LR, but the removal of 2-MIB was good, with an average removal rate of 95.88%.

(4) The effluent of the copolymerization floating filter was more stable than that of the conventional flotation filter, and the removal efficiency of turbidity and algae was increased to varying degrees. The filtration cycle time of the copolymerization floating filter was longer than that of the conventional flotation filter.

Acknowledgements

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Supplementary information

Supplementary information 1

In view of the removal of turbidity, it is very effective to use the process of copolymerization air flotation filter for water diversion from south to north. The combined process can get part of the dissolved gas in the flocculation stage. The addition of microbubbles increases the probability of collisions and accelerates the coalescence rate. In the reaction stage, micro-flocs form, and with the organic combination of flotation and flocculation, the flocculation process and effect are strengthened. Therefore, the removal of turbidity is closely related to coagulation conditions and the coagulation effect, and the effect on air flotation is mainly reflected in the points below.

(1) The colloidal particles in water usually have negative charges, while the negative potential on the surface of microbubbles is usually about –100 mV. The electrostatic repulsion between the two is stronger, which is unfavorable for their collision and adhesion. Coagulation significantly reduces the value of the surface of the colloid particles, thereby greatly weakening the adverse effects of the electrostatic repulsion. (2) In the process of coagulation, a large amount of organic pollutants adsorbed by the floc enhance the hydrophobicity of the surface, which is beneficial to the adhesion of the floc. (3) The size of floc formed in the coagulation process is larger than that of the original colloidal contaminants, which is beneficial to the collision of the floc. Based on the above three points, the condition of coagulation has a direct effect on the operational effect of the air flotation process. In the integrated process of the copolymerization air flotation filter, the bubble directly participates in the agglomeration and flocculation, and the micro bubbles are sandwiched between the flocs in the process of copolymerization and flocculation. The organic combination of flocculation and copolymerization air flotation is achieved. Foam flocculation is not only stable in the floating process but also not easy to sink; the flotation water effect is more obvious. In the process of air flotation, the particle material is taken away with the slag, which effectively reduces the pollutant load of the carbon sand filter. This lengthens the filter period, and the effect on the effluent is improved.

Supplementary information 2

As shown in Fig. S1 (c), SEM images of algae before and after air flotation and filtration showed that the number of algae decreased significantly after air flotation. However, the outer wall of algal cells before and after air flotation is smooth, the algae body is full, the algal body does not deform, and the morphology of the algal cells remains intact. After filtering, some algae cells no longer appear smooth and no longer have a full outer wall shape like algae cells before flotation, but they rather appear wilted and damaged. This appearance indicates that some algal cells in the filter layer are damaged or dead due to wear, extrusion and deposition and other reasons, further result in intracellular protoplasm, organic matter and other substances appearing in the effluent.

Supplementary information 3

In the combined process, the appearance of MC-LR first decreased and then increased, and the overall process for the removal of MC-LR was limited. The combined process has two stages: air flotation and filtration. After the air flotation unit, the microbubbles physically adhered to the algae and were removed, and the MC-LR was partially removed

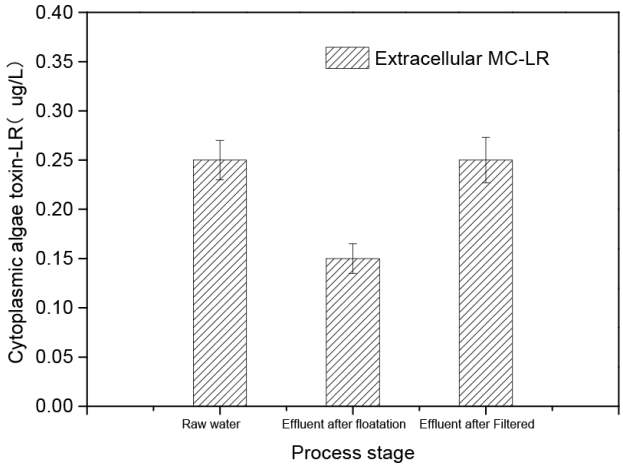

Fig. S2. Removal rule of extracellular MC-LR in combined process each unit.

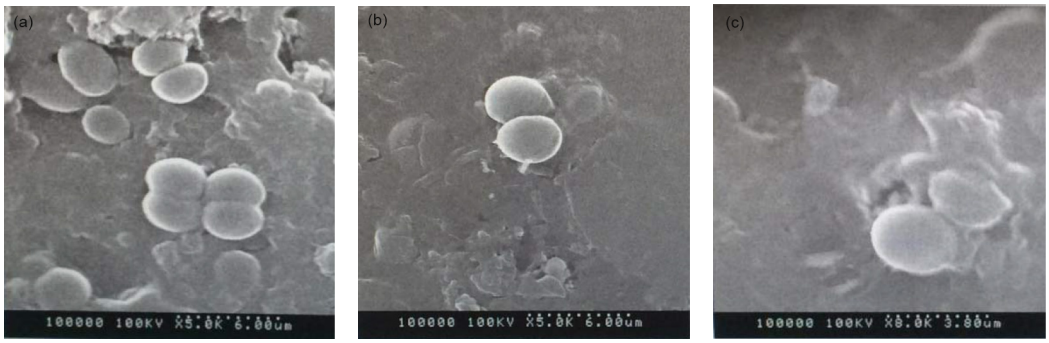

Fig. S1. SEM images of algae before and after the flotation filtration.