

Effect on water quality and control of chemically enhanced backwash by-products (CEBBPs) in the adsorption-ultrafiltration process

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Abstract

The overall purpose of this research was to investigate the typical types of chemically enhanced backwash by-products (CEBBPs) produced in the chemically enhanced backwash (CEB) process and the influence of variability of CEB factors on typical CEBBPs in the adsorption-ultrafiltration process. Moreover, health risk assessment was utilized to assess the potential adverse health effects from exposure to effluent after the optimal online CEB. The results of the study found the NaClO backwash reagent could react with organic matter to produce CEBBPs, including 9 kinds of volatile halogenated organic compounds (VHOCs) and 9 kinds of haloacetic acids (HAAs) during the CEB process. After a comprehensive consideration of the influence of a single factor on the CEBBPs formation and membrane cleaning effect, the optimal CEB parameters were 6 min of BD, 120 min of BI, 30 L/(m²·h) of BF and 50 mg/L of RC. Under the optimum CEB cleaning parameters, the effluent does not pose a non-carcinogenic risk and posed potential carcinogenic risk to local residents. The lifetime carcinogenic risk (LCR) value for HAAs (6.68E-06) is very close to the LCR value of CEBBPs (6.78E-06), indicating that the HAAs are the main substances in the effluent after CEB.

Key words: adsorption-ultrafiltration process, CEB cleaning parameters, chemically enhanced backwash by products, health risk assessment

Highlights

- The NaClO could react with organic matter to produce CEBBPs in the process of CEB.
- The CEBBPs included 12 species of VHOCs and 9 species of HAAs.
- The CEB removal of membrane foulants effectively mitigated membrane fouling.
- The optimal CEB parameters were 6 min of BD, 120 min of BI, 30 L/(m²·h) of BF and 50 mg/L of RC.
- Under the optimum CEB cleaning parameters, the effluent could pose potential carcinogenic risk.

INTRODUCTION

Currently, there is considerable attention focusing on the pollution problems of everyday potable water sources (Alzahrani *et al.* 2013; Wei *et al.* 2016). Because many pollutants, especially organic pollutants, get into the surface water through different ways, the potential risk of water source pollution is becoming more and more prominent; this contaminated surface water is referred to as micro-polluted surface water (Zhang *et al.* 2015; Kan *et al.* 2016). However, conventional water

purification technology (coagulation – sedimentation – filter – disinfection) has some limits in treating micro-polluted surface water (Wang *et al.* 2016). Compared with conventional water purification technology, ultrafiltration (UF) and microfiltration (MF), which are representative of low-pressure membrane technology, can simplify the process, improve the utilization rate of raw water and occupy much less processing power of a traditional craft unit (Masindi *et al.* 2015).

Many studies showed that adsorption combined with membrane can increase the membrane flux and the removal efficiency of organic matter, which is the advantage of the adsorption-UF combination technology (Li *et al.* 2016). Meanwhile, membrane cleaning is an effective way to control membrane fouling and restore membrane filtration (Gibert *et al.* 2016).

Membrane cleaning methods include physical and chemical cleaning. The physical cleaning can only restore the reversible membrane fouling and the irreversible membrane fouling can only be accomplished through the chemical cleaning method (Kimura *et al.* 2016). Owing to the disadvantages of conventional chemical cleaning CIP (clean in place), including the high amount of time required, the complicated operation and the low degree of automation, the online chemical cleaning method, namely chemically enhanced backwash (CEB), has been paid more and more attention by people (Touffet *et al.* 2015). Compared with CIP, CEB required a relatively lower concentration of chemical reagent, which has a short contact time with membrane and can be conducted at room temperature. The transfer of chemical cleaning reagents to the membrane surface in the cleaning mechanisms was a crucial step. In chemical cleaning, oxidant-type cleaning reagents (such as sodium hypochlorite) with strong oxidation ability can effectively remove organic matter on the membrane surface and in the pores (Porcelli & Judd 2010). The sodium hypochlorite solution can effectively remove organic matter from the fouling of an irreversible membrane and recover the flux in the membrane (Kimura *et al.* 2004). Furthermore, the NaClO removal effect on organic pollutants under a higher pH value was better, and natural organic matter (NOM) degraded to carboxyl, ketone, and the aldehyde group by NaClO oxidation (Strugholtz *et al.* 2005).

Chemical cleaning is undoubtedly an effective method to solve membrane fouling, compared with the large amount of membrane fouling research, but there is very little on the study of membrane chemical cleaning. Meanwhile, the potential secondary pollution and the safety of drinking water quality because of membrane chemical cleaning is not yet a cause for concern. The research status of membrane chemical cleaning shows that the main membrane pollution is caused by NOM during drinking water membrane processing and NaClO is widely used for a cleaning reagent (Kan *et al.* 2016). In the CEB process, membrane cleaning reagents may react with membrane pollution to generate by-products. For instance, NaClO reacts with organic matter in membrane cleaning water to generate disinfection by-products that contain toxicity, mutagenicity, carcinogenicity and teratogenicity components. To ensure the water production rate, membrane filtration water is commonly used as backwash water during CEB and the wash water after CEB will not be discarded but go back to the raw water. Therefore, the potential impact of chemically enhanced backwash by-products (CEBBPs) produced in the cleaning process on water quality needs to be further evaluated.

The overall purpose of this project was to examine the typical types of CEBBPs produced during CEB in the adsorption-ultrafiltration process and analyse the influence of CEB hydraulic parameters (backwash interval, backwash duration, and backwash flux) and a cleaning reagent parameter (cleaning reagent concentration) on typical CEBBPs in the CEB regulation process. Meanwhile, the backwashing parameters of CEB were able to be optimized for the regulation of membrane cleaning technology by analysing the correlativity between the control of CEB parameters and typical CEBBPs concentration, examining the influence of parameters on membrane cleaning, and comparing the change of different membrane cleaning effects under CEB regulation. Human health risk assessment (HRA) was applied to assess the potential adverse health effects from exposure to effluent after the optimal online backwashing of CEB. This research topic will help complement the theory of adsorption/UF and improve the security of drinking water quality.

MATERIALS AND METHODS

Experimental set-up

An adsorption-UF system was used in this study. Powdered activated carbon was utilized for adsorption. The adsorption-UF system is denoted as PAC/UF. A schematic diagram of the adsorption-UF is shown in Figure 1. The hollow fibre modules of a polyvinylidene fluoride (PVDF) UF membrane (Litree, China) UF membrane with 0.1 m² membrane area (20 cm length and 100 fibres) and a nominal pore size of 0.01 μm was used. Raw water was fed into a constant-level tank to maintain the water head for the membrane reactor. Certain doses of PAC were continuously fed into the UF membrane reactor with an effective volume of 1 L. The permeation through the submerged membrane module was continuously withdrawn using a peristaltic pump at a constant flux of 20 L/(m²·h). The trans-membrane pressure (TMP) was continuously monitored with a pressure sensor.

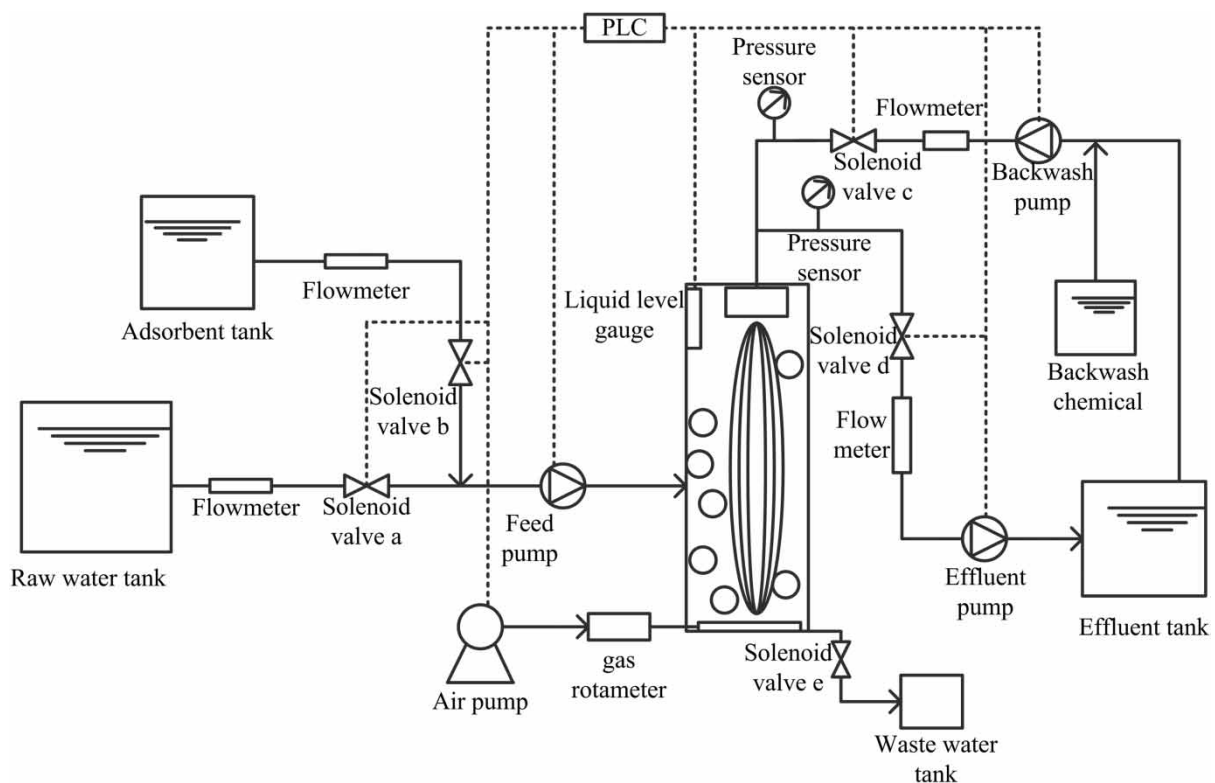


Figure 1 | Schematic diagram of the adsorption-UF process.

NaClO with an effective chlorine concentration of 10–200 mg/L was used as the cleaning reagent due to its widespread application in UF for membrane cleaning. The CEB hydraulic parameters were regulated by a programmable logic controller (PLC) system programmed with timing, counting and scaling code. The PLC system was used to automatically generate the required profiles and to control the valves, pumps and liquid level gauge of the system. To determine the optimum doses of PAC in the reactor, the influence of PAC doses (0, 2, 4, 6, 8, 10 and 12 mg/L) on the DOC and UV₂₅₄ removal rate of raw water was pre-examined through jar tests. The jar test results of different PAC doses are summarized in Table 1. It was found that when the dose of PAC was 6 mg/L, the DOC and UV₂₅₄ removal were the highest in the tested doses.

Table 1 | The jar tests result of different PAC doses

Water quality indexes	Dosage of PAC agent						
	0	2	4	6	8	10	12
DOC (mg/L)	3.661	3.236	3.177	2.516	2.529	2.551	2.543
UV ₂₅₄ (cm ⁻¹)	0.190	0.182	0.181	0.162	0.164	0.165	0.166

Single factor experiment

To confirm the optimum CEB cleaning parameter, a single factor experiment was used to analyse the influence of backwash duration (BD), backwash interval (BI), backwash flux (BF) and reagent concentration (RC) on CEBBPs concentration and membrane fouling. The single factor experiment of CEB parameters is shown in Table 2. Each level of factors was operated for 72 h.

The trans-membrane pressure growth rate (K) was used to represent the CEB cleaning effect and calculated according to Equation (1)

$$K = \frac{\text{TMP}_2 - \text{TMP}_1}{T} \quad (1)$$

where K is the growth rate of trans-membrane pressure (TMP), in kPa/h; TMP₁ is the value of TMP after the membrane was running for a period of time, in kPa. TMP₂ is the value of TMP at an initial time without the membrane running, in kPa. T is membrane running time, in h. In the single factor experiment, the membrane was washed off-line, and thus the TMP₂ value was 0 kPa.

Table 2 | Single factor experiment of CEB parameters

Operating steps	Parameters			
	BD (min)	BI (min)	BF (L/(m ² ·h))	RC (mg/L)
Step 1	2, 4, 6, 8, 10	120	20	50
Step 2	4	30, 60, 120, 240, 480	20	50
Step 3	4	120	5, 10, 20, 30, 40	50
Step 4	4	120	20	10, 25, 50, 100, 200

Analytical methods

Fourteen types of volatile halogenated organic compounds (VHOCs) were investigated, including 1,1-dichloroethene (1,1-DCE), methylene chloride (DCM), trans-1,2-dichloroethene (trans-DCE), chlorobutadiene (CBD), cis-1,2-dichloroethene (cis-DCE), chloroform (TCM), tetrachloromethane (CCl₄), 1,2-dichloroethane (1,2-DCA), trichloroethylene (TCE), bromodichloromethane (BDCM), tetrachloroethylene (PCE), dibromochloromethane (DBCM), tribromomethane (TBM), and hexachlorobutadiene (HCBD). The 14 VHOCs were analyzed by a static head-space gas-chromatographic technique (SHS-GC) using a Varian 3380 gas chromatograph equipped with a 63Ni electron-capture detector (ECD) and a Vocol capillary column (30 m × 0.53 mm I.D., film thickness: 3.0 m-Supelco). Quantitative and qualitative analyses of VHOC were managed using Dionex Chromeleon 6.0 software. Calibration was performed according to the external standard method. Standards of VHOCs were prepared with pure analysis reagents (Supelco) in specific concentrations of methanol. The detection limit for each VHOC was 0.1 µg/L. Aliquots of 5 cm³ from the water sample, external standard and control blank (vials with VHOCs-free water) were each placed into a 10 cm³ glass vial,

sealed, and heated to a specific temperature (1 h at 37 °C). After incubation, 100 µL of the head-space sample was injected directly into the GC using a gas-tight syringe.

Nine types of haloacetic acids (HAAs) were investigated, including monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and chlorodibromoacetic acid (CDBAA). The 9 HAAs were analysed using a modified version of EPA Method 552.3, which involves liquid-liquid extraction of the acids with methyl tert-butyl ether (MTBE), followed by derivatisation of the acids into their corresponding methyl esters using acidic methanol, and subsequent analysis of the HAA methyl esters by GC-MS (Kristiana *et al.* 2011). All of the tests were conducted at least in duplicate. The relative standard deviations (RSD) for different batches were normally < 10%. All of the aqueous solutions were prepared in Milli-Q water.

Hazard quotient for CEBBPs

A standard health risk assessment method, recommended by the USEPA, assessing the potential adverse health effects from exposure to contaminated water, was applied in this paper (Kavcar *et al.* 2009). Individuals are exposed to organic pollutants in water by the following main pathways: (1) direct ingestion of water through drinking; (2) incidental ingestion of surface water while swimming; and (3) dermal absorption of contaminants from water adhered to exposed skin. The amount of pollutants ingested via the second pathway is minor, and incidental ingestion rates (IR) while swimming have not been found in the available literature, so this pathway has been ignored in this study.

Raw water

Water was sampled from the water source of a drinking water treatment plant in northern China during the period of study. During the experiment, the raw water was kept at a temperature in the range of 16.2–18.5 °C and the pH was kept in the range of 7.1–7.3; other water quality characteristics; for example, turbidity, conductivity, DOC, COD_{Mn}, UV₂₅₄, SUVA (specific UV absorbance), and zeta potential were in the range of 2.52 ± 0.92 NTU, 82 ± 5 µS/cm, 3.52 ± 1.51 mg/L, 2.98 ± 1.09 mg/L, 0.187 ± 0.009 cm⁻¹, 1.152 ± 0.005 L/mg·m, and -15.6 ± 0.5 mV, respectively.

RESULTS AND DISCUSSION

Identify the typical CEBBPs

To determine the main types of CEBBPs, the research used time-of-flight mass spectrometry (TOF-MS) to analyse membrane filtered water quality after CEB. According to the result of the TOF-MS, some VHOCs and HAAs were detected in the filtered water. Thus, the research selected 14 types of VHOCs and 9 types of HAAs to detect which types of material were in the membrane CEB effluent.

To accurately identify the types of CEBBPs generated by the reaction of NaClO and organic matter, an experiment was conducted using a CEB and adopting a high RC (100 mg/L), long BD (10 min), short BI (30 min) and high BF (40 L/(m²·h)). The results showed that 9 types of VHOCs (except 1, 1-DCE, trans-DCE, CBD, cis-DCE and HCBD) and 9 types of HAAs were detected in the membrane effluent. The 9 types of VHOCs can be divided into two classes: THMs (TCM, BDCM, DBCM and TBM) and VHOC₅ (DCM, CCl₄, 1,2-DCA, TCE and PCE). The HAAs can be divided into two classes: HAA₅ (MCAA, DCAA, TCAA, MBAA and DBAA) and HAA₄ (TBAA, BCAA, BDCAA, and CDBAA).

The CEEBPs concentration in the membrane effluent (C_e) without CEB, the concentrations of CEEBPs after CEB at 0 and 24 h (C_0 and C_{24}), the average concentrations of CEEBPs (C_{ave}) after CEB during 24 h and the standard limit concentration (C_{sl}), referring to USEPA, are shown in the following table.

As seen from Table 3, some species of CEEBPs had been detected in the membrane effluent before CEB, which indicates that there were certain concentrations of pollutants in the raw water. In addition the concentrations of each species increased greatly even though some species (DCM, CCl_4 , 1,2-DCA, MCAA and TCAA) were much higher than the standard limit, indicating that the cleaning agent would react with organic matter in raw water to generate CEEBPs. After CEB, the THMs concentration (17.373 $\mu\text{g/L}$) was much lower than the standard limit concentration (80 $\mu\text{g/L}$), indicating that the content of the primary THMs precursor (hydrophobic organic matter) was low in raw water, and the DBCM was the main by-product, accounting for 43% in the THMs. The DCM, CBD and cis-DCE concentration increased significantly and accounted for more than 90% of the total VHOCs in the membrane effluent after CEB. Among the nine identified HAAs, the production of TCAA was highest (1.86 mg/L) and the concentrations of several other materials were relatively high.

Table 3 | Classes and species of CEEBPs

CEEBPs class	Species	Concentrations				
		C_{sl} ($\mu\text{g/L}$)	C_e ($\mu\text{g/L}$)	C_0 ($\mu\text{g/L}$)	C_{24} ($\mu\text{g/L}$)	C_{ave} ($\mu\text{g/L}$)
THMs		80	0.122	17.373	3.654	8.948
	TCM	80	0.122	0.547	ND	0.109
	BDCM	80	ND	2.847	ND	1.587
	DBCM	80	ND	7.395	1.411	4.171
	TBM	80	ND	6.584	1.243	3.081
VHOC ₅		–	0.981	393.218	63.230	118.294
	DCM	5	ND	344.981	56.309	100.547
	CCl_4	5	0.113	11.258	1.847	5.124
	1,2-DCA	5	ND	30.694	4.559	10.618
	TCE	5	0.868	3.588	0.515	1.128
	PCE	5	ND	2.697	ND	0.877
HAA ₅		60	2.615	2,150.304	410.402	978.731
	MCAA	60	0.196	133.684	33.127	63.815
	DCAA	60	0.26	40.857	6.891	15.287
	TCAA	60	0.382	1,863.845	349.457	824.854
	MBAA	–	0.977	100.956	10.946	64.857
	DBAA	–	0.8	10.962	9.981	9.918
HAA ₄		–	2.975	1,189.176	285.538	622.589
	TBAA	–	0.647	549.646	238.625	324.184
	BCAA	–	ND	454.158	15.814	188.297
	BDCAA	–	0.988	130.814	10.228	79.551
	CDBAA	–	1.34	54.558	20.871	30.557

– No data.

ND, Not detected.

As can be seen from Figure 2, the total concentration of CEEBPs reached approximately 3,800 $\mu\text{g/L}$. The CEEBPs in the membrane effluent reduced rapidly at one hour after CEB and then the

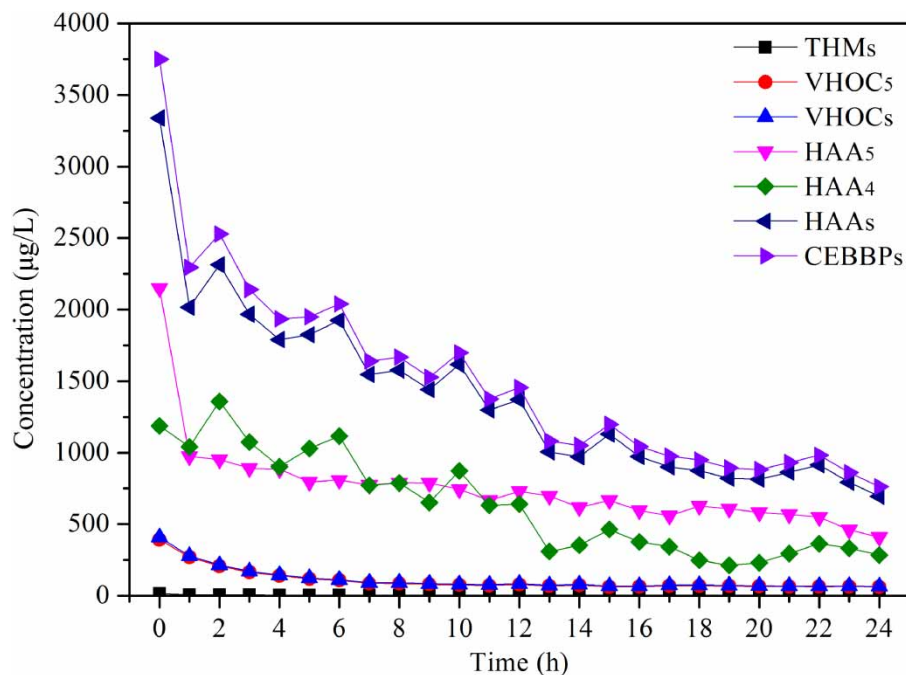


Figure 2 | The concentration change of the CEBBPs classes during 24 h.

concentration stabilized. The concentration of all detected CEBBPs gradually reduced with the extension of the water membrane filtration timer, indicating that CEBBPs had accumulated in the membrane reactor after the CEB, leading to the CEBBPs existing in the membrane effluent. Among the 9 types of VHOCs, the content of four types of THMs proportions was very small (less than 5%), but the VHOC₅ proportion accounted for more than 95%. This indicated that the THMs with strong carcinogenic properties were not the main by-product in the VHOCs generated by the reaction of the NaClO cleaning reagent and organic matter at the time of membrane chemical cleaning. At the initial stage of membrane effluent after CEB, the total concentration of HAAs reached approximately 3,339.48 µg/L. With the extension of time, the average concentration of HAAs showed a linear decreasing trend and finally reached 695.94 µg/L. The total amount of five types of risky carcinogenic substances (HAA₅) showed not much difference with the other four types (HAA₄). Compared to VHOCs, especially THMs, the HAAs were more likely to be generated due to the reaction of the cleaning reagent and organic matter, indicating that the content of primary HAAs precursor (hydrophilic organic matter) was high in raw water and the adsorption process did not lower the hydrophilic organic matter concentration.

CEB cleaning mode

To confirm the optimum CEB cleaning parameters, a single factor experiment was used to analyse the influence of backwash duration (BD), backwash interval (BI), backwash flux (BF) and reagent concentration (RC) on the production of CEBBPs and membrane fouling.

The influence of BD, BI, BF, RC on CEBBPs generation

The CEBBPs concentrations ($C_{2 \text{ min}}$, $C_{4 \text{ min}}$, $C_{6 \text{ min}}$, $C_{8 \text{ min}}$, and $C_{10 \text{ min}}$) under different BD (2 min, 4 min, 6, 8 and 10 min), the CEBBPs concentrations ($C_{30 \text{ min}}$, $C_{60 \text{ min}}$, $C_{120 \text{ min}}$, $C_{240 \text{ min}}$ and $C_{480 \text{ min}}$) under different BI (30 min, 60 min, 120, 240 and 480 min), the CEBBPs concentrations (C_5 , C_{10} , C_{20} , C_{30} and C_{40}) under different BF (5 L/(m²·h), 10 L/(m²·h), 20 L/(m²·h), 30 L/(m²·h)

and 40 L/(m²·h)), the CEBBPs concentrations ($C_{10 \text{ mg/L}}$, $C_{25 \text{ mg/L}}$, $C_{50 \text{ mg/L}}$, $C_{100 \text{ mg/L}}$ and $C_{200 \text{ mg/L}}$) under different RC (10 mg/L, 25 mg/L, 50 mg/L, 100 mg/L and 200 mg/L) are summarized in Table 4.

The concentration of all types of CEBBPs increased with the increment of BD time. When the BD time reached a certain value, the by-product formation rate significantly decreased and the concentration essentially remained unchanged. This might be because the high concentration of the backwash reagent had almost consumed all the organic matter that could react with NaClO. The higher the amount of backwash reagent entering in the membrane reactor because of the increment of BD, the more CEBBPs were generated in the membrane effluent. In all types of CEBBPs, the HAAs proportion was much higher than VHOCs, reaching more than 93%. This was consistent with the recognition rule of typical CEBBPs. When the BD time was 8 min, the total CEBBPs were approximately 160 µg/L, which was triple the concentration than when the BD time was 2 min. However, under these parameter conditions, the generation amounts of all the by-products were below the standard limit value.

As seen in Table 4, under the same condition of BD time, the amount of CEBBPs generated by CEB, on account of the high-frequency backwash, was much higher than the low-frequency backwash. The amount of CEBBPs when the BI time was 30 min was 14 times higher than when the BI time was 480 min. However, under the same BI time, prolonging the BD time did not make by-product generation rapidly increase. For example, under the condition of a 120 min BI time, when the BD time was increased by 10 min the total CEBBPs was still less than 160 µg/L. This is probably because the frequent backwash not only increased the dose of the backwash reagent, but the CEB backwash reagent was also exposed to the new raw water from the filter in the reactor every time. Specifically, the excessive reagent could react with the organic matter of the new raw water in the filter, and it was difficult to test the complete consumption of the organic matter, in which case the by-product concentration would no longer continue to increase. With a long BI time (e.g., more than 60 min), some kinds of CEBBPs were generated below the detection limit. However, when the BI was shortened, the amount of certain CEBBPs began to increase beyond the standard limit concentration of drinking water. For instance, the DCM concentration and TCAA concentration were higher by approximately 19 and 130 µg/L than the standard limit concentration when the BI time was 60 and 30 min, respectively. This indicated that when the BI was less than or equal to 60 min, the effluent was not in conformity with the drinking water health standards.

The larger the BF, the greater the total amount of CEBBPs generated because the amount of backwash reagent entering into the membrane reactor greatly increased with the larger BF under the same condition of BD, BI and RC. This promoted the reaction of the reagent with the organic matter to generate by-products (Zhang *et al.* 2016). Among the 21 types of CEBBPs, the content of four types of THMs (proportionally) was very small, less than 1%, and the VHOCs proportion accounted for more than 99%. Meanwhile, under this condition, the amount of all of the generated by-products was below the standard limit concentration, indicating that the PAC in the reactor can adsorb a certain amount of CEBBPs, which reduces the CEBBPs concentration in membrane effluent.

The higher the RC, the greater were all the typical by-products of CEBBPs generated. Utilizing a high concentration of reagents for the backwash greatly increased the total amount of NaClO in the membrane reactor, which promoted its reaction with the organic matter in the water and generated by-product CEBBPs. When the RC was 30 mg/L, the concentration of certain VHOCs was below the detection limit. This was probably because the absorbent in the raw water after adsorption can adsorb the backwash chemical agent, leading to the decrease of the oxidative ability of ClO⁻ (Xu *et al.* 2013; Dogan *et al.* 2015). Under a similarly BF condition, the proportion of four types of THMs among 21 types of CEBBPs was very small, less than 1%, and the HAAs proportion accounted for more than 95% under all the different RC conditions.

Table 4 | The CEBBPs concentration under different BD, BI, BF, RC(ug/L)

Species	Concentrations under different BD						Concentrations under different BI					Concentrations under different BF					Concentrations under different RC				
	C _{sl}	C _{2 min}	C _{4 min}	C _{6 min}	C _{8 min}	C _{10 min}	C _{30 min}	C _{60 min}	C _{120 min}	C _{240 min}	C _{480 min}	C ₅	C ₁₀	C ₂₀	C ₃₀	C ₄₀	C _{10 mg/L}	C _{25 mg/L}	C _{50 mg/L}	C _{100 mg/L}	C _{200 mg/L}
TCM	80	ND	ND	ND	ND	ND	0.03	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BDCM	80	0.05	0.06	0.07	0.13	0.15	0.38	0.28	0.06	0.04	0.03	ND	ND	0.03	0.05	0.08	ND	0.02	0.05	0.08	0.17
DBCM	80	0.12	0.15	0.18	0.33	0.38	0.99	0.73	0.16	0.11	0.07	0.02	0.04	0.07	0.12	0.22	0.03	0.05	0.14	0.21	0.45
TBM	80	0.09	0.11	0.13	0.24	0.28	0.73	0.54	0.12	0.08	0.05	ND	ND	0.05	0.09	0.16	ND	0.04	0.10	0.15	0.34
DCM	5	ND	ND	ND	7.94	9.20	23.92	17.50	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10.96
CCl ₄	5	0.15	0.18	0.22	0.40	0.47	1.22	0.89	0.19	0.13	0.09	ND	0.04	0.09	0.15	0.27	0.04	0.06	0.17	0.25	0.56
1,2-DCA	5	ND	ND	ND	ND	ND	2.53	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TCE	5	0.03	0.04	0.05	0.09	0.10	0.27	0.20	0.04	0.03	0.02	ND	ND	0.02	0.03	0.06	ND	ND	0.04	0.06	0.12
PCE	5	0.03	0.03	0.04	0.07	0.08	0.21	0.15	0.03	ND	ND	ND	ND	ND	0.03	0.05	ND	ND	0.03	0.04	0.10
MCAA	60	1.90	2.30	2.80	5.04	5.84	1.90	15.18	11.11	2.41	1.67	ND	ND	1.14	1.85	3.35	ND	ND	2.16	3.14	6.96
DCAA	60	0.46	0.55	0.67	1.21	1.40	0.46	3.64	2.66	0.58	0.40	ND	ND	0.27	0.44	0.80	ND	ND	0.52	0.75	1.67
TCAA	60	24.55	29.70	36.13	65.18	75.46	196.21	143.56	31.18	21.63	14.54	3.83	7.21	14.69	23.94	43.28	5.87	9.68	27.96	40.61	89.90
MBAA	-	1.93	2.34	2.84	5.12	5.93	1.93	15.43	11.29	2.45	1.70	0.30	0.57	1.16	1.88	3.40	0.46	0.76	2.20	3.19	7.07
DBAA	-	0.30	0.36	0.43	0.78	0.91	2.36	1.73	0.37	0.26	0.17	ND	0.09	0.18	0.29	0.52	ND	0.12	0.34	0.49	1.08
TBAA	-	9.65	11.67	14.20	25.62	29.66	77.12	56.42	12.25	8.50	5.72	1.50	2.83	5.77	9.41	17.01	2.31	3.81	10.99	15.96	35.33
BCAA	-	5.60	6.78	8.25	14.88	17.23	44.79	32.77	7.12	4.94	3.32	0.87	1.64	3.35	5.47	9.88	1.34	2.21	6.38	9.27	20.52
BDCAA	-	2.37	2.86	3.48	6.29	7.28	18.92	13.85	3.01	2.09	1.40	0.37	0.69	1.42	2.31	4.17	0.57	0.93	2.70	3.92	8.67
CDBAA	-	0.91	1.10	1.34	2.41	2.80	7.27	5.32	1.16	0.80	0.54	0.14	0.27	0.54	0.89	1.60	0.22	0.36	1.04	1.50	3.33
THMs	80	0.26	0.32	0.38	0.70	0.81	2.13	1.57	0.34	0.23	0.15	0.02	0.04	0.15	0.26	0.46	0.03	0.11	0.29	0.44	0.96
VHOC _s	-	0.47	0.57	0.69	9.20	10.66	30.28	20.31	0.60	0.39	0.26	0.02	0.08	0.26	0.47	0.84	0.07	0.17	0.53	0.79	12.70
HAAs	-	47.67	57.66	70.14	126.53	146.51	380.92	278.71	60.53	41.99	28.23	7.01	13.30	28.52	46.48	84.01	10.77	17.87	54.29	78.83	174.53
CEBBPs	-	48.14	58.23	70.83	135.73	157.17	411.2	299.02	61.13	42.38	28.49	7.03	13.38	28.78	46.95	84.85	10.84	18.04	54.82	79.62	187.23

- No data.

ND, Not detected.

The influence of cleaning mode on membrane cleaning effect

Figure 3 shows the total amount of CEBBPs and TMP growth rate under different BD, BI, BF, RC. When the BD time was less than 6 min, the amount of CEBBPs grew slowly. However, when the BD time was between 6 and 10 min, the CEBBPs concentration increased rapidly. This is probably because a small amount of backwash reagent (NaClO) reacted with the organic matter; the CEBBPs concentration increased slowly when the BD time was short. With the increase of BD time, the NaClO concentration gradually increased and the backwash reagent was fully in contact with organic matter in the membrane reactor, which led to a rapid increase in the total amount of CEBBPs. Meanwhile, as seen from the figure, when the device ran for 72 hours without CEB, the K reached 0.132 kPa/h. However, when the BD time increased from 0 to 6 min, the K decreased rapidly, indicating that the CEB can remove the membrane chemical pollutants and effectively reduce membrane fouling. Membrane cleaning was improved with increased BD time. However, when the BD time was greater than 6 min, the K slowed down significantly. After a comprehensive consideration of the effect of BD time on the typical CEBBPs production and membrane cleaning, it was determined that the optimal BD time was 6 min.

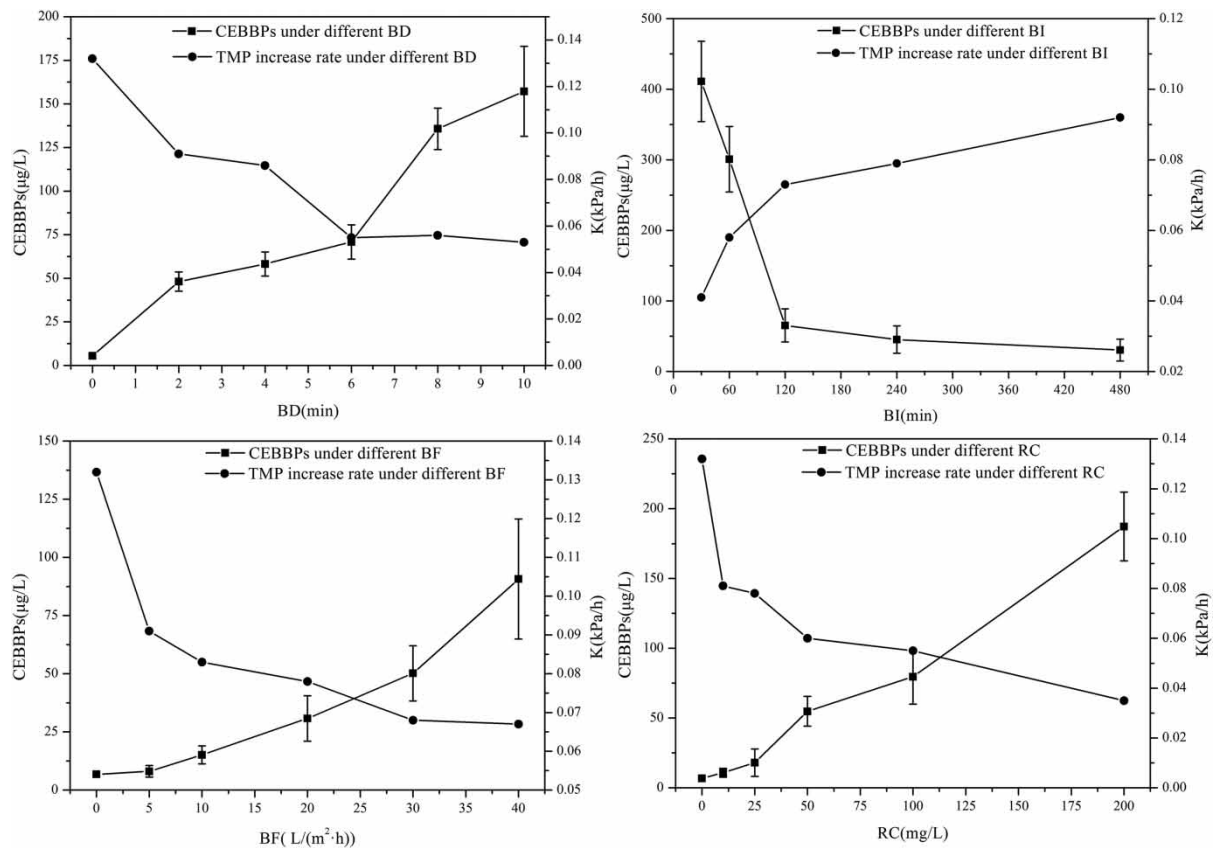


Figure 3 | The total amount of CEBBPs and the TMP growth rate under different BD, BI, BF, RC.

When the BI was less than 120 min, the CEBBPs generation rate rapidly decreased with the increase of BI. However, when the BI time was greater than 120 min, the CEBBPs concentration basically remained unchanged, indicating that the frequent use of CEB promoted the formation of CEBBPs. Meanwhile, when the BI time was less than 120 min, the TMP growth increased significantly, but when the BI time was between 120 and 480 min, the growth rate of TMP was slow. When the BI time was greater than 240 min, the growth rate of TMP eventually reached

0.092 kPa/h. After a comprehensive consideration of the effect of BI time on the typical CEBBPs production and membrane cleaning, the optimal BI time was 120 min.

When the BF increased from 0 L/(m²·h) to 30 L/(m²·h), the TMP growth rate was rapidly reduced from 0.132 kPa/h to 0.068 kPa/h. However, when the BF was higher than 30 L/(m²·h), the TMP growth rate decreased slowly, indicating that utilization of a lower BF achieved a better membrane cleaning effect. Meanwhile, when the BF was 40 L/(m²·h), the total CEBBPs concentrations reached approximately 100 µg/L. Because the organic matter in the water was not completely consumed by the quantity of chemical reagents selected in the BF range, the variation curve of the CEBBPs did not show a flat stage and the total amount of typical CEBBPs showed a linear growth trend with the increase of BF. Because all the CEBBPs were below the standard limit, the highest BI possible was chosen for CEB on the premise of the guarantee of a better membrane cleaning effect. After a comprehensive consideration of the effect of BF on the typical CEBBPs production and membrane cleaning, the optimal BF was 30 L/(m²·h).

With the increase of backwash reagent concentration, the overall generation of typical by-products CEBBPs showed an increasing trend. When the backwash reagent concentration was less than 200 mg/L, the total amount of typical CEBBPs showed a linear growth trend with the increase of RC. This is probably because there was redundant organic matter reacting with the backwash reagent to produce CEBBPs and the generation of by-products gradually increased. Meanwhile, when the backwash reagent concentration increased from 0 mg/L to 50 mg/L, the growth rate of TMP quickly reduced from 0.132 kPa/h to 0.060 kPa/h. However, when the backwash reagent concentration was higher than 50 mg/L, the growth rate of TMP decreased slowly, indicating that utilization of a lower concentration of backwash reagent could achieve a better cleaning effect. Although the amount of all generated by-products, except DCM and TCAA, was below the standard limit concentration, a lower concentration of chemical should be chosen as the backwash reagent on the premise of guaranteeing a good membrane cleaning effect. After a comprehensive consideration of the effect of RC on the typical CEBBPs production and membrane cleaning, the optimal RC was 50 mg/L.

Human health risk assessment

To determine the health risk levels posed by CEBBPs, a HRA (Health Risk Assessment) was applied to assess the potential adverse health effects from exposure to the effluent (Viana *et al.* 2009). In this study, the concentrations of CEBBPs were measured in the membrane effluent after CEB operating under the optimum CEB cleaning parameters and shown in Table 5. The non-carcinogenic HQ (Hazard Quotient) and LCR (Lifetime Carcinogenic Risk) were used for the primary human HRA and are also shown in Table 5.

Under the optimum CEB cleaning parameters, the CEBBPs concentration measured in the effluent after CEB was 172.94 µg/L. The proportion of HAAs in the CEBBPs was approximately 93%, indicating that HAAs should be the main focus in the effluent after CEB. The HRA was only undertaken for pollutants where appropriate toxicity values were available because of the limit of toxicity values for some pollutants. Because some parameters were not available for some kinds of CEBBPs, the HQs for these species are not provided in Table 5. The HQ values for each species of CEBBPs were all less than one; meanwhile, the HI for THMs, VHOC₁₂, HAAs and CEBBPs were 4.50E-05, 4.45E-04, 1.20E-03 and 1.65E-03, respectively. These results show that the concentrations of CEBBPs measured in the effluent under the optimum CEB cleaning parameters in this study pose no health risk to local consumers through ingestion or dermal adsorption. The measured HI may be lower than actual risk because the CEBBPs, which were evaluated in this study, were only a portion of the total by-products in the effluent.

The SFs for the many species of CEBBPs were limited; therefore, the LCRs for only 9 types of CEBBPs were calculated through Equation (8). Under most regulatory regimes, an LCR value over

Table 5 | Concentrations of CEBBPs, non-carcinogenic risks and carcinogenic risks in the effluent

Species	C ($\mu\text{g/L}$)	HQ _s	LCR _s
TCM	ND	–	–
BDCM	0.40	6.74E-06	7.43E-09
DBCM	1.50	2.70E-05	3.32E-08
TBM	0.90	1.13E-05	2.15E-08
DCM	8.50	3.80E-04	–
CCl ₄	0.08	5.98E-06	1.70E-10
1,2-DCA	ND	–	–
TCE	2.10	1.38E-05	7.66E-09
PCE	0.06	2.94E-07	7.94E-09
MCAA	12.00	5.22E-04	3.70E-06
DCAA	3.10	3.86E-04	5.83E-07
TCAA	19.10	2.93E-04	2.40E-06
MBAA	10.60	–	–
DBAA	5.10	–	–
TBAA	56.80	–	–
BCAA	24.30	–	–
BDCAA	18.80	–	–
CDBAA	9.60	–	–
THMs	2.80	4.50E-05	7.98E-08
VHOC ₁₂	13.54	4.45E-04	9.56E-08
HAAs	159.40	1.20E-03	6.68E-06
CEBBPs	172.94	1.65E-03	6.78E-06

– No data.

1.00E-05 indicates a potential carcinogenic risk (Wang *et al.* 2014). In this study, the LCR values for all kinds of CEBBPs are all below 1.00E-05, indicating that these individual species of CEBBPs in the effluent may not pose a carcinogenic health risk to local consumers based on results shown in Table 5. Meanwhile, many species of CEBBPs did not have appropriate parameter values; therefore, the true RI value of CEBBPs may be over 1.00E-05, indicating that the CEBBPs in the effluent may pose a potential carcinogenic risk to local consumers even though the concentration of the species of CEBBPs is much lower than the standard limit concentration. The LCR value for HAAs (6.68E-06) is very close to the LCR value of CEBBPs (6.78E-06), indicating that the HAAs are the main substances in the effluent after CEB and pose a potential carcinogenic risk to local consumers.

CONCLUSIONS

The main conclusions of this study are as follows:

1. In the process of CEB, the NaClO backwash reagent could react with organic matter to produce CEBBPs, including 9 species of VHOCs and 9 species of HAAs. Compared to VHOCs, especially THMs, the HAAs were more likely to be generated due to the reaction of the cleaning reagent and organic matter, indicating that the content of primary HAAs precursor (hydrophilic organic matter) was high in raw water and the adsorption process did not lower the hydrophilic organic matter concentration.
2. The CEB removal of membrane foulants can effectively mitigate membrane fouling. Within a certain range, with the increase of BD, the decrease of BI, and the rise of BF and RC, the TMP grew

slowly after the membrane operation for a period of time and the K was gradually reduced. After a comprehensive consideration of the influence of a single factor on the CEBBPs formation and membrane cleaning effect, the optimal CEB parameters were 6 min of BD, 120 min of BI, 30 L/(m²·h) of BF and 50 mg/L of RC.

3. Under the optimum CEB cleaning parameters, the effluent does not pose a non-carcinogenic risk and potential carcinogenic risk to residents. The LCR value for HAAs (6.68E-06) is very close to the LCR value of CEBBPs (6.78E-06), indicating that the HAAs are the main substances in the effluent after CEB. A further purification process should be implemented to ensure the safety of drinking water after CEB, even though the CEB can reduce the membrane fouling effectively and the concentration of species of CEBBPs is much lower than the standard limit concentration.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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