

## Preparation of cellulose nanofiltration membranes and their removal of typical pollutants from drinking water

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### ABSTRACT

Cellulose membranes have the advantages of good hydrophilicity, excellent mechanical properties, and biodegradability. Therefore, they are the first choice to replace petroleum polymer membranes. In this study, cellulose (BC) and chitosan (CS) were used as raw materials, and N-methylmorpholine-N-oxide (NMMO) was used as solvent. A new kind of cellulose nanofiltration membrane (BC-NFM), cellulose/chitosan nanofiltration membrane (BC/CS-NFM), and interfacial polymerized cellulose/chitosan composite nanofiltration membrane (IP-BC/CS-NFM) were successfully prepared by NaOH hydrolysis and chloroacetic acid carboxymethylation modification, piperazine (PIP), and 1,3,5-trimellitic chloride (TMC) interfacial polymerization, respectively. These two methods were used for the preparation of cellulose nanofiltration membranes for the first time. We also studied their structure, separation performance and their capacity to remove typical pollutants. The results showed that obvious holes appeared on the surface of the nanofiltration membrane obtained by alkali hydrolysis and chloroacetic acid carboxymethylation modification, and the cross-section showed a spongelike structure. The surface of the nanofiltration membrane obtained by interfacial polymerization formed a rough and dense separation layer. The rejection rates of the three kinds of nanofiltration membranes were all over 30% for monovalent salt ions, over 60% for divalent salt ions, over 92% for methyl orange, and over 98% for methyl blue. They had good removal effects for typical pollutants in drinking water.

**Key words:** cellulose, drinking water, interfacial polymerization, modification of carboxymethylation, nanofiltration membrane, separation performance

### HIGHLIGHTS

- Three kinds of cellulose nanofiltration membranes have been prepared.
- The removal ability of three kinds of cellulose nanofiltration membranes was investigated for typical pollutants in drinking water under different conditions.
- The nanofiltration membranes operated stably and effluent indices met the requirements of Drinking Water GB5749-2006.

### INTRODUCTION

Nanofiltration membrane is a new membrane separation material that was developed in the 1980s and is widely used in the field of water treatment. Nanofiltration membranes have high retention of calcium and magnesium ions in water, and can remove inorganic pollutants such as heavy metals, salt ions, chloride, and fluoride in drinking water (Xi *et al.* 2012; Kim & Lee 2014). They can also effectively remove chlorobenzene, pesticide residues, toluene, trichloromethane, algin, and natural organic compounds (Pang *et al.* 2010; Maher *et al.* 2014; Hyung *et al.* 2014; Cherunya *et al.* 2015); they preserve minerals in drinking water that are beneficial to human health.

At present, materials used to produce nanofiltration membranes mainly include polyvinylidene fluoride, polysulfone, polyamide, sulfonated polyethersulfone, and polyacrylonitrile, which are organic polymer materials. Zhao *et al.* (2004) performed plasma-radiation treatment on the surface of a polyacrylonitrile ultrafiltration membrane, thus initiating acrylic acid to graft and modify it to prepare the nanofiltration membrane. Li *et al.* (2002) used a polyacrylonitrile ultrafiltration membrane as the base membrane, and the surface layer was coated with charged reagent chitosan to obtain a positively charged nanofiltration membrane. The positively charged nanofiltration membrane was used to treat the organic mixed wastewater of chemical mechanical pulp, and this membrane performed significantly enhanced removal rates of chroma, Chemical Oxygen Demand (COD<sub>cr</sub>) and Biochemical Oxygen Demand (BOD<sub>5</sub>) than the polyacrylonitrile ultrafiltration membrane. In particular, the retention rate of sodium ion was greatly

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increased from 25% to 40%. [He et al. \(2008\)](#) compounded a layer of sulfonated polyetheretherketone on the surface of a polysulfone or polyethersulfone ultrafiltration membrane to obtain a composite nanofiltration membrane. The experimental evidence shows that the composite membrane has a high retention rate for sodium sulfate. Also, the retention rate of the composite membrane to organic dyes was higher than 97%, and the retention rate to three salts decreased in the order of  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{MgCl}_2$ . [Bowen et al. \(2001\)](#) simultaneously dissolved sulfonated polyetheretherketone and polysulfone by using a mixed N-methylpyrrolidone or N-methylpyrrolidone/pyrrolidone solvent, stirred and dissolved, then stopped for defoaming, scraped into a film, and dipped into a deionized water coagulation bath to gel into a film. [Verissimo et al. \(2005\)](#) prepared a polyamide hollow fiber composite nanofiltration membrane by interfacial polymerization on the inner surface of a polyetherimide hollow fiber ultrafiltration membrane with m-phenylenediamine and trimellitic chloride as monomers. The blend film was fabricated by [Shih et al. \(2009\)](#) via employing the cellulose and the chitosan simultaneously dissolved in NMMO hydrate. The antibacterial properties of the blend film against staphylococcus aureus were investigated. When the mass fraction of chitosan was 3% - 5%, the blend film showed a smooth surface with the appearance of a bacteriostatic circle. The sulfonated polysulfone/polyethersulfone (SPS-PES) composite nanofiltration membrane was prepared by [Li et al. \(2016\)](#) through the L-S phase transformation method, which performed a water flux of  $24.45 \text{ L/m}^2\cdot\text{h}$  and a retention rate of 56.77% under the operating pressure of 0.5 MPa and the temperature of  $25^\circ\text{C}$  in sodium sulfate aqueous solution. [Peng et al. \(2013\)](#) obtained a new composite nanofiltration membrane by interfacial polymerization of homobenzotriacryl chloride and piperazine on the hydrolyzed polyacrylonitrile membrane, whose retention rate to magnesium sulfate reached 95.8%. All of the above nanofiltration membranes are biodegradable petrochemical polymer membranes, which cause a great burden on the social environment and energy.

Therefore, it is urgent to find cheap, easily available, green, and environmentally friendly materials to replace petroleum polymer nanofiltration membranes. Cellulose is globally the most extensive natural polymer material, with good physicochemical stability and biocompatibility. Through the functional modification of cellulose, cellulose materials with better performance can be obtained. Cellulose membrane has the advantages of hydrophilicity, air permeability, solvent resistance, and biodegradability, which are not achievable with petroleum polymer membranes. The mechanism of the membrane formation is the strong molecular inter-atomic forces and hydrogen bonding in cellulose and chitosan membrane; after modification, the hydrogen bonding was damaged, which disrupted the crystalline structures of the cellulose and chitosan, and therefore, the internal structure became loose and an enhanced surface hydrophobicity was observed. Therefore, after modification, cellulose and chitosan membrane has the function of nanofiltration. In this study, cellulose and chitosan were used as the main raw materials to prepare three kinds of nanofiltration membrane materials by carboxymethylation modification and interfacial polymerization, respectively, and their morphology and separation performance were tested. At the same time, the removal ability was investigated of three kinds of nanofiltration membranes for typical pollutants, namely, chloroform, nitrate nitrogen, and hardness in drinking water under different conditions. This provides theoretical and technical support for the application of cellulose nanofiltration membranes in the advanced treatment of drinking water.

## MATERIALS AND METHODS

### Materials

Cellulose (DP is 650, Sichuan Tianzhuzhu Resources Development Co., Ltd); chitosan ( $M_w = 2 \times 10^5$  Da, deacetylation degree 90%, Zhejiang Jinke Biochemical Co., Ltd); NMMO (Analytical Pure, Tianjin Hainachuan Technology Development Co., Ltd); propyl gallate, methyl orange, and methyl blue (all analytically pure, Shanghai Aladdin Biochemical Technology Co., Ltd);  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$  (all analytically pure, Tianjin Fuchen Chemical Reagent Factory); chloroacetic acid (analytically pure, Sinopharm Chemical Reagent Co., Ltd); piperazine (PIP) (analytically pure, Chengdu Aikeda Chemical Reagent Co., Ltd); 1,3,5-trimellitic chloride (TMC; purity 98%, Chengdu Aikeda Chemical Reagent Co., Ltd); N-hexane (purity 98%, Tianjin Zhiyuan Chemical Reagent Co., Ltd); trichloromethane and nitrate nitrogen standard solutions (Beijing Yihua Tongbiao Technology Co., Ltd). The water used in this experiment is de-ionized water.

### Preparation of cellulose nanofiltration membrane

First, 6 wt % cellulose was added to 86.7% NMMO solvent and dissolved by stirring at  $110^\circ\text{C}$ . Then, the film coating solution was obtained by standing and defoaming. Second, the coating liquid was coated onto the

nonwoven fabric and scraped into a film, which was quickly immersed in deionized water for solidification, and an asymmetric film with a porous network structure with thickness of about 200  $\mu\text{m}$  is obtained after being fully gelled. The membrane was washed with deionized water to remove residual NMMO solvent and naturally dried to obtain the cellulose membrane (BCM). Lastly, BC-NFM was prepared by alkali hydrolysis (NaOH concentration, 1 mol/L; reaction temperature, 30  $^{\circ}\text{C}$ ; reaction time, 30 min) and carboxymethylation (chloroacetic acid concentration, 3 wt/v %; solution temperature, 60  $^{\circ}\text{C}$ ; reaction time, 1 h) with dense BC/CSM as the original membrane (water flux 0) (Weng *et al.* 2017a).

#### Preparation of cellulose/chitosan nanofiltration membrane

An amount of 6 wt % BC and CS (raw material mass fraction ratio, BC/CS = 6:1) was added to 86.7% NMMO solvent, dissolved by stirring at 110  $^{\circ}\text{C}$  under high temperature and vacuum, and stood for defoaming to obtain coating solution. Coating and modification methods were the same as above, and BC/CS-NFM was obtained (Weng *et al.* 2017b).

#### Preparation of interfacial polymerized cellulose/chitosan composite nanofiltration membrane

First, 6 wt % BC and CS (raw material mass fraction ratio, BC/CS = 6:1) was added to 86.7% NMMO solvent, dissolved by stirring at 110  $^{\circ}\text{C}$  under high temperature and vacuum, and stood for defoaming to obtain coating solution. Second, coating liquid was coated onto the nonwoven fabric and scraped into a membrane, which was quickly immersed in deionized water for solidification, and the residual NMMO solvent in the membrane was washed away to the asymmetric membrane BC/CSM with a porous network structure. Lastly, IP-BC/CS-NFM was obtained by interfacial polymerization on the BC/CSM base film with piperazine (concentration, 2 wt %; water treatment time, 30 min) as water monomer and trimellitic chloride (concentration, 0.15 wt %; organic reaction time, 3 min) as organic monomer (Weng *et al.* 2020).

#### Nanofiltration-membrane electron-microscope scanning

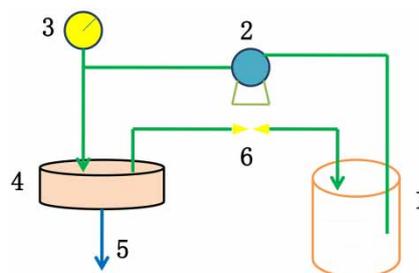
The sample of the nanofiltration membrane material was quenched in liquid nitrogen for 1–3 min, it quickly became brittle, and it was then placed into a freeze dryer for drying. The dried membrane was placed in a high vacuum evaporator, gold was sprayed on the membrane surface and cross-section for pretreatment, and then the membrane was placed in a field emission scanning electron microscope (FE-SEM) to observe the micro-morphology of the surface and cross-section.

#### Detection of separation performance of nanofiltration membrane

The diaphragm was cut with a diameter of 8 cm and placed in the film performance-evaluation device, as shown in Figure 1. Membrane separation performance was tested under operating pressure of 0.5 MPa. Before each test, the nanofiltration membrane needed to be prepressed for at least 30 min to ensure flux stability. The temperature of the feed tank was constant by using the water-bath. The volume of the feed solution was 100 L each time.

The permeability of the nanofiltration membrane is expressed by water flux. The volume of water passing through the membrane in a certain period of time was measured, and water flux was calculated according to Formula (1):

$$J = V/(A \times t) \quad (1)$$



**Figure 1** | Membrane performance evaluation instrument: 1: Feed tank; 2: pump; 3: pressure gauge; 4: membrane cell; 5: permeate end; 6: valve.

where  $J$  is permeation flux ( $L/m^2 \cdot h$ ),  $V$  is permeate volume (L),  $A$  is membrane area ( $m^2$ ), and  $t$  is permeation time (h).

In the experiment, the concentration of inorganic salt was measured by the conductivity method, the absorbance of the initial dye solution and the penetrating solution was measured by ultraviolet spectrophotometry, and rejection rate was calculated according to Formula (2):

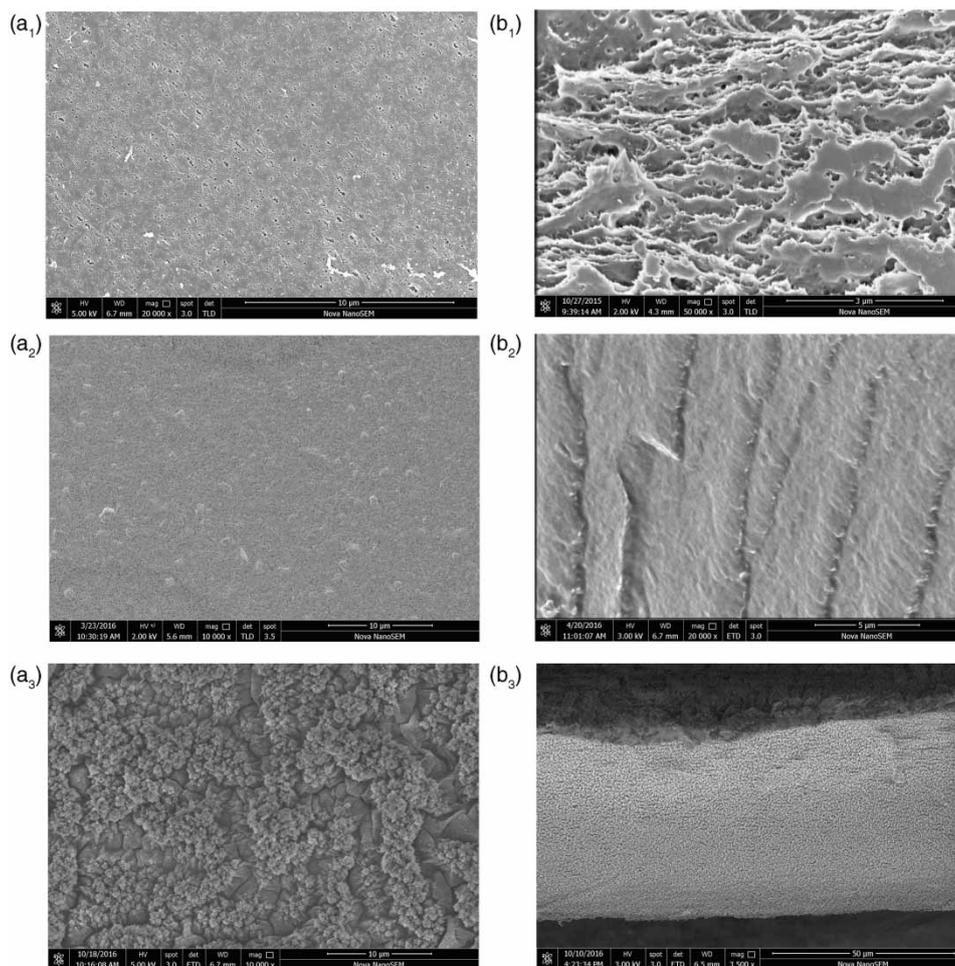
$$R = 100\% \times (C_f - C_p) / C_f \quad (2)$$

where  $R$  is rejection rate (%),  $C_f$  is feed concentration (mg/L), and  $C_p$  is permeate concentration (mg/L). All cross-flow permeation experiments were conducted at room temperature.

## RESULTS AND DISCUSSION

### Micromorphological analysis of nanofiltration membrane

The surface and section morphology of BC-NFM, BC/CS-NFM, and IP-BC/CS-NFM are shown in Figure 2 a<sub>1</sub> and a<sub>2</sub>, and b<sub>1</sub> and b<sub>2</sub> show that obvious holes appeared on the surfaces of BC-NFM and BC/CS-NFM, and sections showed a spongy structure. This was mainly due to the alkaline hydrolysis and carboxymethylation of chloroacetic acid in the base membrane in the modification process. The alkalization and carboxymethylation reaction destroyed the hydrogen bond structure in cellulose macromolecules, so that the crystal lattice of different degrees of swelling and disassembly, the morphology, and supramolecular structure of cellulose irreversibly changed. At the same time, a large amount of aqueous solutions entered the cellulose film, causing violent swelling, resulting



**Figure 2** | SEM images of cellulose nanofiltration membrane (BC-NFM), cellulose/chitosan nanofiltration membrane (BC/CS-NFM), and interfacial polymerized cellulose/chitosan composite nanofiltration membrane (IP-BC/CS-NFM). Surface of (a<sub>1</sub>) BC-NFM, (a<sub>2</sub>) BC/CS-NFM, and (a<sub>3</sub>) IP-BC/CS-NFM. (b<sub>1</sub>) BC-NFM section; (b<sub>2</sub>) BC/CS-NFM cross-section; (b<sub>3</sub>) IP-BC/CS-NFM section.

in its cross-sectional expansion and longitudinal contraction, resulting in cellulose-film cracking and holes, which could form an effective channel. Figure 2 (a<sub>3</sub>) shows that, after the interface polymerization between PIP and TMC, the polyamide layer was formed on the base membrane's surface and became rough. Pores on the surface of the base film were filled with polyamides formed by polymerization, and with the continuous advance of the interface polymerization reaction, an uneven separation layer was accumulated, making the base film surface rough and dense. Figure 2 (b<sub>3</sub>) is the sectional view of the composite nanofiltration membrane, clearly showing that a uniform, dense, and functional layer with a certain thickness was generated on the surface of the base membrane that determined the retention characteristics of IP-BC/CS-NFM. The polyamide layer formed by interfacial polymerization was embedded into the base film surface by a physical and chemical combination, so that it was not easy for the copolymer layer to fall off.

### Separation performance of nanofiltration membrane

The three kinds of nanofiltration membranes prepared by BC-NFM, BC/CS-NFM, and IP-BC/CS-NFM were tested for the separation performance of inorganic salts and dyes NaCl, Na<sub>2</sub>SO<sub>4</sub>, and MgSO<sub>4</sub>. The water flux and rejection rate results are shown in Table 1.

The results showed that IP-BC/CS-NFM obtained by interfacial polymerization had better water flux and retention rate for inorganic salt and dye solutions. IP-BC/CS-NFM interception analysis of inorganic salt ions found that SO<sub>4</sub><sup>2-</sup> ion retention rate was greater than that of Cl<sup>-</sup> because the polypiperazinamide compound nanofiltration membrane was negatively charged, and homologous ions repel each other and retain. The higher the valence state of the inorganic salt ions, the greater the repulsion and the higher the retention rate. Although the Mg<sup>2+</sup> of the hydration radius (0.428 nm) was greater than the Na<sup>+</sup> of hydration radius (0.358 nm), Na<sub>2</sub>SO<sub>4</sub> retention rate was greater than that of MgSO<sub>4</sub> because Mg<sup>2+</sup> had two positive charges, and the shielding effect of IP-BC/CS-NFM was stronger, which reduced the effective negative-charge density on the surface of the composite nanofiltration membrane (Dong *et al.* 2014), which led to a decrease in electrostatic repulsion and thus retention rate. This indirectly indicated that the retention of IP-BC/CS-NFM of inorganic salt was dominated by electrostatic repulsion followed by steric resistance. Although methyl orange is a cationic dye and methyl blue is an anionic dye, IP-BC/CS-NFM had high interception of both methyl orange and methyl blue, which indicated that the interception characteristics of the composite nanofiltration membrane were the result of the joint action of electrostatic and screening effects. Polyethyleneimine/sulfonation of polyethersulphone (PEI/SPES) composite nanofiltration membrane (Tan *et al.* 2010), under the operating pressure of 0.4 MPa at room temperature, water flux of PEI/SPES composite nanofiltration membrane was 5.8 L/m<sup>2</sup> h, the rejections to Na<sub>2</sub>SO<sub>4</sub> and NaCl were 29 and 18%, respectively. Compared to PEI/SPES composite nanofiltration membrane, BC/CS-NFM, BC/CS-NFM, and IP-BC/CS-NFM demonstrated better permeation and rejection.

### Study of removal performance of nanofiltration membrane for three typical pollutants

The chloroform, nitrate nitrogen, and hardness removal capacity of BC-NFM, BC/CS-NFM, and IP-BC/CS-NFM nanofiltration membranes was investigated. Experiments were carried out at room temperature and operating pressure of 0.5 MPa, and the removal effects of the three nanofiltration membranes on different influent concentrations of three typical pollutants were mainly studied.

**Table 1** | Separation properties of three kinds of nanofiltration membranes for inorganic salts and dyes

Type of nanofiltration membrane	NaCl <sup>a</sup> solution		Na <sub>2</sub> SO <sub>4</sub> <sup>a</sup> solution		MgSO <sub>4</sub> <sup>a</sup> solution		Methyl Orange <sup>a</sup> solution		Methyl Blue <sup>a</sup> solution	
	Water flux <sup>b</sup> (L/m <sup>2</sup> h)	Rejection rate (%)	Water flux <sup>b</sup> (L/m <sup>2</sup> h)	Rejection rate (%)	Water flux <sup>b</sup> (L/m <sup>2</sup> h)	Rejection rate (%)	Water flux <sup>b</sup> (L/m <sup>2</sup> h)	Rejection rate (%)	Water flux <sup>b</sup> (L/m <sup>2</sup> h)	Rejection rate (%)
BC-NFM	13.12	34.90	10.32	68.42	10.87	67.54	12.31	93.01	10.12	98.91
BC/CS-NFM	13.51	34.42	12.12	67.71	12.43	66.83	13.64	92.37	12.37	98.79
IP-BC/CS-NFM	15.64	40.26	13.56	71.34	14.03	62.55	13.28	93.65	12.35	98.86

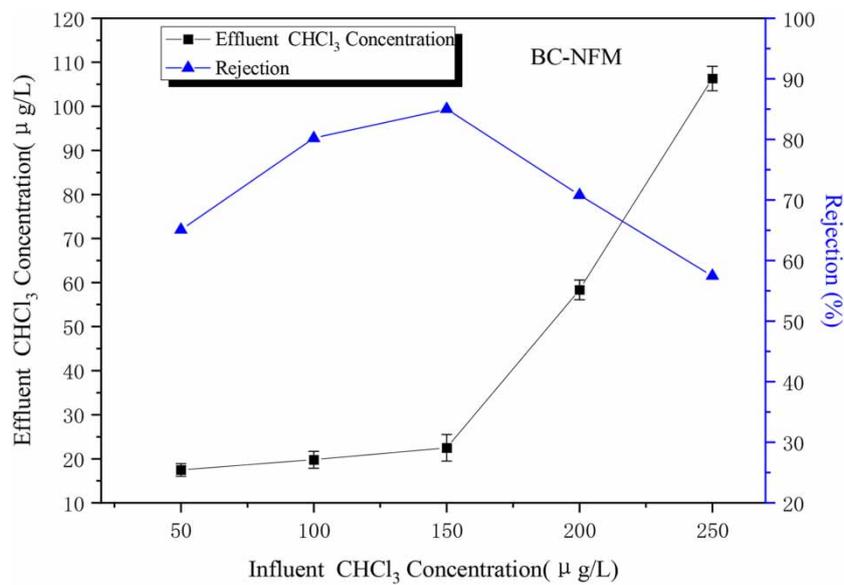
<sup>a</sup>Tested with de-ionized water containing 500 mg/L salt or 100 mg/L dye under 0.5 MPa and room temperature.

<sup>b</sup>Tested with a salt or dye aqueous solution under 0.5 MPa and room temperature.

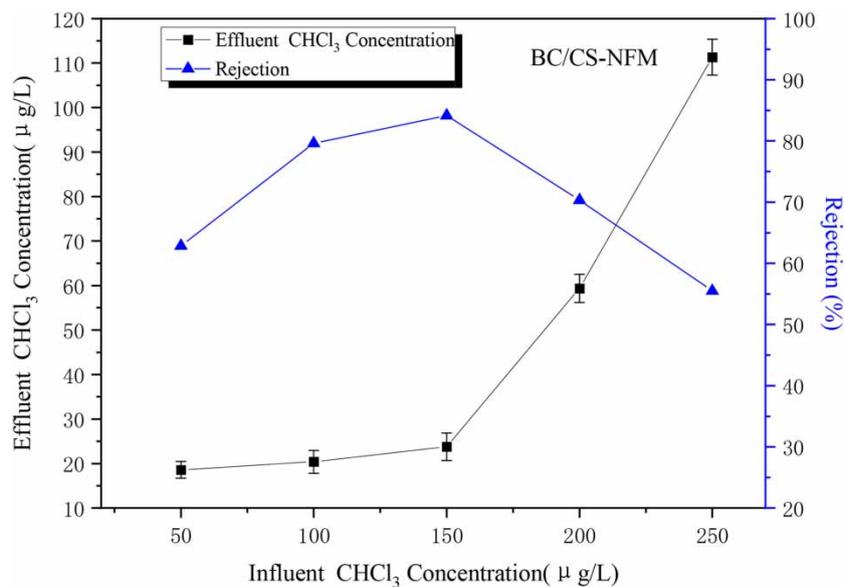
### Trichloromethane removal

In this experiment, deionized water was used to prepare different influent solutions with chloroform, and the retention performance of three nanofiltration membranes for chloroform was studied. The experimental results are shown in Figures 3–5.

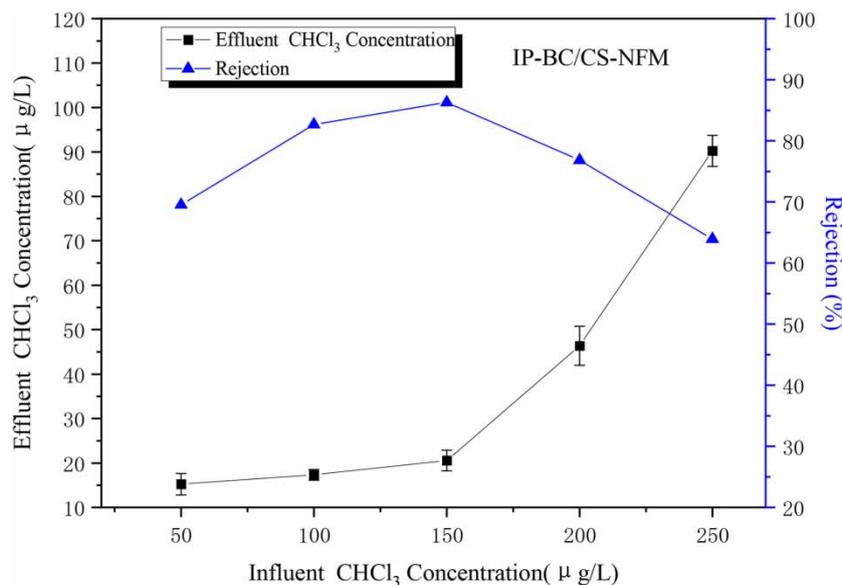
As Figures 3–5 show, before the influent concentration of trichloromethane at 150  $\mu\text{g/L}$ , the effluent concentration of trichloromethane after interception by the three kinds of nanofiltration membranes changed little and was relatively stable, and interception rate gradually increased. With the increase in trichloromethane concentration in the inlet, trichloromethane concentration in the outlet gradually increased, and retention rate gradually decreased. Under normal circumstances, for many materials, the nanofiltration process of solute concentration increase causes the phenomenon of concentration polarization, leading to a decrease in intercept rate.



**Figure 3** | Removal of different chloroform concentrations with BC-NFM. Testing conditions employed were: 50, 100, 150, 200, and 250  $\mu\text{g/L}$  chloroform solution as feed.



**Figure 4** | Removal of different chloroform concentrations with BC/CS-NFM. Testing conditions employed were: 50, 100, 150, 200, and 250  $\mu\text{g/L}$  chloroform solution as feed.



**Figure 5** | Removal of different chloroform concentrations with IP-BC/CS-NFM. Testing conditions employed were: 50, 100, 150, 200, and 250  $\mu\text{g/L}$  chloroform solution as feed.

The experimental results of withholding rate changes in chloroform concentration showed it decreasing after first rising, which may have been due to the low concentration when the concentration polarization phenomenon was not obvious. Chloroform diffusion rate through the nanofiltration membrane had almost no change, so the effluent concentration of chloroform changed little, the withholding rate increased with increase in feed concentration of chloroform to a certain degree of concentration polarization, and the withholding rate began to drop.

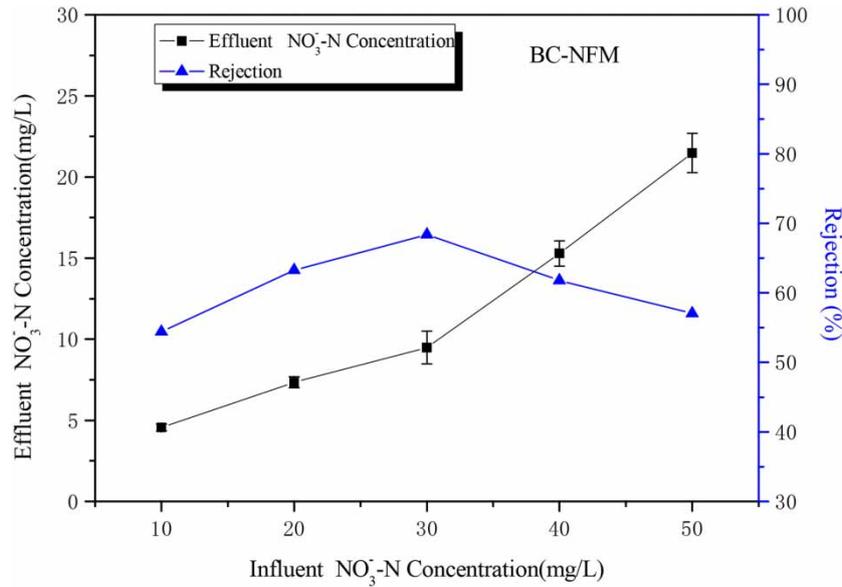
The removal of trichloromethane under the same influent concentration showed IP-BC/CS-NFM > BC-NFM > BC/CS-NFM. All three kinds of nanofiltration membrane with influent concentration of 200  $\mu\text{g/L}$  could control the effluent trichloromethane concentration below 60  $\mu\text{g/L}$ , which indicated that the three kinds of nanofiltration membrane prepared by controlling influent concentration could effectively remove trichloromethane and control its concentration within the national safety standard of drinking water.

### Nitrate nitrogen removal

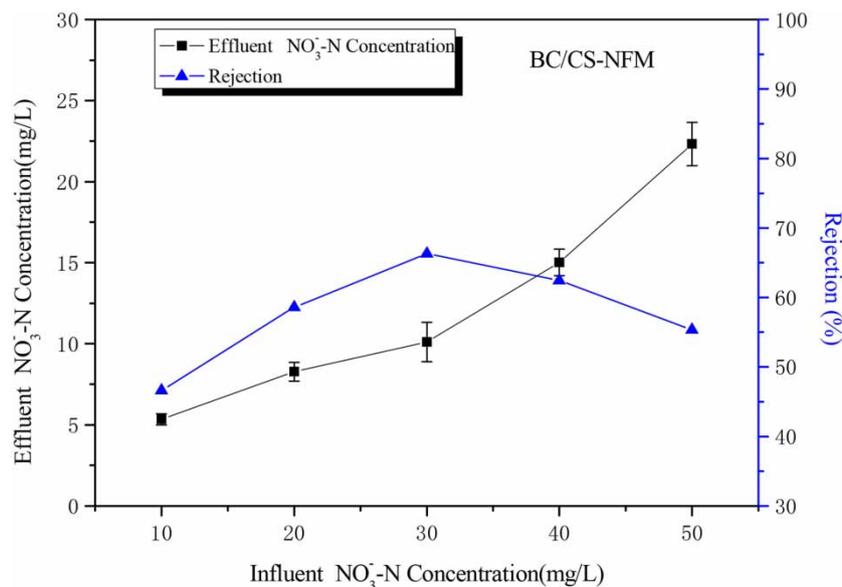
Different aqueous solutions containing nitrate nitrogen were prepared by using deionized water, and the retention of nitrate nitrogen by three kinds of nanofiltration membranes was studied. The experimental results are shown in Figures 6–8.

According to the results in Figures 6–8, with the increase in nitrate nitrogen concentration in the influent, the concentration of nitrate nitrogen in the effluent of the three kinds of nanofiltration membranes gradually increased, and the corresponding concentration of nitrate nitrogen in the effluent first increased and then decreased. As the concentration of nitrate nitrogen in the influent increased, the concentration of nitrate nitrogen in the influent side of the membrane increased, resulting in a difference between the concentrations of nitrate nitrogen on both sides of the membrane and an increase in the driving force of nitrate nitrogen ions passing through the membrane. Therefore, the concentration of nitrate nitrogen in the water accordingly increased. In addition, the increase in nitrate nitrogen concentration in the process of nanofiltration led to concentration polarization, which led to a decrease in interception rate.

The results showed that the maximal nitrate nitrogen retention rates of BC-NFM, BC/CS-NFM, and IP-BC/CS-NFM were 68.37%, 66.30%, and 78.40%, respectively. Under the same level of influent concentration, the removal of nitrate nitrogen was as follows: IP-BC/CS-NFM > BC-NFM > BC/CS-NFM. All three kinds of nanofiltration membrane could control the effluent nitrate nitrogen concentration below 10 mg/L if influent concentration was less than 30 mg/L, which indicated that the three kinds of nanofiltration membranes, prepared by controlling the influent concentration, could effectively remove nitrate nitrogen and control its concentration within the scope of the national safety standards for drinking water.



**Figure 6** | Removal of different nitrate nitrogen concentrations with BC-NFM. Testing conditions employed were: 10, 20, 30, 40, and 50 mg/L nitrate nitrogen solution as feed.



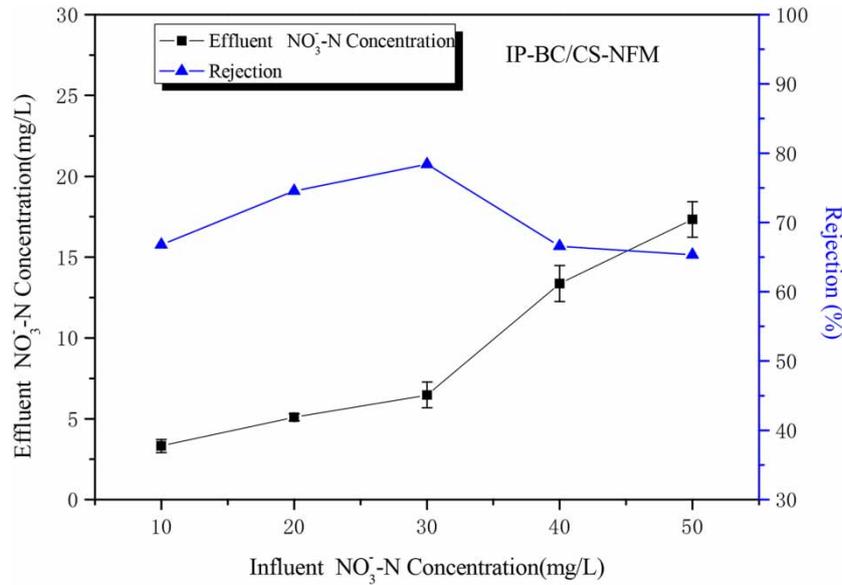
**Figure 7** | Removal of different nitrate nitrogen concentrations with BC/CS-NFM. Testing conditions employed were: 10, 20, 30, 40, and 50 mg/L nitrate nitrogen solution as feed.

### Total hardness removal

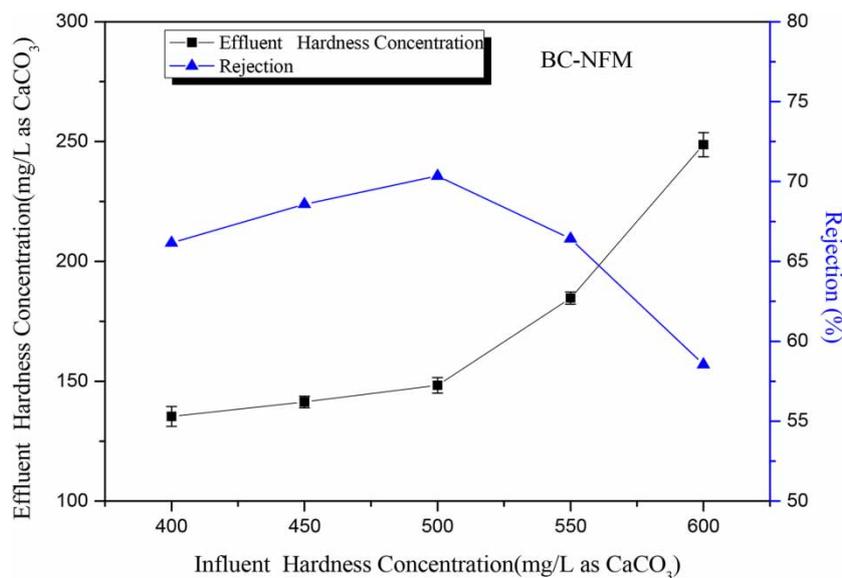
In this study, deionized water was used to prepare aqueous solutions with a total hardness, and the hardness-retention performance of three kinds of nanofiltration membranes was studied. The experimental results are shown in Figures 9–11.

According to the results in Figures 9–11, before the water inlet concentration of hardness was 500 mg/L as  $\text{CaCO}_3$ , and after the three kinds of nanofiltration membranes were retained, effluent hardness changed little and was relatively stable, and retention rate gradually increased. As the hardness of the inlet water continued to increase, the hardness of the outlet water gradually increased, and interception rate gradually decreased. This was mainly due to the concentration polarization phenomenon caused by a change in solute concentration.

Maximal retention rates of BC-NFM, BC/CS-NFM, and IP-BC/CS-NFM on hardness were 70.34%, 69.95%, and 72.49%, respectively. Under the same influent concentration, hardness was removed as follows:



**Figure 8** | Removal of different nitrate nitrogen concentrations with IP-BC/CS-NFM. Testing conditions employed were: 10, 20, 30, 40, and 50 mg/L nitrate nitrogen solution as feed.



**Figure 9** | Removal of different hardness concentrations with BC-NFM. Testing conditions employed were: 400, 450, 500, 550, and 600 (mg/L as  $\text{CaCO}_3$ ) total hardness solution as feed.

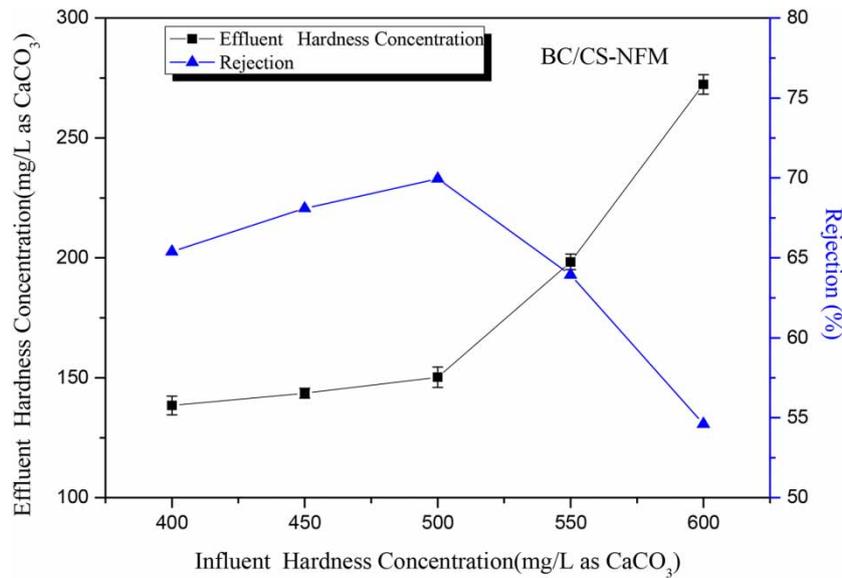
IP-BC/CS-NFM > BC-NFM > BC/CS-NFM. The three prepared kinds of nanofiltration membranes could effectively remove hardness and control the concentration within the national safety standard of drinking water.

#### Influence of operating conditions on nanofiltration-membrane separation performance

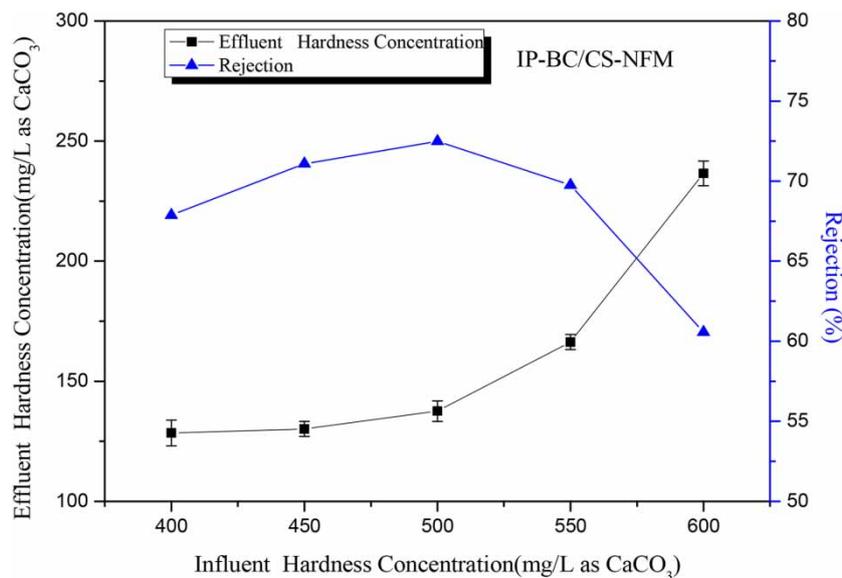
In this section, pH value, temperature, and operating time were selected as the experimental targets to study the influence of operating conditions on the performance of nanofiltration membranes in removing trichloromethane pollutants, operated under inlet water pressure of 0.5 MPa.

#### Influence of inlet pH value on nanofiltration-membrane retention performance

Different pH values of an aqueous solution were adjusted by sodium hydroxide and hydrochloric acid. The interception of chloroform solution with different pH values by BC-NFM, BC/CS-NFM, and IP-BC/CS-NFM is illustrated in Figure 12.

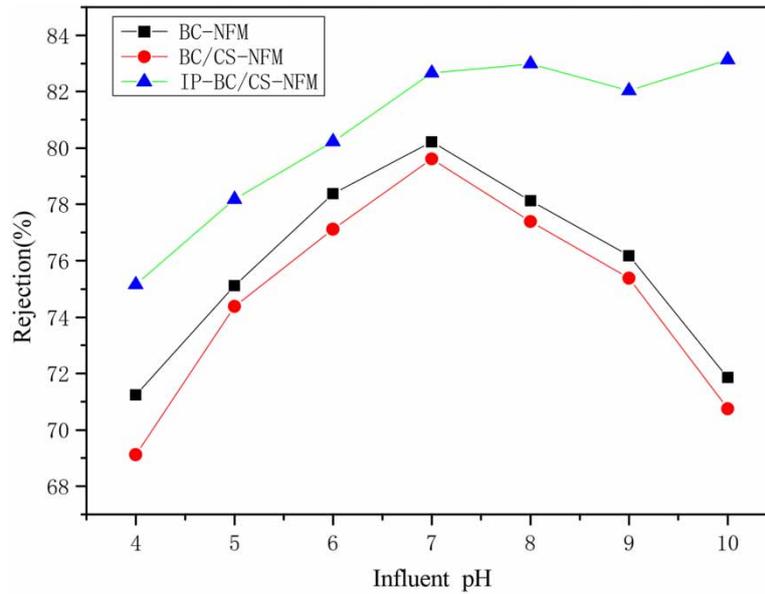


**Figure 10** | Removal of different hardness concentration with BC/CS-NFM. Testing conditions employed were: 400, 450, 500, 550, and 600 (mg/L as CaCO<sub>3</sub>) total hardness solution as feed.



**Figure 11** | Removal of different hardness concentrations with IP-BC/CS-NFM. Testing conditions employed were: 400, 450, 500, 550, and 600 (mg/L as CaCO<sub>3</sub>) total hardness solution as feed.

In Figure 12, the results show that the removal rate of chloroform in the solution by BC-NFM and BC/CS-NFM gradually decreased with the decrease in influent pH value, which was mainly due to the acid hydrolysis of cellulose under acidic conditions, which increased pores on the membrane surface and water flux, but decreased the rejection rate. With the increase in influent pH value, the removal rate of chloroform in the solution by BC-NFM and BC/CS-NFM also gradually decreased, which was due to the alkali hydrolysis of cellulose under alkaline conditions, which increased the pores on the membrane surface and water flux, but decreased the rejection rate. With the decrease in influent pH value, IP-BC/CS-NFM gradually reduced the removal rate of chloroform in the solution, which was due to the acidic conditions. Groups such as -NH- and -NH<sub>2</sub>- can easily combine with water and transform into -NH<sub>2</sub><sup>+</sup>- and -NH<sub>3</sub><sup>+</sup>-. Positively charged micropores on the membrane surface became larger under the electrostatic repulsion of H<sup>+</sup> in the solution, and the rejection rate decreased, thus increasing water flux. With the increase in influent pH value, the removal rate of chloroform in the solution by IP-BC/CS-NFM remained



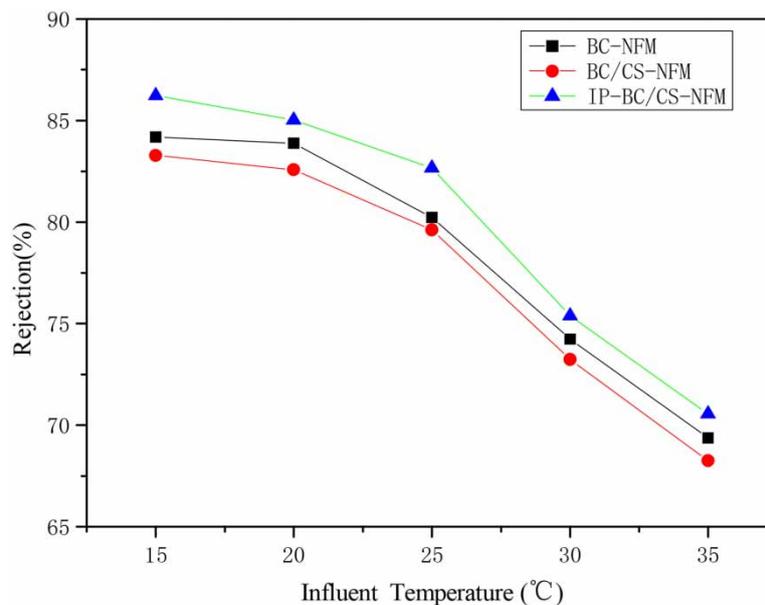
**Figure 12** | Influence of influent pH value on chloroform removal by nanofiltration membrane. Testing conditions employed were: Chloroform concentration in the aqueous solution was 100 g/L, with pH values of 4, 5, 6, 7, 8, 9, and 10, respectively, and the solution was at room temperature.

basically unchanged, due to the decrease in positive charge on the membrane surface, the weakening of electrostatic repulsion, the corresponding flux being relatively stable, and the rejection rate tending to be stable.

#### Influence of inlet water temperature on nanofiltration-membrane retention performance

Different temperatures of the inlet water solution were adjusted by a constant-temperature water tank. Figure 13 shows the interception of the chloroform solution by BC-NFM, BC/CS-NFM, and IP-BC/CS-NFM at different temperature levels.

The Figure 13 results show that the removal rate of chloroform in the solution by the nanofiltration membrane was higher when the temperature of the inlet water solution was low, and the removal rate of chloroform in the



**Figure 13** | Influence of influent temperature on chloroform removal by nanofiltration membrane. Testing conditions employed were: Chloroform concentration in the prepared inlet water solution was 100  $\mu$ g/L, the temperature levels of the solution was 10, 15, 20, and 25  $^{\circ}$ C, respectively, and the pH value of the solution was neutral.

solution by the three nanofiltration membranes decreased slightly when the temperature rose from 15 to 20 °C, but there was little change. When the temperature rose from 20 to 35 °C, the removal rates of chloroform by the three nanofiltration membranes significantly decreased, from 83.88% to 69.37% for BC-NFM, from 82.58% to 68.25% for BC/CS-NFM, and from 85.02% to 70.56% for IP-BC/CS-NFM. Temperature had significant influence on the performance of nanofiltration membrane in removing chloroform, which could be explained by the dissolution–diffusion model.

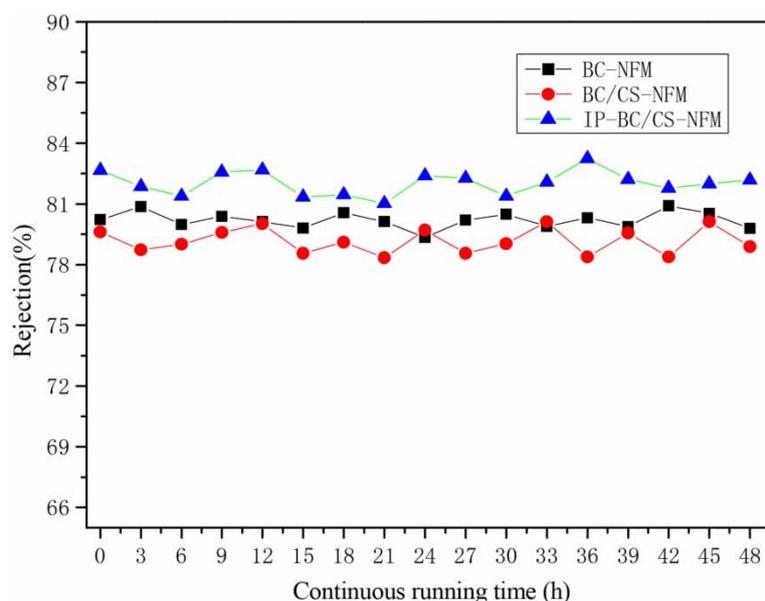
### Influence of operating time on nanofiltration-membrane retention performance

Chloroform concentration in the prepared aqueous solution was 100 µg/L, pH value was neutral, and the solution was at room temperature. The interception of chloroform by BC-NFM, BC/CS-NFM, and IP-BC/CS-NFM was observed by continuous and intermittent operations. Figure 14 shows the continuous-operation mode, keeping the nanofiltration membrane running continuously, and testing the interception every 3 hours during this period. Figure 15 shows the intermittent-operation mode. The nanofiltration membrane ran intermittently, during which interception conditions were tested every 3 days.

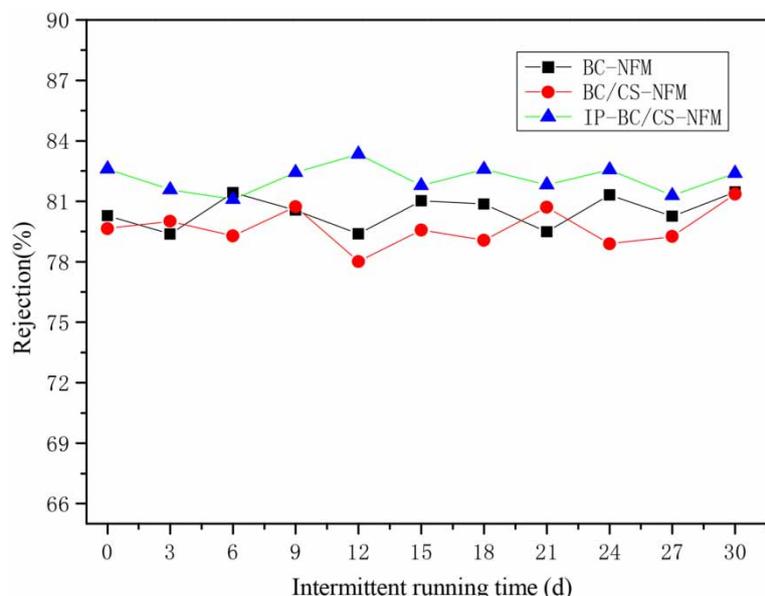
The results in Figures 14 and 15 show that BC-NFM, BC/CS-NFM, and IP-BC/CS-NFM kept relatively stable chloroform retention rates in the continuous and intermittent operation modes. According to the retention conditions of the three nanofiltration membranes within the currently set operation time range, operation time had little influence on the removal of chloroform by the nanofiltration membranes. On the one hand, the interception of chloroform by the three nanofiltration membranes was a physical interception behavior; on the other hand, chloroform solution was prepared, and the solute in the solution was single, which had little influence on the membrane pore structure of the nanofiltration membranes. For the membrane fouling, we investigated the effect of fouling on the flux attenuation of nanofiltration membrane. The results showed that the flux attenuation of a nanofiltration membrane is mainly caused by concentration polarization and adsorption fouling.

## CONCLUSIONS

Nanofiltration membranes can be obtained by alkali hydrolysis and chloroacetic acid carboxymethylation modification of dense BCM and BC/CSM, or by interfacial polymerization with piperazine as aqueous monomer and trimellitic chloride as organic monomer on the surface of asymmetric membrane BC/CSM with porous network structure. At a pressure of 0.5 MPa, the retention rates to NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, Methyl Orange and Methyl Blue were good, and the water flux were also good.



**Figure 14** | Influence of continuous running time on chloroform removal by nanofiltration membrane. Testing conditions employed were: 100 µg/L chloroform solution as feed, running continuously for 48 hours, the operating pressure was 0.5 MPa.



**Figure 15** | Influence of intermittent running time on chloroform removal by nanofiltration membrane. Testing conditions employed were: 100 µg/L chloroform solution as feed, running continuously for 30 days, the operating pressure was 0.5 MPa.

Three nanofiltration membranes – BC-NFM, BC/CS-NFM, and IP-BC/CS-NFM – had good removal effects on chloroform, nitrate nitrogen, and hardness, and could control the removal of pollutants within a certain influent concentration range within the national drinking-water safety standards. The rejection rate of nanofiltration membranes were relatively stable under long operation time, which show their good anti pollution performance.

The separation performance of the nanofiltration membrane obtained by interfacial polymerization was better than that of the membrane obtained by alkali hydrolysis and the carboxymethylation of chloroacetic acid, and it was relatively stable in long-term operation, so it has broad application prospects in the advanced treatment of drinking water.

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## DATA AVAILABILITY STATEMENT

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

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