# A Graphene Oxide Nanofiltration Membrane Intercalated with Cellulose Nano-crystals

Yan Lyu, Qinqin Zhang, Zhenxing Wang, and Junwen Pu \*

Graphene oxide (GO)-based nanofiltration (NF) membranes have simple fabrication and excellent performance in broad applications. However, the tight stacking of GO lamellae leads to low water flux. In this study, the interlamellar spacing of GO was increased by intercalating carboxylmodified nano-crystalline cellulose (CCNC) to increase the membrane flux, which were prepared using vacuum filtration self-assembly. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images showed that GO and CCNC uniformly covered the holes of the substrate membrane. The maximum water flux of the CCNC-intercalated graphene oxide nanofiltration membrane was 12.74 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, which is higher than most commercial nanofiltration membranes. The membrane attained high rejection rates for organic dyes with various charges (≥ 95% for sunset yellow (SY) and ≥ 90% for methylene blue (MB) and rhodamine B (Rh B)). In contrast, the negative GO-CCNC membrane showed a moderate rejection ratio for salt ions (e.g., 80.6% for Na<sub>2</sub>SO<sub>4</sub> and 75.5% for MgSO<sub>4</sub>). The antifouling property of the GO-CCNC nanofiltration membrane was tested using 1 g L<sup>-1</sup> bovine serum albumin (BSA) solution. The membrane intercalated with CCNC showed better antifouling performance. The pure water flux of the membrane was recovered by more than 90% by washing.

Keywords: Nano-crystalline cellulose; Graphene oxide; Nanofiltration membrane; Antifouling

Contact information: Department of Materials Science and Technology, Beijing Forestry University, 100083, P.R. China; \*Corresponding author: 13681243864@126.com

## INTRODUCTION

As the water resources crisis has intensified and environmental water quality has deteriorated, water resources have become an environmental problem attracting worldwide attention (Zhu et al. 2015). The use of nanofiltration (NF) membranes is a new watertreatment technology that has played an important role in drinking-water and waste-water treatment because of their low energy consumption and high efficiency. Therefore, sustained efforts have been made to prepare new nanofiltration membranes with high flux, selectivity, and stability. Graphene oxide (GO)-based membranes are promising options for molecular separation and filtration applications because of their mechanical strength and practical prospects for industrial scale production (Akbari et al. 2016; Fathizadeh et al. 2017; Hong et al. 2017). The surface of GO contains a large number of oxygencontaining functional groups, which can expand the interlamellar spacing (Joshi et al. 2014). The interlayer spacing of dry GO lamella is 0.9 nm  $\pm$  0.1 nm (Nair *et al.* 2012). Graphene oxide, in one-atom-thick carbon materials, has good mechanical properties, chemical resistance, and no permeability to gas and water (Surwade et al. 2015; Anand et al. 2018; Song et al. 2018). In production, however, there are holes and wrinkles in the graphene oxide layer, but the size of the pores and degree of the wrinkles are controllable (Cohen-Tanugi and Grossman 2012; Pacakova *et al.* 2017). Studies have shown that the degree of wrinkles can be controlled by different experimental processes and treatment times, so as to control the lamellar spacing (Pacakova *et al.* 2017; Chen *et al.* 2018). GO folds can lead to changes in pure water flux from dozens to hundreds. Namely, the permeability of GO basement membranes could be controlled by controlling the wrinkles and interlayer spacing of GO sheets (Cohen-Tanugi and Grossman 2012; Pacakova *et al.* 2017). With its unique two-dimensional structure and excellent properties, GO, a promising candidate for next-generation separation nanomaterials, has attracted many researchers' interests in its application in novel nanofiltration membranes.

Great progress has been achieved in water nanofiltration through GO membranes because of its ultrafast permeation for water (Sun et al. 2016; Fathizadeh et al. 2017). Graphene membranes (GMs) are usually formed through simple stacking of graphene, graphene oxide (GO), and reduced graphene oxide (rGO) (Zhu et al. 2018). The layered structure of GO offers unique ion transport properties, and its excellent water dispersibility makes it easy to prepare in the form of membranes (Tsou et al. 2015). Due to the high aspect ratio of GO sheets, GMs can be easily obtained by vacuum filtration or spin-coating (Sun et al. 2007; Chen et al. 2015). Vacuum filtration is a fast and environmentally friendly method that can assemble a highly ordered and homogeneously layered structure on a polymer/inorganic carrier, and it can be produced on a large scale (Dikin et al. 2007; Zhan et al. 2018; Zhu et al. 2018). Oiu et al. (2011) prepared a wet graphene membrane using wrinkled hydrazine-reduced GO via vacuum filtration and studied its potential application in nanofiltration for nanoparticles and dyes. The channels of water are considered to be made up of the wrinkles formed during the reduction process. The degree of corrugation can be easily controlled at the nm scale by controlling the temperature of the hydrothermal reduction. Han et al. (2013) fabricated a neat graphene nanofiltration membrane (GNm) using rGO via vacuum filtration. The prepared GNm showed a well packed layer structure and comparable rejection ratio to commercial NF membranes (60% for 0.01 mol/L Na<sub>2</sub>SO<sub>4</sub> and 99% for dyes), but water flux was only 3.3 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>. It was supposed that the narrow channels between tightly packed rGO sheets may be the reason for low water flux. Additionally, the high pressure during usage of the NF membrane (usually 0.5 MPa to 2 MPa) may lead to shrinkage of the nanochannels, as reported by Huang et al. (2013). Han et al. (2015) fabricated a high-flux, graphene-based NF membrane with intercalation of carbon nanotubes (GCNTm) by assembling refluxed graphene oxide (rGO) and multiwalled carbon nanotubes (MWNTs) on a porous substrate. The water flux of GCNTm was 11.3 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, more than twice that of the neat graphene nanofiltration membrane (GNm). The GCNTm films maintained high rejection rates for dyes (>99% for direct yellow and > 96% for methyl orange) and salt ions (> 83.5% for Na<sub>2</sub>SO<sub>4</sub> and > 51.4% for NaCl). Zhao et al. (2015) also increased the GO lamellar spacing by intercalation of carbon nanotubes. In this case, extending the layer spacing of graphene sheets through the intercalation of nanomaterials is an effective way to increase the flux of membranes (Gao et al. 2015; Zhu et al. 2018). Chen et al. (2018a) prepared a free-standing sandwichstructured polyamide 6 (PA 6)@GO@PA 6 nanofiltration membrane intercalated with nanoparticles(NP). The x-ray diffraction patterns indicated that the interlayer spacing of the GO lamellae increased with the TiO<sub>2</sub> nanoparticle (NP) intercalating. The membrane showed a pure water flux up to 13.77 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, which was 80.7% greater than that of the membrane without NP intercalation, and had excellent organic dye retention rates (> 85% for basic fuchs n and > 92% for methyl orange). In addition, the researchers found that intercalation with other nanoparticles, such as  $SiO_2$  and  $Si_3N_4$ , could also increase water flux and maintain high rejection rates for organic dyes.

Cellulose is the most abundant environmentally friendly material in nature and has good hydrophilicity (Habibi *et al.* 2006; Xia *et al.* 2018). Cellulose nano-crystals (CNC) possesses the excellent properties of cellulose and is in nanometer size. They are long, rod-like structures with a diameter of less than 100 nm, and a large ratio of length to diameter (Ioelovich 2008; Peng *et al.* 2011). The physical shape is similar to carbon nanotubes, and the surface contains a large number of hydroxyl groups, which can be modified by carboxylation (Habibi *et al.* 2006; Zhu *et al.* 2017). Many studies on cellulose and GO have shown that they have good compatibility (Kafy *et al.* 2017; Zhu *et al.* 2017; Chen *et al.* 2018b). Fang *et al.* (2016) prepared freestanding bacterial cellulose-graphene composite membranes for selective ion permeation. They found that the water stability and mechanical strength of composite membrane is better than pure GO membrane. It has been shown that the thermal and mechanical properties were improved with the addition of GO (Marian *et al.* 2016). Furthermore, the result indicated that the retention rate after 90 min increased from 78% (pure cellulose acetate membrane) to 99% (composite membrane 1wt% GO added).

In this study, to further increase the water flux of GNm, graphene/nano-crystalline cellulose composite membranes were designed by assembling GO and CNC on a porous substrate *via* a vacuum-filtration-induced self-assembly process, as shown in Fig. 1. The CNC, which was carboxylated (CCNC), was used as an intercalation structure to increase the layer spacing of GO. There are three reasons for the choice of CCNC. First, CCNC has a strong rod structure that could effectively maintain the interlayer spacing. Second, CCNC has a large number of hydroxyl groups, which can bond with GO through hydrogen bonds. Third, CCNC is a hydrophilic substance that could enhance the hydrophilicity of a membrane, which is conducive to improving water flux. The operating pressure of nanofiltration membrane is generally 0.5 MPa to 2 MPa. Considering the relatively high pressure that the NF membrane bore, commercialized polyvinylidene fluoride (PVDF) ultrafiltration membrane was used as support layer.

#### EXPERIMENTAL

#### Materials

Graphene oxide (300-mesh, 0.1 wt% water dispersion) was provided by Beijing Carbon Century Technology Co., Ltd (Beijing, China). Cellulose nano-crystals (CNC) gel (4.3 wt%) was provided by Technical Institute of Physics and Chemistry (Beijing, China). The 2,2,6,6-tetramethyl-1-(pyperidinyloxy) radical (TEMPO) was purchased from Sigma-Aldrich (St. Louis, MO, USA). NaClO solution (8%) and MgSO<sub>4</sub> were purchased from Xilong Scientific Co., Ltd (Shantou, China). NaBr was purchased from Tianjin Jinke Fine Chemical Research Institute (Tianjin, China). NaOH was purchased from Tianjin Guangfu Science and Technology Development Co., Ltd (Tianjin, China). Polyvinylidene fluoride (PVDF) ultrafiltration (UF) membranes with a pore size of 50 nm were purchased from the Beijing Hai Cheng Shi Jie Co., Ltd (Beijing, China). Sunset yellow and rhodamine B were obtained from Shanghai Ruji Biotechnology Development Co., Ltd (Shanghai, China). Methylene blue and MgCl<sub>2</sub> were purchased from Tianjin Yongda Chemical Regent Co., Ltd (Tianjin, China). NaCl and Na<sub>2</sub>SO<sub>4</sub> were obtained from Beijing OBO Biotech Co., Ltd (Beijing, China). All reagents were analytical reagents unless otherwise specified.

## Preparation of Carboxyl-Modified CNC (CCNC)

The CNC gel (23.3 g, including 1 g of CNC) was prepared as a dispersion of 0.5 wt% to 1 wt%. Then, 0.025 g of TEMPO and 0.5 g of NaBr were mixed into the dispersion. The mixture was stirred at room temperature by magnetic stirring. The NaClO solution was dripped slowly until the content of NaClO was 1 g. The oxidation started when NaClO reached the desired amount. Then, 3 mol  $L^{-1}$  NaOH and 1 mol  $L^{-1}$  NaCl solution were used to adjust the pH of the mixture to 10 to 10.5. The mixture was stirred at room temperature for 4 h to ensure that the oxidation reaction was fully carried out. The CCNC gel was obtained by vacuum filtration after the end of the reaction and rinsed three times with water. The concentration of the CCNC gel was measured using the drying and weighing method.

## Fabrication of GO-CCNCm

To fabricate a series of GO-CCNCm with varying CCNC contents, diluted dispersions of GO and CCNC were prepared. The 0.1-mg mL<sup>-1</sup> GO and CCNC dispersions were prepared by bath-sonication and stirring dilution for 30 min. The GO and CCNC solutions were used for membrane fabrication immediately after sonication. For uniform dispersion, 2.5 mL of GO solution (0.1 mg mL<sup>-1</sup>) was added into 200 mL of deionized water (DI H<sub>2</sub>O) and bath-sonicated for 30 min. Different volumes of CCNC solution were subsequently added into the fully diluted GO solution and bath-sonicated for 5 min. Then, the mixed dispersion was subjected to pressure-assisted filtration at 1 bar pressure on PVDF membranes (50-nm pore size, 90-mm diameter), which were fixed on the plate filter instrument to yield GO-CCNC membranes. The preparation process is shown in Fig. 1. To produce 10, 30, 50, and 80 wt% GO-CCNC membranes, 0.25, 0.75, 1.25, and 2 mL of CCNC solution were added, respectively. As a contrast, a pure GO membrane was prepared using 2.5 mL of the GO solution and was likewise diluted and filtered without the addition of CCNC. The as-prepared membranes were dried in a vacuum drying device with temperature controlled at 40 °C for 24 h. The membranes were then cut into circular samples with a diameter of 6.5 cm and seal-stored under room temperature for performance evaluation.



**Fig. 1.** Schematic representation of the preparation of GO-CCNC nanofiltration membranes by a vacuum filtration method.

## Flux and Rejection Ratio Test

All of the NF performance evaluations were conducted with self-made cross-flow filtration equipment that has an effective area of 26.4 cm<sup>2</sup>. The NF membrane was fixed

onto the equipment and filtered pure water for 20 min under a pressure of 5 bar, so that the performance of the membrane reached a stable state. The water flux (J) was measured by collecting the permeate water through the membrane in a certain period of time and weighing it using an electronic balance (0.01 g). The pure water was calculated using the following equation,

$$J(Lm^{-2}h^{-1}bar^{-1}) = V/(A \times T \times P)$$
<sup>(1)</sup>

where V is the permeation of pure water (L), A is the effective membrane area ( $m^2$ ), T is the sampling time (h), and P is the operating pressure (bar). Flux changes with pressure were also measured by changing pressure.

Then, 0.01 mol L<sup>-1</sup> NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>, and MgSO<sub>4</sub> solutions were used as feed solutions to test the ion interception performance. The capabilities of the membranes to separate organic dyes from water were tested using 0.05 g L<sup>-1</sup> of sunset yellow (42.37 Da), methylene blue (373.90 Da), and rhodamine B (479.01 Da) solutions. All experiments were carried out under a pressure of 5 bar. When the feeding solution was switched, the membrane was washed with pure water in the filtration cell for 30 min to eliminate the effect of the former solute. Permeate concentration ( $C_p$ ) was recorded when the retention rate became stable. The concentrations of the salt and organic dye solutions were measured using a conductivity meter and ultraviolet spectrophotometer, respectively. The rejection ratio (R) was calculated using the following equation,

$$R(\%) = (1 - C_p) / C_o$$
<sup>(2)</sup>

where  $C_p$  is the permeate concentration (mol L<sup>-1</sup>) and  $C_o$  is the original concentration (mol L<sup>-1</sup>) of the salt or dye solution. The flux and rejection ratio under various concentrations were measured under the same conditions using Na<sub>2</sub>SO<sub>4</sub> solutions of various concentrations.

#### **Fouling Resistance Test**

Bovine serum albumin was selected as the contaminant to characterize the antifouling property of the membranes. The BSA feed solution was 1 g L<sup>-1</sup>. At first, the pure water flux ( $J_0$ ) of a new membrane was measured every 20 min for 1 h. Then, the tank was fed with BSA solution, and the water flux ( $J_1$ ) of the BSA solution was measured every 20 min for 100 min. After filtration, the membrane was washed with DI water for 30 min. Then, the pure water flux ( $J_2$ ) of the membrane was measured again.

The flux recovery ratio (FRR) of the membrane was measured to characterize the antifouling property of the nanofiltration membranes. The FRR was calculated using the following equation,

$$FRR(\%) = J_2 / J_0 \times 100\%$$
(3)

where  $J_0$  and  $J_2$  are the pure water flux (L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>) before and after BSA feed solution, respectively. Higher FRR indicated that the flux of membrane was easier to recover by washing.

#### Characterization

The chemical structure of CNC and CCNC were characterized using Fourier transform infrared spectroscopy (FTIR) (Vertex 70v, Bruker, Billerica, MA, USA).

The surface morphology of the membranes was investigated using scanning electron microscopy (SEM) (SU8010, Hitachi, Tokyo, Japan). All samples received 45 s

of gold coating.

The morphology and roughness of the membranes, as well as the thickness of the functional layer were observed using atomic force microscopy (AFM) (Bruker Multimode 8, Billerica, MA, USA).

The hydrophilicity of the membrane surface was characterized by the contact angle. The contact angle was measured with a contact angle measuring system (OCA 20, DataPhysics Corporation, San Jose, CA, USA). For each sample, 5 different locations were tested and averaged for accuracy.

Zeta-potential was tested using a zeta potentiometer (Zetasizer Nano Z, Malvern Panalytical, Malvern, UK) to characterize the electronegativity of the membrane. Each sample was tested five times and averaged for accuracy.

## **RESULTS AND DISCUSSION**

## **Carboxyl Modification of CNC**

In the process of vacuum filtration, whether the dispersant is dispersed uniformly or not is a major factor in film formation and performance. Graphene oxide is a hydrophilic, two-dimensional substance that can be dispersed evenly in water. However, CNC has many hydroxyl groups on the surface and large specific surface area, and it is very easy to reunite in water. Carboxylation of CNC can effectively relieve agglomeration and make it disperse evenly in water. Additionally, modified CNC contains more surface charge (mainly provided by carboxyl groups on the surface of CCNC) and leads to higher salt rejection because of the stronger Donnan exclusion. Figure 2 shows the FTIR spectra of the CNC and CCNC. It is obvious that the CCNC carboxyl content was significantly higher than that of CNC. The hydroxyl absorption peak at 3400 cm<sup>-1</sup> was reduced in the modified nanocrystalline cellulose relative to the unmodified sample, indicating a decrease in the hydroxyl content. The carboxyl absorption peaks of CCNC at 1600 cm<sup>-1</sup> and 2900 cm<sup>-1</sup> increased compared with the unmodified samples, and the cumulative double bond stretching vibration peak at 2400 cm<sup>-1</sup> increased, indicating that the carboxyl content increased. The FTIR results indicated that the selective oxidation of TEMPO oxidized the hydroxyl groups at the C6 position of CNC to carboxyl groups, and the content of carboxyl groups increased significantly. Macroscopically, the dispersion of CCNC in water was significantly better than that of CNC, as shown in Fig. 3.



Fig. 2. FTIR spectra of (a) CNC and (b) CCNC



**Fig. 3.** Digital photos of CNC and CCNC dispersions. Ultrasonic-dispersed CCNC (left) and CNC (right) (a) immediately after dispersion and (b) after 10 min of quiet

## **Fabrication of GO-CCNCms**

Figure 4 shows the formation of the GO-CCNC membrane at a microscopic scale. Figure 4a shows visible holes on the surface of the PVDF basement membrane. Figure 4b is the SEM image of the junction between the functional layer and the basement membrane. The right portion of Fig. 4b shows the porous basement membrane (a PVDF UF membrane with a pore size of 50 nm) that was not covered with GO. The typical cavernous structure of the basement membrane is shown in Fig. 4b. As shown in the left portion, when the pores were uniformly covered with GO, the pore size of the membranes decreased obviously. As shown in Fig. 4 (c, d), the as-prepared membranes exhibited a smooth surface without any visible defects. Visible defects would significantly reduce the retention of the membranes. At the same time, the functional layer of the membrane must be as thin as possible to ensure a high water flux. The loading dosage of GO was 44.1 mg m<sup>-2</sup> in this experiment, which was the boundary value of the membrane with no defects. The average thickness of the membrane without CCNC was only 122 nm, which was measured using AFM (Fig. 4e). After intercalation of CCNC (10, 30, 50, and 80%), the thicknesses of the membranes significantly increased, to 128, 137, 144, and 165 nm, respectively.



**Fig. 4.** (a) SEM image of the PVDF supporting membrane with a pore size of 50 nm. (b) SEM image (top view) of GO-CCNCm(0%) at the juncture. SEM images of (c) GO-CCNCm (0%) and (d) GO-CCNCm (50%). (e) AFM image of the edge of the functional layer (GO-CCNCm (0%)).

Five different GO-CCNC membranes were fabricated with CCNC addition ratios ranging from 0% to 80%, and the loading of GO for all these films was 44.1 mg m<sup>-2</sup>. Figure 5 shows the surface images of the ultrathin selective layer with varying CCNC additions. The content of CCNC is shown in parentheses. For example, GO-CCNC (10%) denotes that the amount of CCNC added in the film was 10% of GO content. As shown in Fig. 5(a-e), the nano-structured membranes of various CCNC loadings all appeared uniform and smooth. This was a result of the good synergy and flexibility of CCNC and GO. The CCNC modified by carboxylation was able to form a stable system with the GO. The uniform distribution of CCNC can also be observed in the AFM image (Figure 5f).



**Fig. 5.** SEM images of (a) GO-CCNC (0%), (b) GO-CCNC (10%), (c) GO-CCNC (30%), (d) GO-CCNC (50%) and (e) GO-CCNC (80%). (f) AFM image of GO-CCNC (50%).

## NF Performance of GO-CCNCm

The flux and rejection ratio of the GO-CCNC membranes were systematically measured. NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub> and MgSO<sub>4</sub> were used to test the salt retention rate of the membranes. Sunset yellow (SY), methylene blue (MB), and rhodamine B (Rh B) were used to test the ability of the membrane to separate dyes. The dyes (SY, MB, and Rh B) have similar molecular weights, but different charges, which are anionic, cationic, and electroneutral, respectively. These salts and dye solutions were deliberately chosen based on their various charges and molecular weights so that the separation mechanism of the membranes could be explored. The results are summarized in Table 1.

Membrane	Flux (L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	Rejection of Salts (%)				Rejection of Dyes (%)		
		Na <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>	NaCl	MgCl <sub>2</sub>	S Y(-)	M B(+)	Rh B
GO-CCNC (0%)	7.64	94.3	83.9	52.3	24.1	99.7	98.4	99.2
GO-CCNC (10%)	8.17	80.6	75.4	47.5	16.2	98.8	96.2	98.4
GO-CCNC (30%)	9.84	71.0	55.1	30.2	10.4	98.1	93.6	96.5
GO-CCNC (50%)	9.96	67.6	43.2	22.5	8.3	96.5	91.5	93.4
GO-CCNC (80%)	12.74	53.4	28.7	19.8	7.2	95.9	90.1	92.3

 Table 1. NF Performance of GO-CCNCm with Varying CCNC Loading

When GO lamellae are stacked, the interlayer spacing is mainly determined by functional groups on the surface (Joshi et al. 2014). The 2D nanochannels formed by GO layer are narrow, which is not conducive to the passage of water molecules. Consequently, compared with some high-performance commercialized nanofiltration membranes, GObased NF membranes have excellent separation performance, but low water flux (Han et al. 2013). In this experiment, carboxyl-modified CNC was used as an intercalation material to increase the lamellar spacing of the GO and further increase the water flux of the membrane. As shown in Table 1, the pure water flux of the GO-CCNC membranes increased with increased CCNC loading. In order to further understand the intercalation effect of CCNC, the flux was also tested with the change in operating pressure. As shown in Fig. 6b, the flux of pure water increased as operating pressure increased from 5 bar to 7 bar, and the growth rate of CO-CCNC (10%) and GO-CCNC (50%) was larger than that of GO-CCNC (0%). When operating pressure increases, the GO layer is compressed to narrow the water channels (Huang et al. 2013). However, the support of CCNC slowed down the contraction of channels. This result indicates that the intercalation of CCNC increases and holds the spacing between GO lamellae, which is consistent with the thickness variation of the membranes. Within the limitations of the instrument, the maximum pressure measured was 7 bar, and there was no damage to the membrane under this pressure. Generally, the thin separation layer supported by nanoporous pads cannot bear high pressure (Tian *et al.* 2015), but the GO-CCNC membranes can handle at least 7 bar pressure.

The desalination performance of the NF membrane was between that of the ultrafiltration membrane and the reverse osmosis membrane. The moderate desalination performance is very suitable for drinking water treatment (Giagnorio et al. 2018). In addition, the retention properties of salts could reflect the structures and mechanisms of the membrane. Thus, the rejection of GO-CCNCm to four kinds of salts (Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, NaCl, and MgCl<sub>2</sub>) under the pressure of 5 bar at 0.01 mol L<sup>-1</sup> concentration were systematically tested. As shown in Table 1, the retention properties of salt ions of the membranes were in the order of R ( $Na_2SO_4$ ) > R ( $MgSO_4$ ) > R (NaCl) > R ( $MgCl_2$ ), which is a typical performance for a negatively charged NF membrane. This result is consistent with the result of the  $\zeta$ -potential test (Fig 6a), which indicated that the GO-CCNC membranes were highly negatively charged. The negative charge was mainly attributable to the large number of carboxyl groups on the surface of GO and CCNC. The results of salt retention can be ascribed to the Donnan exclusion. On the basis of the Donnan exclusion effect, when the solution passes through the NF membrane under pressure, the charges on the surface of the membrane will prevent the passage of ions with the same charge, and the ions with opposite charge are also intercepted in order to ensure the electrical neutrality of the solution (Schaep et al. 1998; Song et al. 2016). The GO-CCNC membranes showed higher retention of MgSO<sub>4</sub> than NaCl (Table 1), which could be ascribed to the steric hindrance effect. According to the steric hindrance effect, particles with diameter larger than the aperture are intercepted, and particles with diameter smaller than the pore diameter pass through. The hydrated radius of Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup> and Cl<sup>-</sup> are 0.43 nm, 0.38 nm, 0.36 nm, and 0.33 nm, respectively (Schaep *et al.* 1998). The hydration radius of  $Mg^{2+}$  and  $SO_4^{2-}$ ions are larger than that of Na<sup>+</sup> and Cl<sup>-</sup> ions. Therefore, steric hindrance should also be considered in the retention of salts. As shown in Table 1, with increasing CCNC content, the rejection rates of the four salts decreased, which indicates that the intercalation of the CCNC increased the spacing of the GO lamellae, and the steric hindrance of the ions was reduced. The rejection of Na<sub>2</sub>SO<sub>4</sub> and NaCl dropped from 94.3% to 53.4% and from 52.3%

to 19.8%, respectively, which are more moderate decreases than those of MgSO<sub>4</sub>, from 83.7% to 28.7%, and MgCl<sub>2</sub>, from 24.1% to 7.2%. This result likely occurred primarily because  $Mg^{2+}$  has the largest hydration radius, and steric hindrance plays a major role.

The effect of feed solution concentration on the permeate flux and the rejection of Na<sub>2</sub>SO<sub>4</sub> solution by GO-CCNC membranes are shown in Fig. 6(c, d). With increasing Na<sub>2</sub>SO<sub>4</sub> concentration, the flux and rejection rate decreased significantly. At first, with increasing feed concentration, the osmotic pressure increases, and the hydrodynamic resistance increases, resulting in a decrease in permeation flux. In addition, the presence of Na<sub>2</sub>SO<sub>4</sub> would reduce the spacing of the GO electrostatic double layer because of the charge-screening effect (Zheng *et al.* 2017). The decline of the interception rate could be explained by the Donnan theory. The concentration of Na<sup>+</sup> increased with increasing concentration of the solution, shielding the negative charge on the membrane surface, resulting in a decrease in the surface charge density and rejection effect of the anions (Wang *et al.* 1997; Miao *et al.* 2013).



**Fig. 6.** (a) Zeta potential of GO-CCNC membranes with varying content of CCNC. (b) The effect of pressure on flux. The effect of solution concentration on (c) flux and (d) rejection

The retention properties of dyes with different charges were also systematically tested. As shown in Table 1, all of the films showed excellent retention of dye molecules ( $\geq$  95% for SY,  $\geq$  90% for MB and Rh B). The retention properties of the dyes were in the order of R (SY) > R (Rh B) > R (MB). These three dyes have similar molecular weights, so they are similar in terms of steric hindrance. The difference in interception rates was mainly caused by the Donnan effect. The negatively charged SY had the strongest

electrostatic repulsion, so the rejection rate was the highest. The second strongest repulsion was the neutral Rh B. The electrostatic repulsion of MB with positive electricity was the smallest.

#### **Antifouling Property of GO-CCNCm**

In practice, membrane fouling is the most important factor to reduce membrane performance and shorten service life. Therefore, good antifouling performance is particularly important for efficient membrane operation (Werber *et al.* 2016; Wang *et al.* 2018). As a typical simulated pollutant, BSA was used to evaluate the antifouling performance of the GO-CCNC membranes. The antifouling performance of each membrane was characterized by the change in water flux after the filtration process of 1 g  $L^{-1}$  BSA solution. As shown in Fig. 7(a), the flux of GO-CCNC (0%) and GO-CCNC (50%) decreased significantly when the BSA solution was filtered, but both of the fluxes were greatly restored after direct washing. This result was attributed mainly to the deposition of BSA molecules on the surface of the membrane through a variety of interactions, increasing the transmembrane resistance of the water molecules, reducing the flux. The FRR value of GO-CCNC (0%) was 89.7%, which was slightly lower than the 91.2% of GO-CCNC (50%). The results indicated that the addition of CCNC could enhance the antifouling performance of the membrane, which could be explained by the following factors.



**Fig. 7.** (a) Fouling characterization of GO-CCNC (0%) and GO-CCNC (50%) with 1 g/L BSA solution under 5 bar. (b) Water contact angle of GO-CCNC membranes with varying loadings of CCNC. Typical surface AFM images and surface roughness analysis for (c) GO-CCNC (0%) and (d) GO-CCNC (50%)

As shown in Fig. 7(b), with the addition of CCNC, the contact angle of the membrane decreased, indicating the hydrophilic enhancement of the film. Hydrophilic membranes generally have better antifouling property, because the formation of water layer, preventing the attachment of pollutants (Ostuni *et al.* 2001). Meanwhile, surface roughness is the key factor in the antifouling performance of the membrane. And smooth surfaces are less likely to block contaminants than rough surfaces (Feng *et al.* 2004). As shown in Fig. 7(c, d), the roughness of GO-CCNC (0%) was 34.5. After intercalation with CCNC, the roughness of GO-CCNC (50%) dropped to 27.6. In addition, the surface of CCNC contains a large number of carboxyl and hydroxyl groups. After adding CCNC, the film surface had a strong electronegative property, and BSA also has a negative charge (Wang *et al.* 2018). The repulsion between negative charges reduced the adhesion of BSA onto the membrane surface. Based on the above analysis, the intercalation membranes. After cleaning, the flux of GO\_CCNC (50%) membrane was recovered by more than 90%.

## CONCLUSIONS

- 1. In this study, CCNC-intercalated GO nanofiltration membranes were prepared using a vacuum pressure self-assembly method. The CCNC and GO were evenly distributed on the surface of the membrane, and the GO lamellar spacing was increased by the intercalation of the CCNC. The maximum water flux of the GO-CCNC nanofiltration membrane was 12.74 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, which is higher than most commercial nanofiltration membranes.
- 2. The GO-CCNC membrane attained high rejection rates for three types of organic dyes with different charges ( $\geq 95\%$  for SY, and  $\geq 90\%$  for MB and Rh B) and moderate rejection ratios for salt ions (*e.g.*, 80.6% for Na<sub>2</sub>SO<sub>4</sub> and 75.5% for MgSO<sub>4</sub>).
- 3. The intercalation of CCNC effectively reduced the roughness of the membrane surface and improved the antifouling performance of the membrane. After washing, the pure water flux of the membrane was recovered by more than 90%.

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