



# Performance of ceramic nanofiltration membrane for desalination of dye solutions containing NaCl and Na<sub>2</sub>SO<sub>4</sub>

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## HIGHLIGHTS

- Ceramic nanofiltration membrane was used for desalination of dye solutions containing NaCl and Na<sub>2</sub>SO<sub>4</sub>.
- Dye EBT solutions with mixture of salts showed higher flux than that with single salt.
- Self-aggregation and salting-out due to decrease of zeta potential of dye were responsible for the high rejection of EBT.
- Ceramic nanofiltration membrane showed better separation performance compared with DK and DL membranes.

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## ABSTRACT

Removing mixture salts from dye solutions using membrane technology still need to be improved for high dye rejection and low salt rejection. In this work, ceramic membrane with pore size of 1.5 nm presented a satisfactory desalination of dye solutions containing NaCl and Na<sub>2</sub>SO<sub>4</sub> compared with two commercial organic nanofiltration membrane elements (DK and DL). Effect of salt content, salt type, molar ratio of NaCl and Na<sub>2</sub>SO<sub>4</sub>, dye concentration and pH on performance of ceramic membrane for desalination of Eriochrome black T (EBT) were investigated. The results showed that dye rejection decreased by increasing salt content, dye concentration and solution pH. Compared with dye–NaCl solutions, a relative high flux and low rejection of dye were observed when treating dye–Na<sub>2</sub>SO<sub>4</sub> solutions. For the mixture salt–dye solutions, the flux, which was higher than that for the single salt–dye solutions, first increased then decreased with decreasing  $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$  due to the change of structure of cake layer. Supper-molecule aggregates of EBT formed by hydrogen-bond is mainly responsible for the high rejection of EBT (>99%) at acid conditions. The rejection of NaCl and Na<sub>2</sub>SO<sub>4</sub> was below 20% and 40%, respectively. These promising results demonstrates that the new ceramic membrane has a potential application in dye purification.

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## 1. Introduction

Most dyes are produced by chemical synthesis which also produces byproduct salts (typical NaCl and Na<sub>2</sub>SO<sub>4</sub>) as impurities [1] due to salt-generation reactions, solution neutralization by acid/base or salt addition for promoting a chemical reaction [2,3]. To obtain the dye as a solid, it is common to add electrolyte (usually NaCl) to the dye solution in order to precipitate the dye, known as the salting-out process. However, the purity of the dye product is low and could contain salt as high as 30% [1,4]. This results in a product of much lower colour intensity relative to pure dye and varying dyeing characteristics [5].

Nanofiltration (NF) based process are widely used for dye desalting and purification as alternative separation techniques to the conventional salting-out processes [6]. Most of the commercially available NF membranes are made of polymeric materials and have high retention

of multivalent anions (e.g. sulfate) and organic molecules with molecular weights above 300 g/mol, and low retentions to most monovalent anions (e.g. chloride) [3,7], which are suitable for purification and concentration of dye products containing monovalent salts. For example, commercial DK (Osmonics) NF membrane was used for desalination and purification of reactive black 5 and 96.0% rejection of dye and 21.1% retention for salt (NaCl) were observed [8], but with high rejection of Na<sub>2</sub>SO<sub>4</sub> (>98%) [9].

With the development of ceramic membrane, more ceramic NF membranes are commercially available [10]. Several researches were focused on dye wastewater treatment and separation of dye and salt using ceramic NF and ultrafiltration (UF) membranes [11,12]. Ceramic membranes are made of a mixture of diverse mineral oxide (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>), and compared with polymeric membranes, they are characterized with the high thermal, chemical and mechanical resistance, outstanding separation characteristics and higher lifespan [13, 14]. More important, ceramic NF and UF membranes showed low rejection of NaCl and Na<sub>2</sub>SO<sub>4</sub> [15–17], showing great promises for

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desalination of dye. Majewska-Nowak et al. [18,19] studied the performance of three single-channel ceramic membranes (MWCO of 1 kDa, 15 kDa, and 50 kDa) for nine anionic organic dyes with molecular weights ranging from 327 to 1060 Da with or without salts. The results indicated that all the membranes provides 95–99% retention of high-molecular-weight organic dyes (>700 Da) without salt, while the membranes with MWCO of 15 kDa and 150 kDa showed a high rejection of Direct Black DB (>95%) with the presence of  $10 \text{ g} \cdot \text{L}^{-1}$  NaCl. Da et al. [11] prepared a tubular ceramic NF membrane with molecular weight cut-off of 800 Da for separation of fluorescent brightener and NaCl and the fluorescent brightener recovery of 99% was obtained while the NaCl removal was >98% at a temperature of  $60^\circ\text{C}$ .

Membrane performance was significantly affected by the dye-salt-membrane interaction in the membrane application for separation of dye and salt [12]. Several phenomenon including charge screening [20], change of aggregation state of dye [21,22], salting-out [23,24] and interaction between dye molecules and membrane [12] were reported in dye-salt-membrane system which influence the flux of membrane and rejection of solutes.

In this study, a tubular ceramic NF membrane was compared with two commercial spiral-wound organic NF membrane elements (DK and DL) for rejection of salts and six dyes with different molecular weight and charge. The effect of different solution environment (salt type, salt content, dye concentration, and pH) on the dye state and performance of ceramic membrane were discussed. The dye-salt-membrane interactions were discussed and their effect on membrane performance was investigated.

## 2. Materials and methods

### 2.1. Chemical and feed solutions

Four anion dyes Eriochrome black T (Shenyang Le Heng Technology Co., Ltd. (PRC)), Reactive brilliant blue KN-R (Shanghai Eighth Dyestuff Chemical Plant), Reactive black 5 (Zhejiang Runtu Co., Ltd. (PRC)) and Evercion red H-E7B (Everlight Chemical) and two cationic dyes Methylene blue (Aladdin) and Basic Green 4 (Aladdin) with different

molecular weight were used in this study as shown in Table 1.  $\lambda_{\text{max}}$  of dye was obtained with dye concentration in the range of Beer's law. NaCl of analytical grade was provided by Xilong Chemical Co., Ltd. (PRC).  $\text{Na}_2\text{SO}_4$  of analytical grade was supplied by Sinopharm Chemical Reagent Co., Ltd. (PRC). All the chemicals were used without further purification.

The feed solutions were prepared before each experiment by dissolving the corresponding solutes in pure water (conductivity under  $5 \mu\text{S} \cdot \text{cm}^{-1}$ ) until the desired concentration were reached. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust the pH of dye solutions.

### 2.2. Membranes

In this study, one multi-channel tubular ceramic membrane (length of 0.5 m, external diameter of 30 mm and 19 channels of 4.0 mm inner diameter) with pore size of 1.5 nm provided by Jiangsu Jiuwu High-tech Co. Ltd. (PRC) was used. The material of active layer and support of the membrane were  $\text{TiO}_2$  and  $\alpha\text{-Al}_2\text{O}_3$  respectively. The effective filtration area of membranes was  $0.1 \text{ m}^2$ . Two commercial organic spiral-wound membrane elements (DK1812 and DL1812, membrane area of  $0.38 \text{ m}^2$ ) were also used.

Water permeability of each membrane was measured at  $25^\circ\text{C}$  using pure water at a cross-flow velocity of 3 m/s before each experiment. The initial flux ( $J_w$ ) of membranes were measured at different operating pressures ( $\Delta P$  of 0.10, 0.15, 0.20, 0.25, 0.30 MPa for ceramic membrane,  $\Delta P$  of 0.40, 0.6, 0.8, 1.0, 1.2 MPa for DK and DL membranes). The pure water permeability was determined by Darcy's law [12] as follows:

$$J_w = L_p \cdot \Delta P = \Delta P / (\mu \cdot R_m) \quad (1)$$

where  $\mu$  is the water viscosity. The slope of the straight line  $J_w$  against  $\Delta P$  gives the pure water permeability coefficient ( $L_p$ ). The  $L_p$  of the five membranes were used to calculate the intrinsic membrane resistance ( $R_m$ ) according to Eq. (1). The permeability coefficient of the membranes were 63, 5.1, and  $6.9 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$  for ceramic membrane used in this study, DK and DL membranes, respectively.

**Table 1**  
Molecular structures and molecular weights of the organic dyes used in this study.

Dye	Molecular structure	Charge	MW (g/mol)	$\lambda_{\text{max}}$
Methylene blue		Positive	319.85	665
Eriochrome black T		Negative	461.38	533
Reactive Brilliant Blue KN-R		Negative	626.54	594
Basic Green 4		Positive	927.03	617
Reactive black 5		Negative	991.82	596
Evercion red H-E7B		Negative	1774.19	544

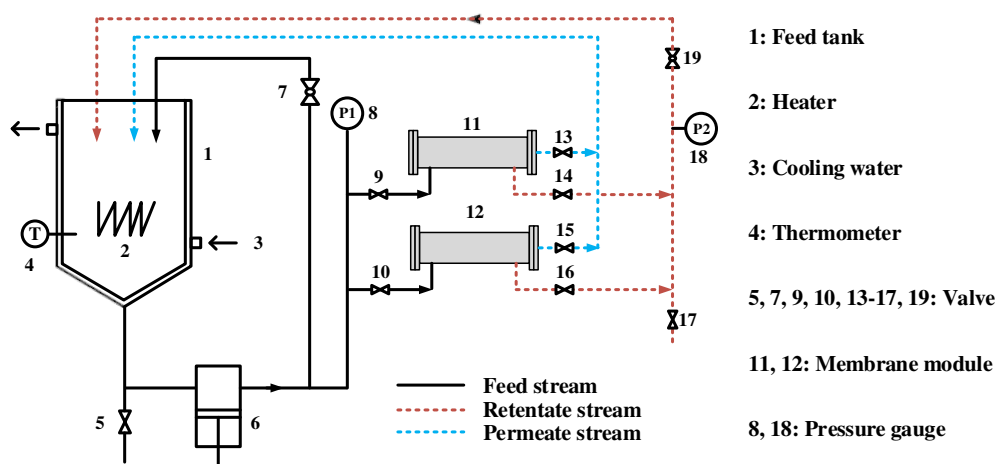


Fig. 1. Scheme of the NF pilot plant with spiral-wound membrane.

### 2.3. Filtration setup and experimental procedure

All experiments with ceramic and polymeric NF membranes were conducted with cross-flow membrane filtration system. The filtration set-up of tubular ceramic membrane was described in our previous work [25], and the experiment set-up for spiral-wound membrane (DK and DL) were as shown in Fig. 1.

All experiments were performed at constant temperature of 25 °C with recirculation mode. Both permeate and concentrate streams were recycled back to the feed tank except the sampled solution during the experiments. The cross-flow velocity of  $3 \text{ m} \cdot \text{s}^{-1}$  and transmembrane pressure (TMP) of 0.3 MPa were fixed for experiments of ceramic membrane, and for experiments of DK and DL membranes, the TMP of 0.30 MPa and flow rate of  $6.5 \text{ L} \cdot \text{min}^{-1}$  were used. The duration of all the experiments was 60 min.

After each filtration experiment, a cleaning procedure for ceramic membrane was performed in order to recover the performance of the membrane. Firstly, the membrane was rinsed with pure water for

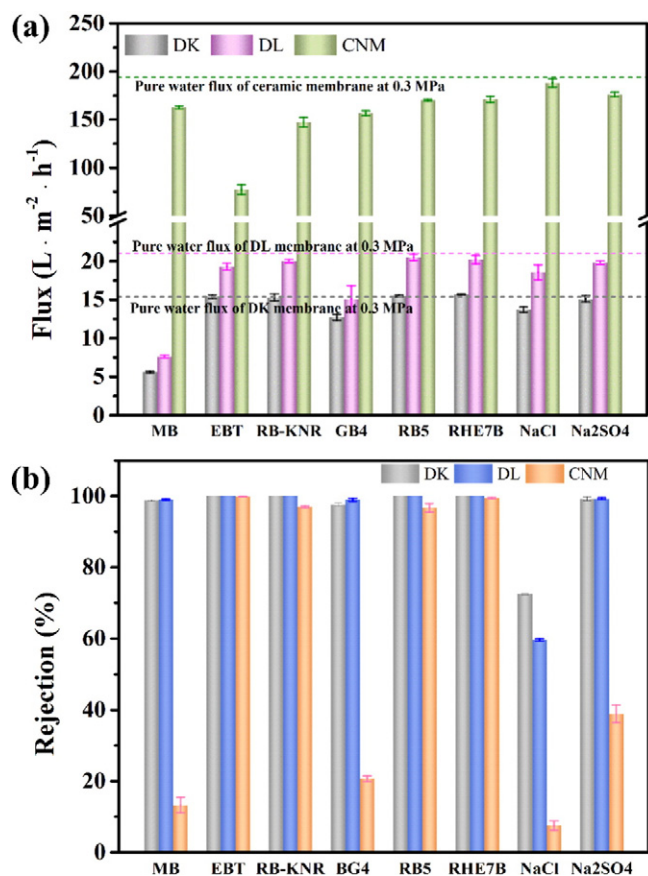


Fig. 2. Evolution of membrane flux (a) and rejection (b) for different pure dyes and salts. Conditions:  $C_{\text{dye}} = 500 \text{ mg} \cdot \text{L}^{-1}$ ,  $C_{\text{(NaCl or Na}_2\text{SO}_4)} = 1.0 \text{ g} \cdot \text{L}^{-1}$ , temperature = 25 °C, TMP = 0.3 MPa, CFV =  $3 \text{ m} \cdot \text{s}^{-1}$  for ceramic membrane and  $6.5 \text{ L} \cdot \text{min}^{-1}$  for DK and DL membranes.

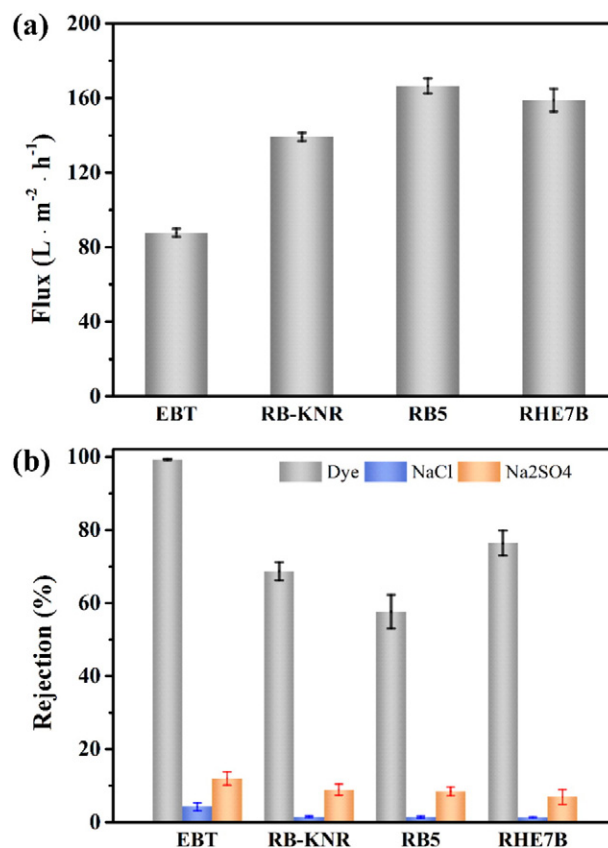


Fig. 3. Performance of ceramic membrane for dye-salt solutions. Conditions:  $C_{\text{(dye)}} = 500 \text{ mg} \cdot \text{L}^{-1}$ ,  $C_{\text{(NaCl)}} = 2.5 \text{ g} \cdot \text{L}^{-1}$  ( $0.0425 \text{ mol} \cdot \text{L}^{-1}$ ),  $C_{\text{(Na}_2\text{SO}_4)} = 6 \text{ g} \cdot \text{L}^{-1}$  ( $0.0425 \text{ mol} \cdot \text{L}^{-1}$ ), Temperature = 25 °C, TMP = 0.3 MPa and CFV =  $3 \text{ m} \cdot \text{s}^{-1}$ .

10 min with a crossflow velocity of  $3 \text{ m} \cdot \text{s}^{-1}$ , temperature of  $25^\circ\text{C}$  and atmospheric pressure in order to remove the reversible foulants. Secondly, pure water flux measurements were performed in order to check the fouled membrane permeability. Subsequently, a chemical cleaning was performed. The first step was a basic cleaning with a NaOH solution ( $\text{pH} = 10\text{--}11$ ) for 10 min at room temperature with a CFV of  $3 \text{ m} \cdot \text{s}^{-1}$  and TMP of 0.5 bar. It was followed by a rinse with pure water until  $\text{pH} 7$  was achieved. The membrane was subsequently rinsed by hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solution (0.5 (v/v) %) at room temperature for 20–60 min based on the degree of fouling and finally it was rinsed again with pure water until  $\text{pH} 7$  was obtained. After the above cleaning procedure, the membrane permeability was reevaluated to determine the initial permeability recovery. For DK and DL membranes, after each experiment, the membranes were rinsed with pure water for 30 min at a flow rate of  $6.5 \text{ L} \cdot \text{min}^{-1}$ , temperature of  $25^\circ\text{C}$ , and atmospheric pressure to remove the foulants, then the pure water flux was tested. If the membrane permeability was not recovered, a basic cleaning solution with  $\text{pH}$  of 10–11 was used to rinse the membrane for 20 min and then the membranes were rinsed with pure water until  $\text{pH}$  of 7. The membrane permeability was then reevaluated.

#### 2.4. Analytical methods

The permeate flux was calculated by Eq. (2) as follow:

$$J_p = V / (A \cdot t) \quad (2)$$

where  $J_p$  is the permeate flux ( $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ),  $V$  is the volume of permeate (L),  $A$  is the effective area of the membrane ( $\text{m}^2$ ), and  $t$  is the permeate collection time (h).

The rejection of dye, NaCl and  $\text{Na}_2\text{SO}_4$ ,  $R$ , is defined by Eq. (3):

$$R(\%) = (1 - C_p / C_f) \cdot 100 \quad (3)$$

where  $C_p$  is the concentration of the permeate and  $C_f$  is the concentration of the retentate.

Orion AquaMate 7000 VIS Spectrophotometer (Thermo Scientific) was used for the measurement of the dye concentration of permeate and retentate at the maximum absorbance wavelength. Before testing the dye samples, the samples were diluted and checked the  $\lambda_{\text{max}}$ . The concentration of NaCl and  $\text{Na}_2\text{SO}_4$  was measured with ion chromatography (ICS-2000, Dionex, USA).  $\text{pH}$  of feed solution was measured using automatic potentiometric titrator (ZDJ-4A, Rex Electric Chemical, China).

#### 2.5. Ionic strength

The ionic strength ( $I$ ) of the aqueous phase empirically estimates the level of interactions between ions [26] and is calculated as in Eq. (4):

$$I = \frac{1}{2} \sum C_i Z_i^2 \quad (4)$$

where  $Z_i$  is the valence of ion  $i$ , and  $C_i$  is the concentration of ion  $i$ .

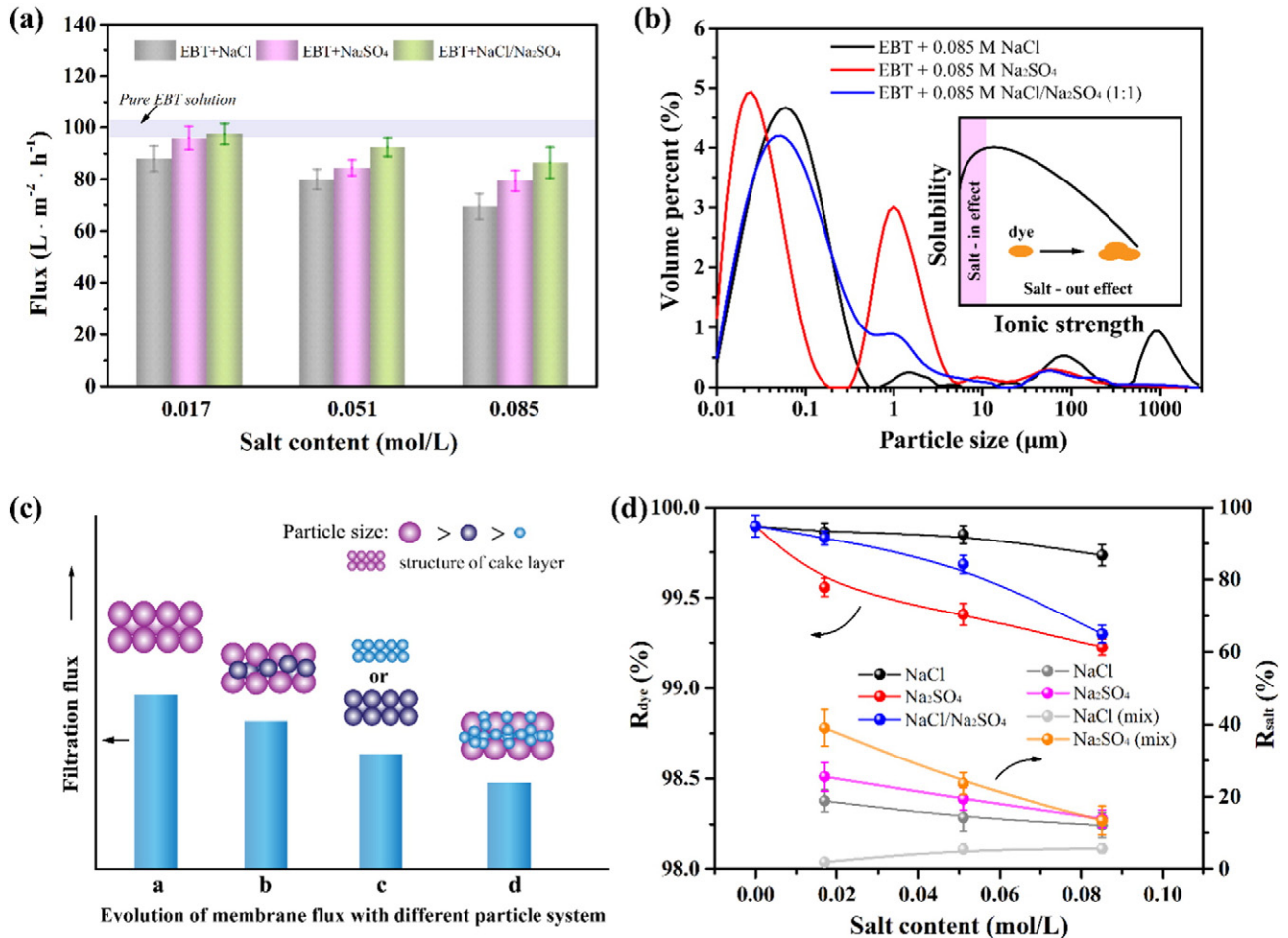


Fig. 4. Evolution of flux (a) and rejection of dye and salt (b), (b) particle size distribution of feed solution, (c) evolution of filtration flux over time with different particles size [28–31]. Conditions: TMP = 0.30 MPa, CFV =  $3 \text{ m} \cdot \text{s}^{-1}$ , temperature =  $25^\circ\text{C}$ , and CEBT =  $500 \text{ mg} \cdot \text{L}^{-1}$  with ceramic membrane.



### 3. Results and discussion

#### 3.1. Membrane performance for different pure dyes and salts

The membranes (DK, DL and ceramic NF membrane) were evaluated using different pure dye and salt solutions. As shown in Fig. 2, six dyes with different molecular weights (from 300 to 1800 Da) and charge were used in this study. It is evident from Fig. 2 (a) that the ceramic membrane showed a high flux compared with organic NF membranes (DK and DL). The properties of polymeric nanofiltration membranes

lie between those of non-porous RO membranes (where transport is governed by a solution-diffusion mechanism) and porous ultrafiltration (UF) membranes (where separation is usually assumed to be due to size exclusion and, in some cases, charge effects) [27]. For ceramic nanofiltration membranes, size exclusion and charge effects were the main separation mechanism and there was not the process of solution-diffusion compared with polymeric nanofiltration membranes. So the flux of ceramic nanofiltration membranes was higher than polymeric nanofiltration membranes. Compared with the ceramic membrane, DK and DL membranes are more negatively charged. When treating

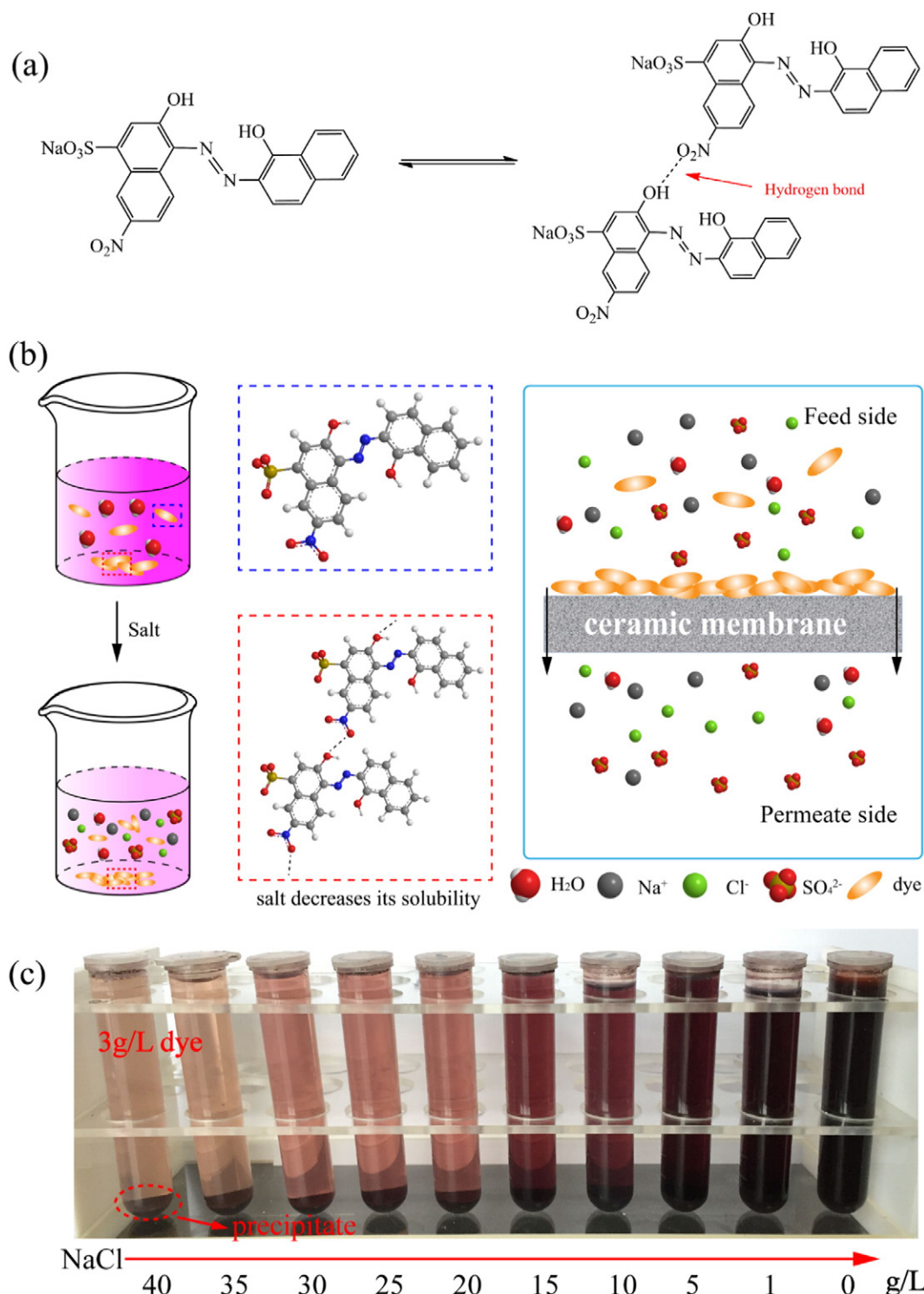
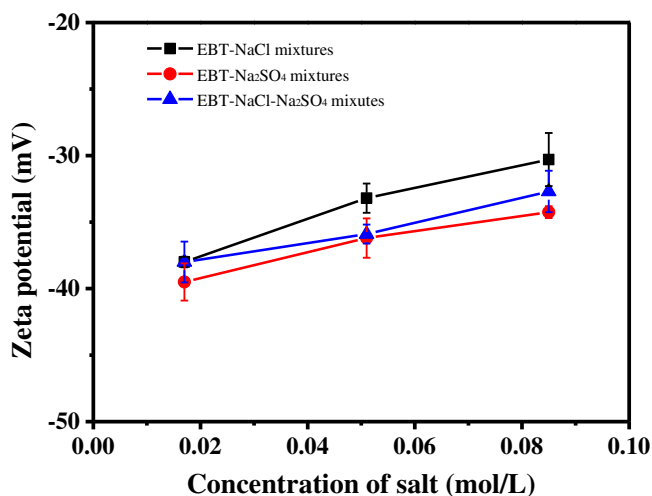


Fig. 5. (a) interaction of EBT molecule in aqueous, (b) diagram of EBT-salt interaction and filtration mechanism, (c) feed solution state with presence of salt after standing for 48 h.



**Fig. 6.** Evolution of dye particles zeta potential with different concentration of salt and a fixed EBT concentration of  $50 \text{ mg} \cdot \text{L}^{-1}$ . In the EBT-NaCl- $\text{Na}_2\text{SO}_4$  mixture, the  $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4} = 1$ .

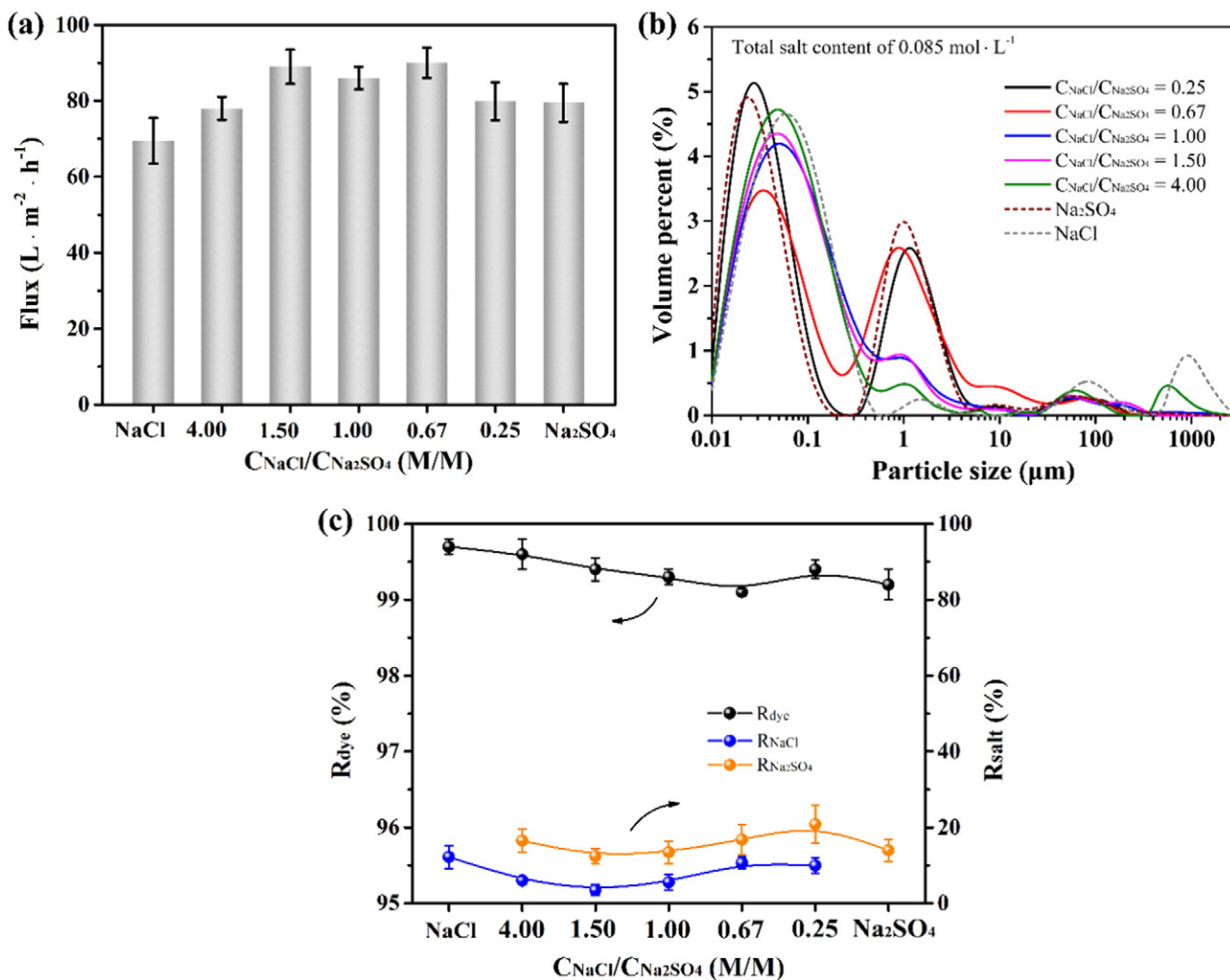
anion dyes (EBT, RB-KNR, RB5, and RHE7B), Fig. 2 (a) showed that flux of DK and DL membranes were close to the pure water flux, indicating a better antifouling property due to the electrostatic repulsion. But when treating cation dyes (MB and GB4), membrane fouling was severe for

DK and DL membranes. The flux of DK and DL membranes decreased by 63.6% and 63.7% for dye MB respectively, and 17.5% and 28.1% for GB4, respectively. For ceramic membrane, the flux decline was 16.6% and 19.7% for dye MB and GB4, respectively.

Considering the rejection of dyes and salts, Fig. 2 (b) shows that DK and DL membrane had a high rejection for all dyes studied (100% for anion dyes, >97% for cation dyes), while the ceramic membrane reject >96.8% anion dyes studied but <20% of cation dyes (MB and GB4). For rejection of salts, DK and DL membranes showed a >60% rejection of NaCl and >98% rejection of  $\text{Na}_2\text{SO}_4$ , compared to 7% and 39% of the ceramic membrane. The results show that the commercial NF DK and DL membranes were suitable for removing NaCl from anion dye solutions due to the severe membrane fouling when desalination of cation dyes and high rejection of  $\text{Na}_2\text{SO}_4$ . On the other hand, the ceramic membrane showed a promising application in removing both NaCl and  $\text{Na}_2\text{SO}_4$  in a single membrane separation step for dye solutions and a high flux compared with DK and DL membranes.

### 3.2. Performance of ceramic membrane for dye-salt solutions.

Fig. 3 presents the membrane performance of ceramic NF membrane for dye/salt mixtures. At all cases, the flux and dye rejection were lower than that of the pure dye solutions (Fig. 2), and rejection of NaCl and  $\text{Na}_2\text{SO}_4$  were kept below 5% and 10%, respectively. With presence of the salt in dye solutions, the shield of membrane charge and the more dispersion of dye [12] would make dye molecule aggregate on



**Fig. 7.** Evolution of flux (a), particle size distribution of feed solution with different ion environment (b), and rejection of dye and salt over  $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$  (c). Conditions: TMP = 0.30 MPa, CFV =  $3 \text{ m} \cdot \text{s}^{-1}$ , temperature =  $25^\circ\text{C}$ ,  $C_{\text{EBT}} = 500 \text{ mg} \cdot \text{L}^{-1}$  and salt content of  $0.085 \text{ mol} \cdot \text{L}^{-1}$  with ceramic membrane.

membrane surface easier and enter membrane pores and block the membrane pores, resulting in the decline of flux and dye rejection. Compared with the flux of pure dye solutions (Fig. 2(a)), the flux of dye-salt mixtures decreased by 13%, 5%, 2% and 7% for EBT, RB-KNR, RB5, and RHE7B, respectively (Fig. 3 (a)). Fig. 3 (b) shows that the rejection of EBT remained above 99% with presence of salt although a slight decline was observed (from 99.9% to 99.3%). On the other hand, the presence of salts has a significant effect on rejection of RB-KNR, RB5 and RHE7B where the rejection decreased from 97.1% to 68.7% for RB-KNR, 96.8% to 57.6% for RB5, and 99.5% to 76.4% for RHE7B (Figs. 2(b) and 3(b)). This phenomenon was also observed by E. Alventosa-deLara, et al. [12] who studied membrane performance of ultrafiltration ceramic membrane for treatment of model dye wastewater containing dye RB5 and salt NaCl. Due to the high rejection of EBT and low rejection of NaCl and Na<sub>2</sub>SO<sub>4</sub> of ceramic membrane, the dye EBT was further studied in the following sections.

### 3.3. Effect of salt concentration and types on performance of ceramic membrane

To study the effect of salt content on performance of ceramic membrane, inorganic salt NaCl and Na<sub>2</sub>SO<sub>4</sub> were used in this experiment. The influence of NaCl, Na<sub>2</sub>SO<sub>4</sub> and the mixture of NaCl and Na<sub>2</sub>SO<sub>4</sub> (molar ratio of 1) on permeate flux and rejection of dye and salt were investigated respectively with a fixed EBT concentration of 500 mg·L<sup>-1</sup> as shown in Fig. 4. It was evident from Fig. 4 (a) and (d) that the presence of salts in the dye solution significantly aggravated the membrane performance that both permeate flux and dye rejection decreased with increasing salt content. For the same dye-salt solution, the flux, dye and salt rejection all decreased with increasing salt content. Comparing different dye-salt solutions indicates that the dye solutions with mixture salt of NaCl and Na<sub>2</sub>SO<sub>4</sub> have the highest flux, followed by dye solutions with Na<sub>2</sub>SO<sub>4</sub> and dye solutions with NaCl.

The dye rejection decreased with increasing ionic strength as shown in Fig. 4 (d). This is because the higher ionic strength would shield the free charge of membrane, resulting in more dye molecules passing through the membrane thus decreasing the dye rejection [32]. Also, the salt ions would couple with the charged dye molecules, dispersing them more uniformly [21]. Thus, the dye particles may pass through the membrane easily, decreasing its dye rejection. Apart from that, the salt rejection decreased with increasing salt content due to the increased concentration gradient across the membrane. The rejection of NaCl and Na<sub>2</sub>SO<sub>4</sub> was below 20% and 40%, respectively.

As shown in Fig. 4 (a), flux decreased with increasing ionic strength for the same dye-salt mixtures system. For different dye-salt mixtures, the ionic strength sequence was  $I_{\text{NaCl}} < I_{\text{mixture of NaCl and Na}_2\text{SO}_4} < I_{\text{Na}_2\text{SO}_4}$  with the same total salt molar concentration and the flux increased first then decreased with increasing ionic strength. Alventosa-delara et al. [12] reported that the charge screening of membrane and more dispersion of dye molecules in presence of salt resulted in higher adsorption of dye particles into the membrane pore walls due to the greater passage of dye particles through membrane, leading to the decrease in the effective pore size and therefore reduced flux. Wang et al. [21] noted that any concentration polarization and membrane fouling would be reduced due to the increase of dye dispersion in the presence of salt and an increase of flux with increasing feed salt was observed when treating mixtures of congo red and NaCl. Apparently, the flux change caused by ionic strength when comparing different dye-salt mixtures was not consistent with results reported by Alventosa-delara et al. [12] and Wang et al. [21]. Besides, considering the low molecule weight of EBT in relation to the MWCO of the membrane and the high rejection of dye (>99%), aggregation of dye and salting-out phenomenon may be responsible for the change of flux and high rejection of dye.

The phenomena that the ionic organic dye molecules tend to aggregate in aqueous solution has been long known [33,34]. This behavior are

generally interpreted as being due to the formation of dimers and higher order aggregates [35], being attributed to van der Waals forces, ion-dipole and dipole-dipole interactions, and dispersion forces arising from delocalized  $\pi$  electrons [36]. The main factors influencing the strength of the dye molecular aggregation was the dye concentration and structure, temperature, solvent and electrolyte concentration [37, 38]. The aggregation of ionic dyes in aqueous solution can be enhanced by decreasing temperature, increasing dye concentration, or adding inorganic salts or certain substrates to the dye solution [39,40], which results in a more serious fouling and therefore the flux was decreased. Besides, the dye would even dissolve out from the solution when salt concentration is high, which is called salting-out phenomenon and it is significantly affected by salt type, salt concentration and dye concentration [23,24]. And enhancement of dye aggregation and salting-out phenomenon due to presence of high concentration of inorganic salt was attributed to decrease of dye particles zeta potential as shown in Fig. 6. As shown in Fig. 6, with increasing concentration of salt, the zeta potential of dye particles decreased. And the decreased zeta potential of dye particles would make dye particles easier to approach and aggregate. This is also the main reason for the salting-out phenomenon.

As shown in Fig. 5 (a), the EBT molecules form super-molecular aggregates in aqueous due to the hydrogen-bond between molecules and this phenomenon is enhanced when pH < 6.3 [41]. For different salt ion, Voet [42] reported that the influence of cation and anions on aggregations was attributed to the effect of salt on hydrophobic interactions, and put forward lyotropic numbers for different ions ( $T$  values for cations and  $N$  values for anions). Relatively large  $T$  values and small  $N$  values correspond to a large hydrophobic effect and favour dye

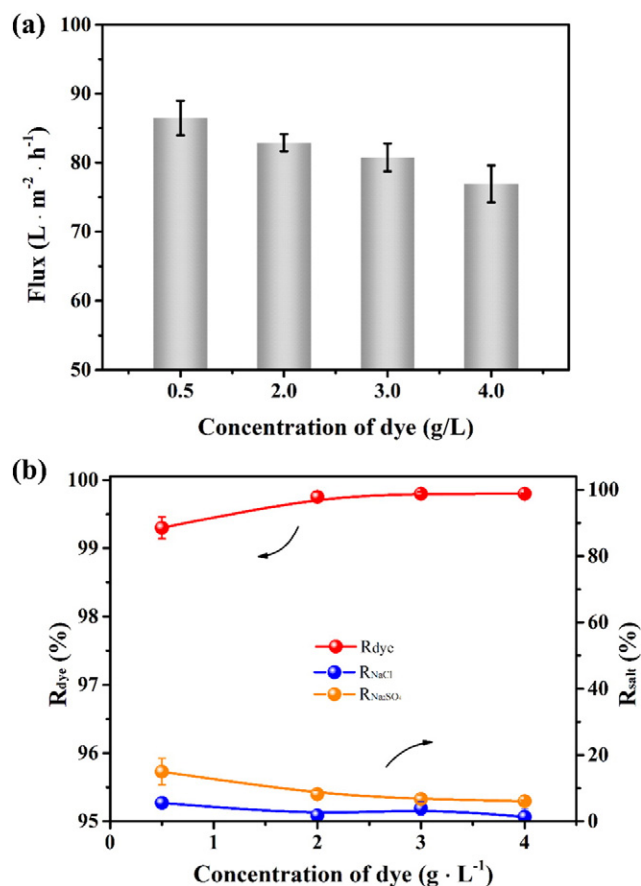


Fig. 8. Evolution of flux (a), resistance contribution on flux decline (b), and rejection of dye and salt over concentration of dye EBT. Conditions: TMP = 0.30 MPa, CFV = 3 m·s<sup>-1</sup>, temperature = 25 °C, C<sub>NaCl</sub> = 0.0425 mol·L<sup>-1</sup>, C<sub>Na<sub>2</sub>SO<sub>4</sub></sub> = 0.0425 mol·L<sup>-1</sup> with ceramic membrane.



aggregation. The results showed that  $\text{SO}_4^{2-}$  ( $N = 2$ ) is more effective on dye aggregation than  $\text{Cl}^-$  ( $N = 10$ ).

The pH of feed solutions in these experiments was in the range of 4–5. As shown in Fig. 5 (b), the EBT molecules in aqueous solution with pH of 4–5 aggregated severely to form dye particles. This was the reason to why the membrane showed a high rejection of EBT (shown in Fig. 5 (d)). When salt was present in EBT solutions, due to the salting-out effect, the solubility of dye particles decreased to form bigger particles and may even precipitate out from the solutions as shown in Fig. 5 (c), maintaining the high rejection of dye. With increasing NaCl content, more dye particles were precipitated on the bottom of sampling tube after standing for 48 h. But the dye molecules and small dye particles in aqueous could pass through the membrane easily, and due to the enhancement of charge screening of membrane with increasing ionic strength, the dye rejection was decreased slightly.

As shown in Fig. 4 (b), the different ionic environment in dye solutions resulted in the different dye particles size distribution. This phenomenon may be responsible for the change of flux of different salt-dye solutions because the dye particles size distribution affects the structure of cake layer directly which was related to the flux. As presented in Fig. 4 (c), many studies [28,30,31] have reported that flux increased with increase in particle size for monodispersed suspensions due to the higher porosity of cake layer formed by the larger particles. The deposit layer on the membrane surface consisting of spheres of varying size will normally have a smaller porosity than one consisting of spheres of a single size [29]. Fig. 4 (b) shows the dye particles size distribution of three dye-salt solutions with the same total molar concentration of salt. It was clear that the dye solution with  $0.085 \text{ mol} \cdot \text{L}^{-1}$

NaCl (with the lowest ionic strength) showed a multimodal distribution of dye particles. With increasing ionic strength ( $I_{\text{NaCl}} < I_{\text{mix}} < I_{\text{Na}_2\text{SO}_4}$ ), dye particles size distribution tend to show a bimodal distribution rather than a multimodal distribution. As shown in Fig. 4 (a), the multimodal distribution of dye particles (dye solution with  $0.085 \text{ mol} \cdot \text{L}^{-1}$  NaCl) resulted in the lowest flux. Compared with the dye particles size distribution of dye solution with presence of  $0.085 \text{ mol} \cdot \text{L}^{-1}$  mixture salt, the  $0.085 \text{ mol} \cdot \text{L}^{-1}$   $\text{Na}_2\text{SO}_4$  (with the highest ionic strength) caused the dye particles to be smaller, forming more compact cake layer and resulting in a relative low flux.

### 3.4. Effect of $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$ on performance of ceramic membrane

Effect of the molar concentration rate of NaCl and  $\text{Na}_2\text{SO}_4$  ( $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$ ) on permeate flux and rejection of dye and salt with total molar concentration of  $0.085 \text{ mol} \cdot \text{L}^{-1}$  of salt was investigated as shown in Fig. 7. From Fig. 7 (a), it was clearly shown that the ratio of  $C_{\text{NaCl}}$  and  $C_{\text{Na}_2\text{SO}_4}$  had a significant effect on flux. When  $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$  was above 1, flux increased with increasing concentration of  $\text{Na}_2\text{SO}_4$ , but when  $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$  was below 1, increasing concentration of  $\text{Na}_2\text{SO}_4$  aggravated the flux. This phenomenon may be attributed to the change of the size distribution of dye particles with different ionic environment as shown Fig. 7 (b), which directly affected the structure of the cake layer. In dye solution with mixture of NaCl and  $\text{Na}_2\text{SO}_4$ , dye particles size distribution changed from a multimodal distribution to a bimodal distribution with decreasing  $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$  when  $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$  was above 1, resulting in the flux improvement. When  $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$  was below 1, the apparent bimodal distribution of dye particles was observed and with decreasing  $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$ , the dye particles became smaller, and the amount of small dye particles increased which decrease the flux. These results were consistent with the results of Chang et al. [29] and Fred et al. [43] (More particles with different size and smaller particles size in suspension result in lower flux). Considering the membrane separation performance, the dye rejection had a slight decrease with decreasing  $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$  (increasing ionic strength) due to the charge screening effect and more dispersion of the dye molecules [21,32]. The rejection of NaCl and  $\text{Na}_2\text{SO}_4$  were below 20%, and the rejection of  $\text{Na}_2\text{SO}_4$  was higher than that of NaCl due to steric effect.

### 3.5. Effect of dye concentration on performance of ceramic membrane

The effect of dye concentration on membrane performance was also investigated as shown in Fig. 8. It was clear from Fig. 8 (a), as expected, that the flux decreased when the dye concentration was increased. Flux decline is known to be caused by the concentration polarization phenomenon and by the deposition of particles within the membrane pores or onto its external surface, forming a cake layer which increases the filtration resistance [12]. The fouling layer is an additional resistive layer to the permeate of dyes [4] and the enhanced dye aggregation with increasing dye concentration [35,37] increased the dye rejection (Fig. 8 (b)).

Fig. 8 (b) illustrates the rejection of dye and salts with different dye concentration. It was clear from the Fig. 8 (b) that dye rejection had no obvious change (all above 99.3%) with a slight increasing trend. The increase of dye concentration would increase the possibility of aggregation of dye, and the aggravation of membrane fouling acted as an additional layer prevents the dye from passing through membrane. These may be the reason for the high rejection of dye and the increasing trend. Fig. 8 (b) also shows that salt rejection decreased with increasing dye concentration. This was because when charged solute (dye) was present, the accumulation of dye molecules near membrane surface would result in the charge screening of membrane, thus decreasing the rejection of salt. It was previously reported that the NaCl retention decreased greatly when charged solute (glutamic acid) was added, but neutral solute (glucose) did not affect the NaCl retention [44].

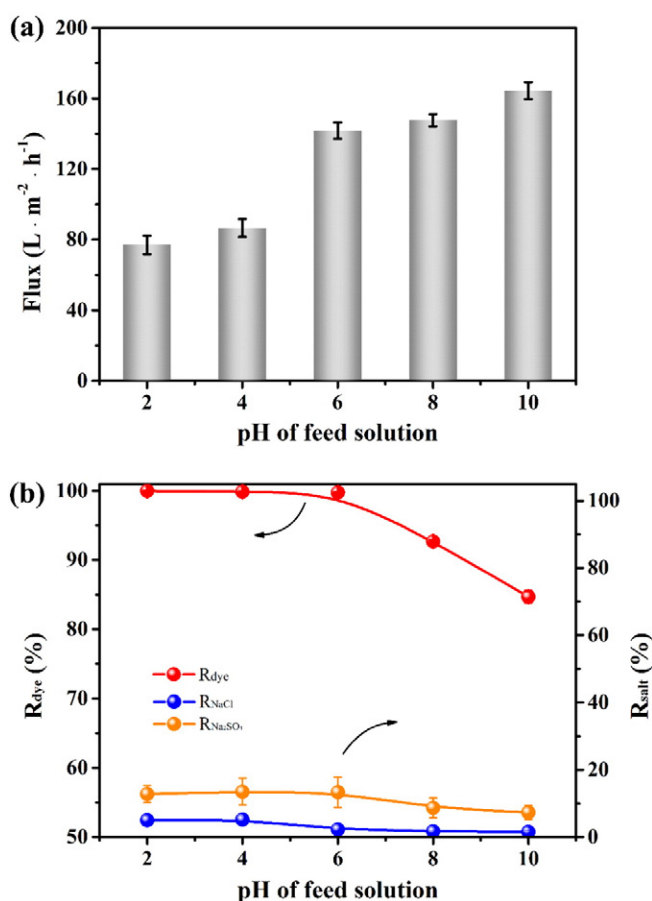


Fig. 9. Evolution of flux (a) and rejection of dye and salt (b) over pH of feed solution. Conditions: TMP = 0.30 MPa, CFV =  $3 \text{ m} \cdot \text{s}^{-1}$ , temperature =  $25^\circ \text{C}$ ,  $C_{\text{EBT}} = 500 \text{ mg} \cdot \text{L}^{-1}$ ,  $C_{\text{NaCl}} = 0.0425 \text{ mol} \cdot \text{L}^{-1}$ , and  $C_{\text{Na}_2\text{SO}_4} = 0.0425 \text{ mol} \cdot \text{L}^{-1}$  with ceramic membrane.



### 3.6. Effect of solution pH on performance of ceramic membrane

In this study, the effect of pH of feed solution on membrane performance was investigated. It is shown from Fig. 9 that the pH of the feed solution has a significant influence on the membrane performance. The flux increased (Fig. 9 (a)) and dye rejection decreased (Fig. 9 (b)) noticeably with increasing pH of feed solutions. The point where the pH was 6 was a transitional region where flux and dye rejection changed evidently. The change of surface charge of membrane and dye state at different pH of feed solution may be responsible for the evolution of flux and rejection.

For ceramic membrane used in these experiments, made of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ , the isoelectric point (IEP, where membrane surface dose not present electrical charge) of membrane is around 6 [45]. The membrane surface is positively charged when  $\text{pH} < \text{IEP}$  and negatively charged when  $\text{pH} > \text{IEP}$  [12]. The dye, EBT, used in this study is shown to have functional group with negative charge as shown in Table 1. When pH is below 6, electrostatic attraction between dye molecules and membrane surface results in the accumulation of dye on the membrane surface, aggravating the membrane fouling and decreasing flux and dye rejection. When pH is above 6, electrostatic repulsion between dye molecules and membrane surface decreases the concentration of dye on membrane surface, alleviating membrane fouling and increasing dye rejection. However, the dye rejection decreased when pH was above 6 (Fig. 9 (b)), indicating that the electrostatic interaction mechanism is not the sole reason to the change of dye rejection.

The dye rejection was above 99% when pH was below 6, and a sharp decline (to 85%) was observed when pH increased from 6 to 10. The degree of aggregation of dye molecules at different pH may be responsible for this. In the work of Xie et al. [41], the aggregation of EBT was aggravated when pH was below 6.3. When pH was above 6.3, the dye molecules aggregation was weakened, resulting in smaller dye particles size. Therefore, the dye rejection was decreased due to the passage of smaller dye particles through membrane. The enhancement of dye dispersion when pH was above 6.3 alleviated the concentration polarization and membrane fouling, leading to the increase in the flux at high pH.

## 4. Conclusions

A ceramic nanofiltration (NF) membrane with MWCO of 900 Da and two commercial NF DK and DL membranes were used in this study for desalination of dye solutions and ceramic NF membrane showed be suitable for desalination of dye solutions containing NaCl and  $\text{Na}_2\text{SO}_4$  simultaneously due to the satisfactory dye rejection and low rejection of both NaCl and  $\text{Na}_2\text{SO}_4$ . The effect of salt content and type,  $C_{\text{NaCl}}/C_{\text{Na}_2\text{SO}_4}$ , dye concentration, and pH of solution on performance of ceramic NF for desalination of dye EBT was studied. The aggregation of dye EBT in aqueous was affected by solution environment (ionic type and concentration, dye concentration and pH) and dye solution showed different particle size distribution. The results revealed that rejection of dye EBT was dominated by the steric effect due to the aggregation of dye molecule. Flux and dye rejection was decreased with increasing salt content, dye concentration and flux increased and dye rejection decreased with increasing pH of solution. The dye solution with mixture of NaCl and  $\text{Na}_2\text{SO}_4$  showed a higher flux than single salt. Dye rejection was all above 99% when pH was below 6 and rejection of NaCl and  $\text{Na}_2\text{SO}_4$  were below 20% and 40%, respectively.

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