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Treatment of ammonia nitrogen wastewater by membrane distillation using PVDF membranes

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ABSTRACT

Three operation technologies based on PVDF membranes including membrane contactor (MC), direct contact membrane distillation with pure water as permeate solution (DCMD), reaction direct contact membrane distillation with sulfuric acid solution as permeate solution (RDCMD) were tested for ammonia removal from water. The effects of feed run parameters (temperature, pH, initial concentration and velocity) and permeate temperature on the ammonia removal rate, mass transfer coefficient and selectivity in RDCMD process were investigated in detail. Results showed that, comparing with MC and DCMD, RDCMD performed the highest ammonia removal efficiency and mass transfer coefficient. In RDCMD, feed pH value was proved to be the most dominant factor, when the pH value increased from 9 to 11, mass transfer coefficient increased noticeably from 0.54×10^{-5} m s^{-1} to 2.2×10^{-5} m s^{-1} and selectivity increased from 1.73 to 6.95, respectively, but with the further increase of pH from 11 to 13, mass transfer coefficient and selectivity increased slightly. Increasing feed temperature could lead to higher ammonia mass transfer coefficient but lower selectivity. Permeate temperature was in favour of the selectivity, but had no remarkable effect on mass transfer coefficient. Feed velocity and initial concentration had a negligible influence on mass transfer coefficient and selectivity. A laboratory scale application of RDMCD was carried for 0.50 mol L^{-1} ammonia wastewater, after 4 h operation at optimal process conditions, 98.5% ammonia was removed, however, the membrane only was polluted a little and can be easily washed by deionized water. In addition, the PVDF membrane can maintain stable properties to resist 0.5 mol L^{-1} sulfuric acid solution, and is potential in the ammonia removal by RDCMD.

Keywords: Ammonia; Direct contact membrane distillation; PVDF membranes; Mass transfer coefficient; Selectivity

1. Introduction

It is well known that ammonia is a general pollutant in waste water, and that excessive ammonia in water leads to eutrophication, which often results in dissolved oxygen deficit and water pollution, thus influences self-purification of water and harms the living of aquatic animal. Some ammonia removal techniques have been applied, such as breakpoint chlorination [1,2], air stripping [3,4], ion-exchange [5,6] and conventional biological denitrogenation process [7,8]. However, these techniques remove ammonia from wastewater with relatively low efficiency but high cost, and removal rate cannot satisfy the increasing effluent criteria. Therefore, new and effective techniques need to be developed to improve efficiency of ammonia removal from wastewater.

In recent years, membrane separation technology has gained great attention in ammonia wastewater treatment,

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the removal of ammonia from wastewater was mainly by the membrane-based stripping processes. Comparing with traditional technologies in ammonia removal, the advantages of membrane separation technology are obvious, such as high efficiency, high removal rate, no secondary pollution of the water, etc. Membrane contact (MC) was the primary membrane-based stripping process that no temperature difference exists between the feed side and the permeate side. In such process, micro-porous hydrophobic membranes are selected as a barrier between liquid and gas, and the volatile components in the feed side diffuses across membrane pores and reacts with the receiving solution. This membrane-based stripping process provide fast ammonia removal efficiency due to the large surface area, which is often the key to any fast separation. MC process have been widely studied and conducted in the removal of many volatile components, including ammonia [9,10], sulfur dioxide [11], chloroform [12], toluene [13], and phenol [14]. In the fields of ammonia removal by MC, many researches had demonstrated that feed pH played an important role in ammonia removal efficiency while the feed flow rate and ammonia concentration had little effects on ammonia removal [15,16].

Although membrane distillation (MD) was firstly introduced as desalination technique to supply clean water, it also may be regarded as a membrane-based stripping separation process based on micro-porous hydrophobic membrane if it is used to remove volatile component from wastewater. In MD process, the volatile components are also driven across the membrane by its vapor pressure gradient between two sides of the membrane. However, different from MC process, MD process lies in the temperature difference between feed side and permeate side, which could intensify the vapor pressure gradient between two sides of membrane, so as to improve the removal efficiency and mass transfer coefficient of volatile component. Compared with conventional volatile component removal technologies, MD process provides many advantages in volatile component removal from wastewater, including complete rejection of nonvolatile components, lower operating temperature and pressures, small vapor space and easy combination with other technology [17,18].

MD has four configuration based on four different ways that the permeated species are carried out of the membrane module. Direct contact membrane distillation (DCMD) is one of the MD configurations, which the warm feed and the cold permeate are in direct contact with hydrophobic porous membrane, permeated components are carried out of the membrane module by cold permeate solution. This configuration is best suited for applications in different volatiles removal based on hydrophobic porous membrane, such as ammonia [19–21], sulfur dioxide [22], toluene [23] and phenol [24–26] et al. In the field of ammonia removal, DCMD had been studied and compared with vacuum membrane distillation and sweeping gas membrane distillation based on hydrophobic membrane. It was found that DCMD showed the highest selectivity. Among different hydrophobic membranes, larger pore size and less thickness membranes led a higher mass transfer coefficient and lower selectivity. As for operation parameters, the effects of pH and feed temperature on ammonia removal were more significant than that of velocity, permeate temperature and feed concentration [27–29]. As the dominant component of DCMD, the materials of hydrophobic membranes have a great influence on the performance of ammonia removal. Polytetrafluoroethylene (PTFE), propene polymer (PP) and polyvinylidene fluoride (PVDF) are three kinds of hydrophobic membranes that are mainly used in DCMD. Pores' shape of PTFE and PP membranes are like a stretched ellipse formed by the stretching method. PTFE and PP membranes have been studied comprehensively in DCMD for ammonia removal, and the mass transfer mechanism also has been investigated in detail [27,28]. As for PVDF membrane, there are two different preparation methods, including the sol-gel method and the thermally-induced phase method. And the membrane structure is corresponding to the membrane preparation method. Hollow fiber PVDF hydrophobic membrane made by sol-gel method has been studied by Qu et al in DCMD for ammonia removal [29], but the researches of PVDF membrane that made by thermally-induced phase method used for ammonia removal in DCMD was little. In this study, a kind of PVDF flat sheet hydrophobic membrane that prepared by thermally-induced phase method was selected for ammonia removal in DCMD, and the mass transfer mechanism was also investigated.

In this study, three operation processes based on PVDF flat sheet hydrophobic membranes including membrane contactor (MC), direct contact membrane distillation (DCMD), reaction direct contact membrane distillation (RDCMD) were tested for ammonia removal from wastewater. RDCMD is named for chemical reaction between ammonia and sulfuric acid existing in its process. The effect of different operating conditions (feed pH, feed temperature, permeate temperature, feed concentration and feed velocity) on mass transfer coefficient and selectivity were evaluated to analyze the RDCMD mass transfer mechanism. In addition, a laboratory scale application was carried to evaluate the practicability of RDMCD to high concentration ammonia wastewater and the change of membrane properties after the process.

2. Experimental

2.1. Membrane and membrane module

The membrane used in this study was the hydrophobic PVDF flat sheet membrane, which was provided by Millipore, and the characteristics were shown in Fig. 1 and Table 1. The membrane module was fabricated from chlorinated polyvinyl chloride material, with an active membrane area of 4.275×10^{-3} m^2 (0.095 × 0.045 m^2).

2.2. The flow sheet and equipments

The flow sheet of the direct contact membrane distillation was given in Fig. 2. The feed solution and permeate solution were driven by two magnetic pumps (MP-55RZM, Shanhai Xinxishan industrial Co, Ltd. China). A thermostatic bath (HHS, Shanghai Boxun industrial Co, Ltd. China) was used to heat feed solution, and a chiller (HWY-10, Shanghai Changji instrument Co, Ltd. China) was used to cool permeate solution. The feed circulation included the feed side of the membrane module, the feed tank and the

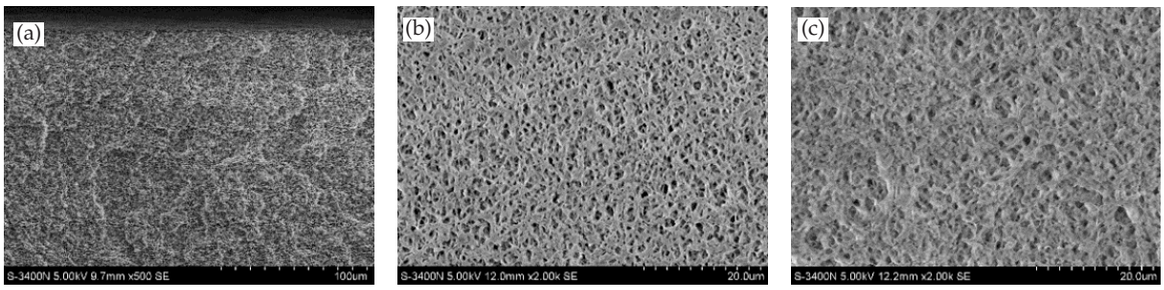

Fig. 1. Cross section (a), top surface (b) and bottom surface (c) morphology of PVDF flat sheet membrane.

Table 1
Properties of the PVDF membrane used in the experiments

Parameter	Value
Membrane thickness (mm)	0.223
Porosity(%)	75.30
Average pore radius (μm)	0.20
Contact angle θ (°)	122.6
LEPw (KPa)	252.5

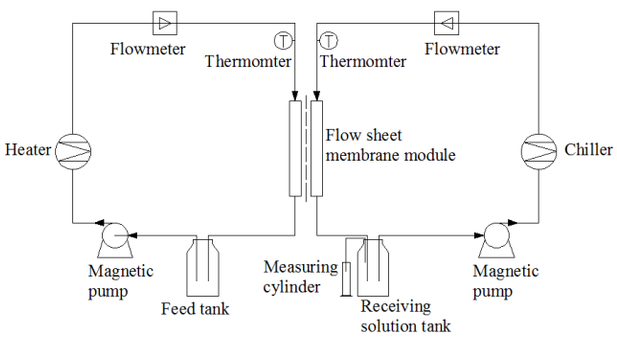

Fig. 2. Experimental flowsheet for ammonia removal.

coil in the thermostatic bath; the permeate solution circulation included the permeate side of the membrane module, the permeate solution tank and the coil in the chiller. There were two thermometers equipped on inlets of feed and permeate sides. Two flow meters were equipped on the feed and the permeate sides, respectively.

2.3. Experimental procedure

The feed solution was ammonia chloride solution, the permeate solution was de-ionized water or dilute sulfuric acid solution. Feed pH was adjusted by HCl or NaOH solution. To make sure there is no considerable leakage, a test was conducted with the corresponding feed solution flowing through the membrane module before DCMD process was started. One feed sample was taken from the feed tank every other 30 min; the sample concentration was analyzed by formaldehyde titration. The average permeate flux was measured by overflow volume of the permeate tank. The mass transfer coefficient (K_a) and selectivity (β) can be calculated by the obtained concentration and mass flux base on the follow equations [27].

$$\frac{JA}{F_f\left[1\text{-}\exp\left(-K_aA/F_f\right)\right]-JA}\ln\frac{c_0}{c_t}=-\ln\left(1-\frac{JAt}{V_0}\right) \quad (1)$$

$$\ln\frac{c_0}{c_t}=-(\beta-1)\ln\left(1-\frac{JAt}{V_0}\right) \quad (2)$$

2.4. Analysis method

The feed concentration was analysis by formaldehyde titration [30] base on follow reaction:

$$4NH_4^{+}+6HCHO=(CH_2)_6N_4+4H^{+}+6H_2O \quad (3)$$

The ammonium salts can react instantly and completely with formaldehyde to yield equimolecular acid. By adding excess formaldehyde in the sample solution that has been adjusted to neutral, the generated acid can be titrated by the solution of sodium hydroxide, with phenolphthalein as indicator. Therefore, the concentration of feed solution can be measured by the amount of sodium hydroxide consumed.

2.5 Membrane characterization

Different parameters (contact angle, membrane thickness, contact angle, mechanical properties, porosity and average pore size) of the PVDF membrane before and after a laboratory scale application experiment was characterize, respectively. The cross-sectional, top and bottom surface morphology of the membranes were observed using a scanning electron microscopy (S-3400N, HITACHT, Japan); The contact angle was measured by the contact angle meter (Shanghai Zhongchen Digital Technology Apparatus Co., Ltd., Shanghai, China); Membrane thickness was analyzed by a micrometer; Pore size measurement of the membranes was carried out by applying the ImageJ software on the top SEM image, approximately 200 pores were randomly selected from the top SEM image and the average value was reported. Porosity was analyzed based on Peng's study [31]. Three pieces of membranes were kept immersed in the butanol for 24 h, then

blotted, weighed and oven dried at 60°C for 24 h, followed by weighing again. The porosity was calculated using the followed equation: Ø(%) = $(m_1 - m_2)/\rho.A.l$, where Ø is the porosity (%), m_1 (g) is the weight of the wet membrane, m_2 (g) is the weight of the dry membrane, ρ (g L^{-1}) is the liquid density (butanol), A (m^2) is the effective surface area of the membrane, and l (m) is the membrane thickness. The liquid entry pressure of water (LEP_w) was measured using a using a laboratory setup, the membrane was place in a dead end equipment, the compressed nitrogen was used to apply pressure, the pressure at which water starts to be transported across the membrane was referred as (LEP_w) for a given membrane sample.

3. Results and discussion

3.1. Comparison of MC, DCMD and RDCMD

By investigating MC, DCMD and RDCMD for ammonia removal from wastewater in the same ammonia concentration of 0.06 mol L^{-1}, RDCMD process showed the highest ammonia removal rate and highest mass transfer coefficient in comparison with MC and DCMD in three hours' operation (Figs. 3, 4). Comparing with MC process, RDCMD is a non-isothermal separation process, and the ammonia partial pressure increased with the rise of ammonia solution temperature, which enhanced NH_3 diffusion from the feed solution to permeate side. Comparing with DCMD, the permeate solution of RDCMD is 0.5 mol L^{-1} sulfuric acid solution, so NH_3 that have transferred across PVDF membrane can react immediately with sulfuric acid to form non-volatile compound ($(NH_4)_2SO_4$). Those effects indicated that RDCMD possessed higher ammonia removal efficiency and mass transfer coefficient. However, the selectivity (β) of MC is much higher than that of DCMD and RDCMD (Fig. 4), which results from higher ammonia partial pressure than

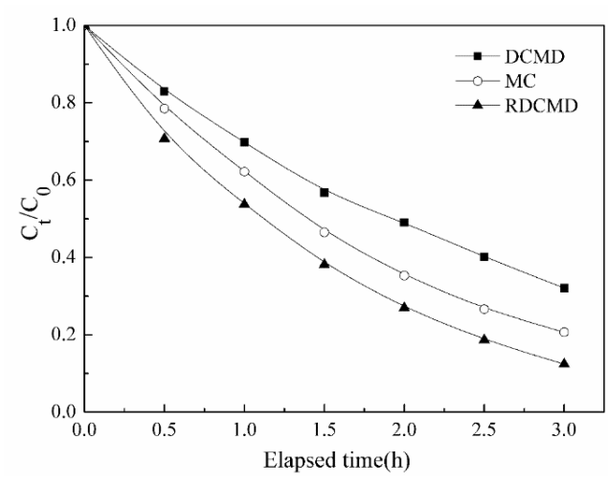

Fig. 3. Variation of feed ammonia concentration in MC, DCMD and RDCMD (MC: C_0 = 0.06 mol L^{-1}, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12; DCMD: C_0 = 0.06 mol L^{-1}, T_f = 53°C, T_p = 22°C, u_f = 0.73 m s^{-1}, up = 0.27 m s^{-1}, feed pH = 12; RDCMD: C_0 = 0.06 mol L^{-1}, T_f = 53°C, T_p = 22°C, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12).

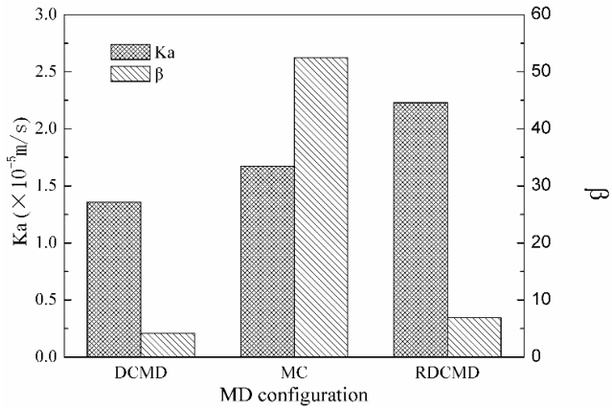

Fig. 4. Mass transfer coefficient and selectivity in MC, DCMD and RDCMD (MC: C_0 = 0.06 mol L^{-1}, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12; DCMD: C_0 = 0.06 mol L^{-1}, T_f = 53°C, T_p = 22°C, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12; RDCMD: C_0 = 0.06 mol L^{-1}, T_f = 53°C, T_p = 22°C, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12).

partial pressure of water vapor in the membrane surface of feed at ambient temperature, and with the increment of feed temperature, partial pressure of water vapor increase more quickly.

3.2. Effect of operating parameters in RDCMD process

3.2.1. Effect of the feed temperature

Increasing the feed temperature favored the ammonia removal (Fig. 5) and it was corresponding with change of mass transfer coefficient at different feed temperatures. It can be found that K_a increased from 1.62 × 10^{-5} m s^{-1} to 2.62 × 10^{-5} m s^{-1} when the feed temperature increased from 38°C to 60°C (Fig. 6). According to Henry's law, NH_3 concentration in membrane pores depends on Henry constant when feed is dilute solution, with the increase of feed temperature, Henry constant increased strongly, and this resulted to a higher NH_3 concentration in membrane. Ammonia has the dissociate equilibration in aqueous solution, because of the endothermic nature of dissociation of ammonium to ammonia, more ammonia was in the feed solution at higher feed temperature. So the higher feed temperature, the higher NH_3 concentration in membrane pores is, and also the higher mass transfer coefficient is. In addition, improving feed temperature can reduce viscosity of feed, so as to enhance NH_3 diffusion in the bulk solution, which resulted in a higher mass transfer coefficient (Fig. 6). Moreover, the average temperature within membrane pores increased with rise of feed temperature, higher diffusivity could be obtained under higher temperature within membrane pores. So hot feed is in favor of ammonia diffusion in membrane pores.

In spite of the positive effect of feed temperature on the transfer mass coefficient, negative effect on selectivity was observed (Fig. 6). Due to the rise of feed temperature from 38–60°C, water vapor partial pressure and diffusion coefficient increased, so the mass transfer of water vapor intensified, selectivity decreased from 12.83 to 6.27 (Fig. 6).

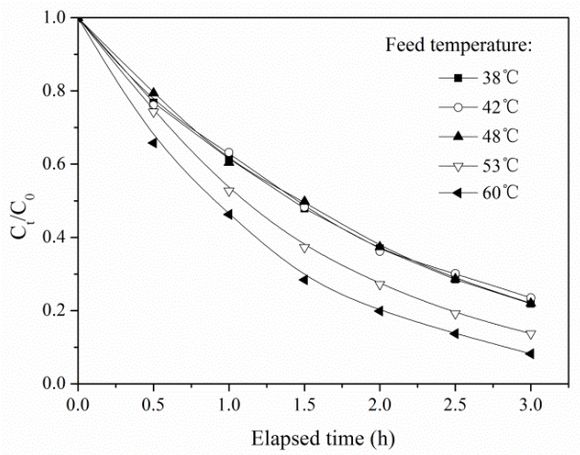

Fig. 5. Variation of feed ammonia concentration at different feed temperatures (C_0 = 0.06 mol L^{-1}, T_p = 22 °C, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12)

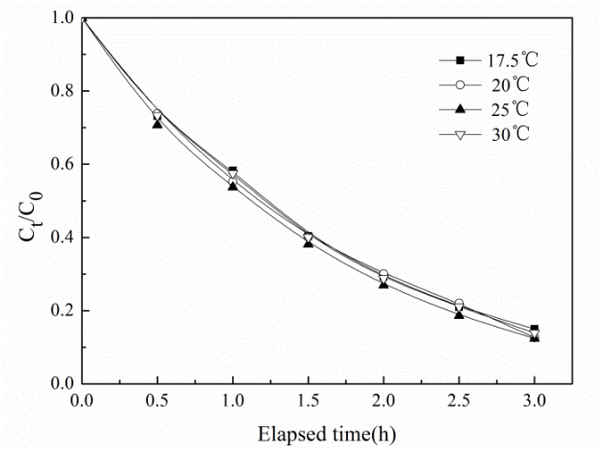

Fig. 7. Variation of feed ammonia concentration at different permeate temperatures (C_0 = 0.06 mol L^{-1}, T_f = 53 °C, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12)

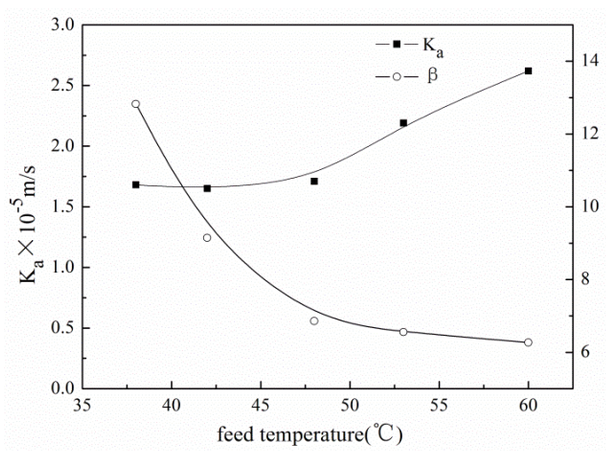

Fig. 6. Effect of feed temperature on ammonia mass transfer coefficient and selectivity (C_0 = 0.06 mol L^{-1}, T_p = 22 °C, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12)

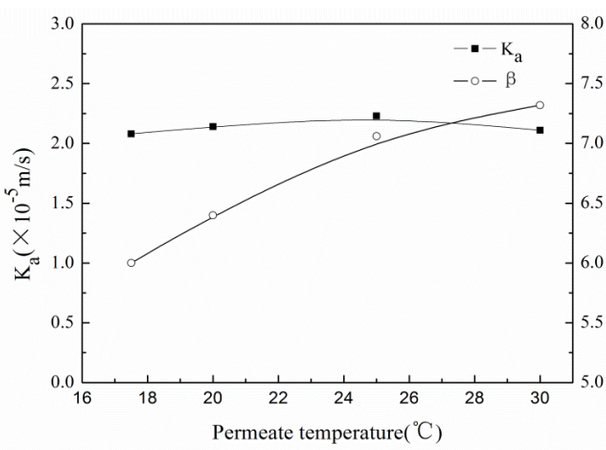

Fig. 8. Effect of permeate temperature on ammonia mass transfer coefficient and selectivity (C_0 = 0.06 mol L^{-1}, T_f = 53 °C, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12)

The negative effect of feed temperature on selectivity exceeded the positive influence of feed temperature on mass transfer coefficient within the range of operating temperature used. Therefore, to guarantee the efficient of ammonia removal, it isn't suitable to select higher temperature.

3.2.2. Effect of the permeate temperature

Permeate temperature has no remarkable influence on ammonia removal rates and over all transfer mass coefficient (Figs. 7, 8). The permeate temperature is lower than feed temperature in RDCMD process, so it is the feed temperature that dominates the membrane pores' temperature, and permeate temperature has little influence on ammonia diffusion in membrane pores. Additionally, permeate temperature can't influence the ammonia diffusion in feed bulk any more. But selectivity has slight increment with the raising of permeate temperature (Fig. 8). With the increase of permeate temperature, the temperature difference between feed and permeate side decreased, leading to a decrease of water vapor partial pressure difference; the transfer of water vapor decreased, leading to the slight increase of selectivity.

3.2.3. Effect of the feed pH

The effect of feed pH on mass transfer coefficient was attributed to the ammonia dissociate equilibration in aqueous solution, as shown by following Eq. (4).

$$NH_4^+ + OH^- = NH_3 + H_2O \tag{4}$$

The molecule of NH_3 can be directly transferred across the membrane, but NH_4^+ must react with hydroxide to form NH_3. Increasing pH value of the aqueous solution in the feed

is beneficial for hydroxide diffusion from the feed bulk to membrane surface, which makes the ammonia dissociation equilibration move towards NH_3 yield. The driving force of the ammonia transfer across the membrane is the ammonia partial pressure difference between two sides of the membrane, and the higher concentration of ammonia in the feed, the higher ammonia partial pressure in the feed side is. More NH_3 exists at the membrane interface of feed side when pH value is high, which results in higher driving force for ammonia transfer. With the increase of feed pH from 9 to 13, mass transfer coefficient increased from 0.54 ×10^{-5} m s^{-1} to 2.36 ×10^{-5} m s^{-1}, selectivity increased from 1.73 to 7.46 and ammonia removal efficiency increased from 21–92% (Figs. 9, 10), respectively. Obviously, when feed pH increased from 9 to 11, ammonia removal efficiency increased from 21–91%, mass transfer coefficient increased from 0.54 × 10^{-5} m s^{-1} to 2.2 × 10^{-5} m s^{-1} and selectivity increased from 1.73 to 7.32, respectively. However, ammonia removal efficiency increase from 91–92%, mass transfer coefficient increased from 2.2 × 10^{-5} m s^{-1} to 2.36 × 10^{-5} m s^{-1}, selectivity slightly increased from 7.32 to 7.46 with the rise of pH from 11 to 13, respectively (Figs. 9, 10), which due to the resistance caused by membrane would gradually dominate the mass transfer process with the feed pH exceeding 11, and Ding et al also found the similar results [27].

3.2.4. Effect of the initial feed concentration

Figs. 11 and 12 showed that there were no remarkable changes of ammonia removal efficiency, mass transfer coefficients and selectivity at different initial feed concentration. On the one hand, when the ammonia concentration in the feed increases, the dissociation equilibration (4) moves towards the ammonia yield, the ammonia partial pressure would be enhanced. But on the other hand, the existence of ammonia in water makes the water vaporize more easily, the water vapor partial pressure also increases [27]. On the whole, the two effects are near and neutralized, thus the effects of initial feed concentration on mass transfer coefficients and selectivity vanished for a specific range of ammonia concentration in the

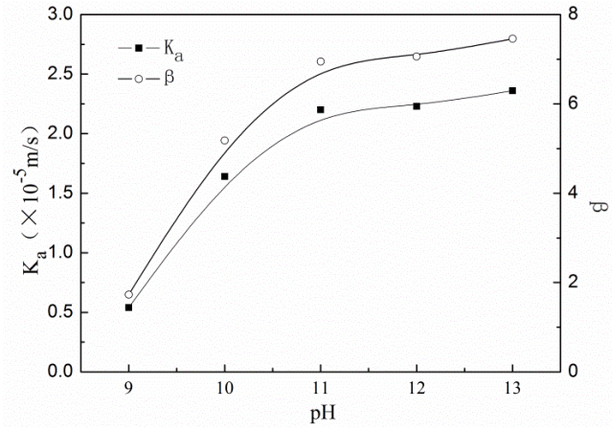

Fig. 10. Effect of feed pH on ammonia mass transfer coefficient and selectivity (C_0 = 0.6 mol L^{-1}, T_f = 53°C, T_p = 22°C, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}).

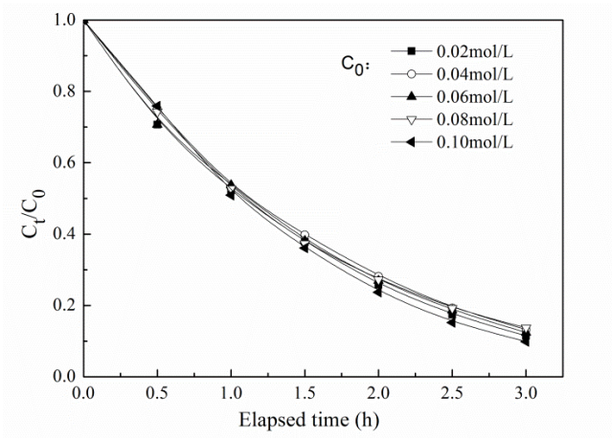

Fig. 11. Variation of feed ammonia concentration at different initial feed concentration (T_f = 53°C, T_p = 22°C, u_f =0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12).

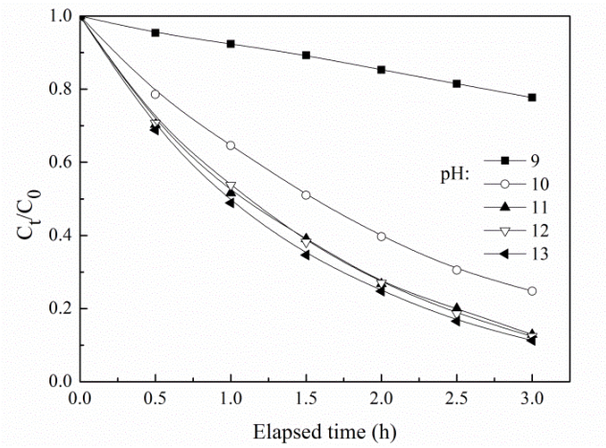

Fig. 9. Variation of feed ammonia concentration at different feed pH (C_0 = 0.6 mol L^{-1}, T_f = 53°C, T_p = 22°C, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}).

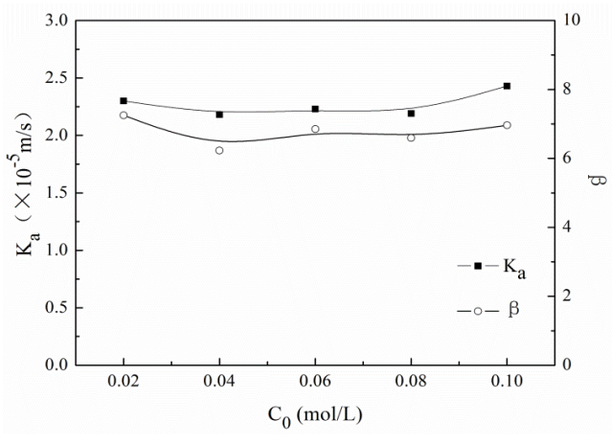

Fig. 12. Effect of initial feed concentration on ammonia mass transfer coefficient and selectivity (T_f = 53°C, T_p = 22°C, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12).

experiment. In addition, the resistant of the membrane was the dominant factor for ammonia transfer, especially when ammonia concentration is high. So the ammonia removal efficiency, mass transfer coefficients and selectivity had a little change with the increase of initial concentration.

3.2.5. Effect of the feed velocity

With the increase of feed velocity, ammonia removal efficiency and mass transfer coefficient only increased slightly, the selectivity has no remarkable change (Figs. 13, 14). As the rise of feed velocity from 0.46 m s^{-1} to 0.73 m s^{-1}, the Reynolds number increased from 1218 to 1915 (Table 2), which reduced the concentration polarization of feed. Therefore the mass transfer resistance from the feed bulk to membrane surface would decrease, leading to the mass transfer coefficient increased from 2.23×10^{-5} m s^{-1} to 2.52×10^{-5} m s^{-1}, and the ammonia removal efficiency increased from 88.5–92.0% (Figs. 13, 14). However, due to high solubility of ammonia in water, the mass transfer resistance of ammonia in feed bulk is slight. Because the main resistance of ammonia transfer comes from resistance in membrane pores, the feed velocity has little effect on mass transfer in gas phase, which can be accounted to the influence of feed velocity on mass transfer coefficient only increased a little (Fig. 14). The above reasons also can be used to explain that selectivity has no remarkable change with the increase of feed velocity.

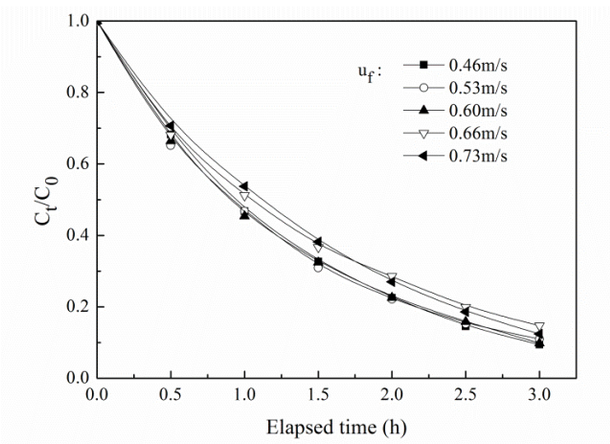

Fig. 13. Variation of feed ammonia concentration at different feed velocity (C_0 = 0.06 mol L^{-1}, T_f = 53°C, T_p = 22°C, u_p =0.27 m s^{-1}, feed pH = 12).

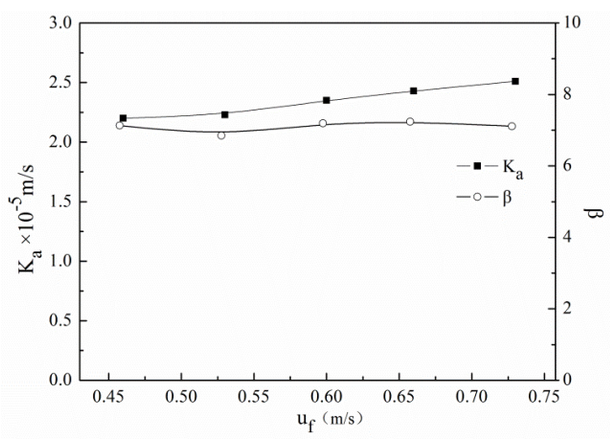

Fig. 14. Effect of feed velocity on ammonia mass transfer coefficient and selectivity (C_0 = 0.06 mol L^{-1}, T_f = 53°C, T_p = 22°C, u_p = 0.27 m s^{-1}, feed pH = 12).

Table 2
Variation of Reynolds number at different initial feed velocity

Feed velocity (m s^{-1})	0.46	0.53	0.60	0.66	0.73
Re	1218	1392	1566	1740	1915

3.3. Laboratory scale application of RDCMD

A kind of simulated ammonia wastewater containing 0.50 mol L^{-1} NH_4Cl, and some other impurities (0.01 mol L^{-1} $FeSO_4$, 0.01 mol L^{-1} $CaCl_2$, and 0.01 mol L^{-1} Na_2SiO_3) was used to test the application of RDCMD for ammonia removal, after 4 h treatment by RDCMD under the optimal conditions (T_f = 53°C, T_p = 22°C, u_f = 0.73 m s^{-1}, u_p = 0.27 m s^{-1}, feed pH = 12), 98.5% ammonia was removed.

3.3.1 Evaluation of the PVDF membrane for RDCMD

The PVDF membrane plays an important role in the implementation of RDCMD for ammonia removal from wastewater, it is necessary to evaluate the membrane fouling and the changes of membrane properties. By comparing the SEM images of PVDF membrane before and after the operation (Figs. 1, 15), it can be seen that only part of top surface was polluted by the impurities, the cross section and bottom surface of the membrane had no change after the operation; moreover, the few contaminants adhered in the membrane top surface can be easily removed by washing with deionized water for ten minutes.

The membranes, used in RDCMD process, should be characterized by the following membrane parameters: membrane material, thickness, porosity–pore size, liquid-entry-pressure of water (LEP_w) [32]. Compared the parameters of the PVDF membrane before and after the operation (Tables 1, 3), only porosity and contact angle decreased a little. In the process of RDCMD, some membrane pores could be blocked by small particles, which accounted to the little decrease of porosity; and the slight fouling of the membrane surface would decrease the hydrophobicity of the membrane, which led to a decrease of contact angle. The thickness of PVDF membrane could give information on mechanical strength of the membrane. It can be observed that there was no changes of thickness after operation, which demonstrated that RDCMD process has little influence on the mechanical strength of the membrane, and the mechanical strength of PVDF membrane is suitable for RDCMD process. Pore size and LEP_w was also related with mechanical property, RCMD is a thermally-driven separation process, and the pressure difference between two sides of the membrane isn't enough to destroy the mechanical property, so the pore size and LEP_w also has negligible change after the operation.

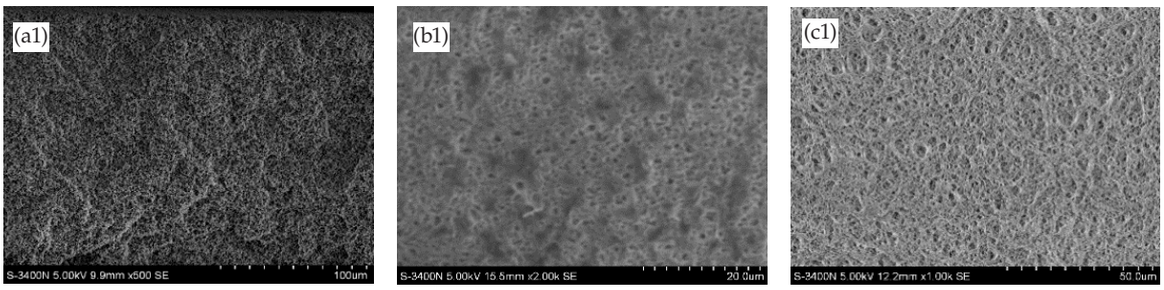

Fig. 15. Cross section(a1), top surface(b1) and bottom surface(c1) morphology of PVDF flat sheet membrane after 4 hours operation

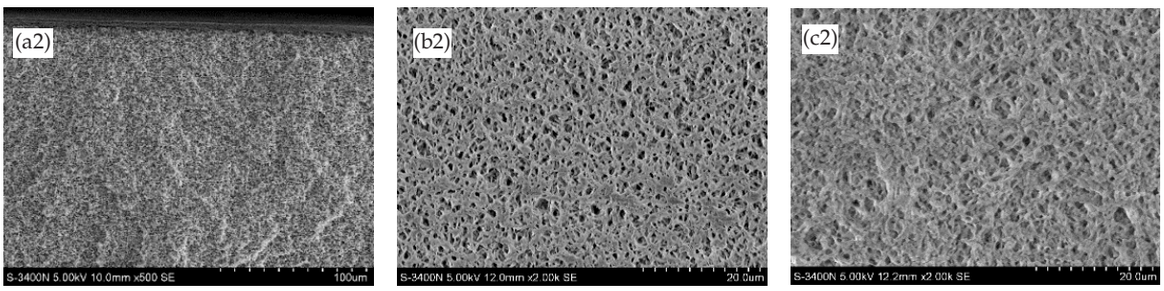

Fig. 16. Cross section (a2), top surface (b2) and bottom surface (c2) after 7 d treatment by 0.5 mol L^{-1} H_2SO_4.

Table 3
Properties of the PVDF membrane after different operation

Parameter treatment	Four hours laboratory scale application	0.5 mol L^{-1} H_2SO_4 for 1 day	0.5 mol L^{-1} H_2SO_4 for 7 days	0.5 mol L^{-1} H_2SO_4 for 15 days
Membrane thickness (mm)	0.218	0.223	0.219	0.220
Porosity(%)	70.15	75.42	74.58	75.82
Average pore radius (μm)	0.22	0.21	0.19	0.20
Contact angle θ (°)	122.2	120.8	109.9	109.5
LEP_w (KPa)	248.8	251.2	249.5	251.8

To further investigate the application of the PVDF membrane, the endurance capacity to sulfuric acid solution was evaluated. A piece of membrane was immersed into 0.5 mol L^{-1} H_2SO_4 for 1, 7 and 15 d, results showed that only the contact angle decreased slightly with the increase of time, and after 7 d, the contact angle maintained about 109.9° (Table 3), other properties have no remarkable change. SEM images also showed that cross section and surface of the membrane changed little. High concentration sulfuric acid can destroy the hydrophobic structure of the membrane, but the sulfuric acid concentration of the receiving solution was only 0.5 mol L^{-1}, the hydrophobicity of membrane couldn't be influence heavily by this sulfuric acid solution, so the contact angle only decreased slightly. Even though the contact angle decrease to 109.9°, the membrane still keep a high hydrophobic property. It can be concluded that the RDCMD process based on hydrophobic PVDF membrane is potential to apply in ammonia wastewater treatment.

3.3.2 Comments of large-scale implementation of RDCMD

Even though the laboratory scale application of ammonia treatment by RDCMD has been investigated in detail and operated successfully, the large-scale implementation in industry is still difficult to be widely realized. The complexity of industry implementation of RDCMD lies in four aspects, including optimization of operating conditions, preparation of novel membranes, design of module configurations, and solutions of membrane scaling and fouling. According to characteristics of different kinds of ammonia wastewater, the proper membrane and module configuration, optimal operating condition, and suitable solutions to control membrane scaling and fouling can be obtained by experimental attempts and pilot-scale test. Many studies have been undertook, and achieved good results for ammonia removal, but that does not mean to apply widely in industrial scale, one of the reasons is its high thermal energy consumption, which is the main production cost. However, one of the advantages of RDCMD is that it can be operated at low temperature. Therefore, with the use of cheap thermal energy, for example, waste heat or renewable energy (geothermal, wind or solar energy), it will realize practical/industrial implementations. In addition, for extreme high and complex ammonia wastewater, other technologies, including biological denitrogenation, breakpoint chlorination, cannot be used or cost too much, MD will be competitive to be economic feasibility and industrially implemented. Therefore, to be widely industrial application, RDCMD should either use cheap/renewable energy or try to be applied in extreme high/complex ammonia wastewater.

4. Conclusions

In this study, a kind of PVDF flat sheet hydrophobic membrane that prepared by thermally-induced phase

method was selected for direct contact membrane distillation to removal ammonia from wastewater. Three operation process (MC, DCMD and RDCMD) were compared for ammonia removal, the developed RDCMD process had the highest ammonia removal efficiency and mass transfer coefficient which was studied in detail to investigate the mass transfer mechanism. In addition, a laboratory scale application was carried to evaluate the practicability membrane properties.

For RDCMD, the influence of operating conditions (feed pH, feed temperature, permeate temperature, feed concentration and feed velocity) on mass transfer coefficient and selectivity were investigated in detail. Results showed that the feed pH is of great importance to ammonia removal performance, both mass transfer coefficient and selectivity could be greatly improved by increasing the feed pH, mass transfer coefficient increased from 0.54×10^{-5} m s^{-1} to 2.2×10^{-5} m s^{-1} and selectivity increased from 1.73 to 6.95, respectively, when the pH value increased from 9 to 11, but after pH up to 11, increasing pH gave no noticeable effect on mass transfer coefficient and selectivity. Feed temperature also had an important influence on mass transfer coefficient and selectivity; higher ammonia removal efficiency and mass transfer coefficient but lower selectivity were observed at higher feed temperature. Increasing permeate temperature had no remarkable effect on mass transfer coefficient, but was favor for the selectivity. Initial feed concentration and feed velocity had a negligible influence on mass transfer coefficient and selectivity.

The laboratory scale application demonstrated that RDCMD process can obtain 98.5% removal rate when treating 0.50 mol L^{-1} ammonia wastewater, and PVDF membrane was capable to resist fouling and maintained stable during the ammonia removal, which indicated that RDCMD process was practical for ammonia removal. However, these results only can support the industrial implementation, which does not mean industrial applications could be economical achieved, it will be necessary to find cheap/renewable energy to reduce the cost. In addition, RDCMD can be considered to use in the treatment of extreme wastewater during which the high cost could be negligible.

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Nomenclature

J — transmembrane flux (m^3 ($m^{-2}.s^{-1}$))
A — membrane area (m^2)
c_0 — initial ammonia concentration of feed (mol L^{-1})
c_t — ammonia concentration of feed at time of t (mol L^{-1})
F_f — feed velocity (m^3 s^{-1})
K — total mass transfer coefficient of NH_3 (m s^{-1})
t — time (s)
V_0 — initial feed volume (m^3)
β — selectivity
LEP_w — liquid-entry-pressure of water(KPa)

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