RESEARCH ARTICLE

VALORIZATION OF BIOGAS THROUGH SIMULTANEOUS CO_2 AND H_2S REMOVAL BY RENEWABLE AQUEOUS AMMONIA SOLUTION IN MEMBRANE CONTACTOR

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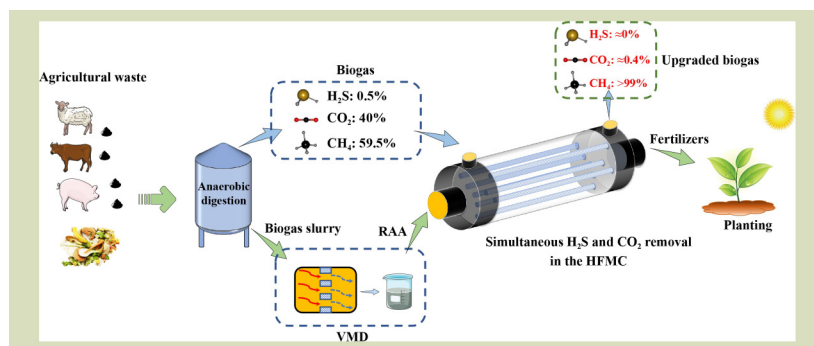
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HIGHLIGHTS

- Simultaneous H_2S and CO_2 removal from biogas is studied.
- Renewable absorbent from biogas slurry is used in membrane contactor.
- More than 98% of H_2S can be removed by membrane absorption.
- The impurities have less influence on H_2S removal efficiency.

GRAPHICAL ABSTRACT

ABSTRACT

Upgrading biogas into biomethane not only improves the biogas utilization as vehicle fuel or natural gas substitute, but also reduces the greenhouse gases emissions. Considering the principle of engineering green energy process, the renewable aqueous ammonia (RAA) solution obtained from biogas slurry was used to remove H_2S and CO_2 simultaneously in the hollow fiber membrane contactor. RAA was mimicked in this study using the ammonia aqueous solution mixed with some typical impurities including ethanol, acetic acid, propionic acid, butyric acid and NH_4HCO_3. Compared with the typical physical absorption (i.e., pure water) removing 48% of H_2S from biogas, RAA with 0.1 $mol \cdot L^{-1}$ NH_3 could remove 97% of H_2S. Increasing the NH_3 concentration from 0.1 to 0.5 $mol \cdot L^{-1}$ could elevate the CO_2 absorption flux from 0.97 to 1.72 $mol \cdot m^{-2} \cdot h^{-1}$ by 77.3%. Among the impurities contained in RAA, ethanol has a less impact on CO_2 absorption, while other impurities like CO_2 and acetic acid have significant negative impacts on CO_2 absorption. Fortunately, the

impurities have a less influence on H$_2$S removal efficiency, with more than 98% of H$_2$S could be removed by RAA. Also, the influences of operating parameters on acid gases removal were investigated to provide some engineering suggestions.

1   INTRODUCTION

Generated from the anaerobic digestion of waste organic compounds, biogas is a typical renewable and green energy[1]. Biogas mainly contains methane with about 60 vol%, and carbon dioxide with about 40 vol%, thus it can be used as fuel for power and heat production[2]. Other trace species including ammonia, dihydrogen, dinitrogen and hydrogen sulfide also exist in biogas[3,4]. Biogas can be used for direct combustion after desulfurization because H$_2$S can cause corrosion in pipelines and equipment[5]. To obtain biomethane from biogas as the pipeline natural gas and vehicle fuel, it is mandatory to remove CO$_2$ and other trace components, a process that is known as biogas upgrading[6]. Upgrading biogas into biomethane not only increases the economic revenues for biogas plant, but also reduces the greenhouse gas emissions[7]. Theoretically, a negative CO$_2$ emission can be achieved by capturing CO$_2$ from biogas followed by CO$_2$ utilization or storage, since biogas is always considered as a typical carbon-neutral fuel[8].

Currently, adsorption, absorption, membrane separation and even cryogenic technology are available on the industrial scale for biogas upgrading[9,10]. These technologies are primarily used for CO$_2$ separation while a pretreatment is required to get rid of the side effects of contaminants like H$_2$S and other trace components[11]. Water scrubbing, pressure swing adsorption and membrane separation processes can be used for simultaneous CO$_2$ and H$_2$S removal[9]. However, they still suffer from the drawbacks of high CH$_4$ loss, generally ranged from 2%–20%. It is known that CH$_4$ has a much higher greenhouse effect than that of CO$_2$[12]. Chemical absorption can achieve a negligible CH$_4$ loss (< 0.1%), high CH$_4$ purity at the atmospheric pressure and temperature, and simultaneous removal of H$_2$S, which may be a good choice for biogas upgrading[10,11]. However, chemical absorption also struggles with a high system energy consumption and CO$_2$ absorbent loss due to the stable salt formation after the chemical reaction between absorbent and acidic gases. In addition, determining how to utilize or store this CO$_2$ separated from biogas should be focused in the future if a negative CO$_2$ emission biogas utilization is targeted[7].

To avoid these drawbacks during CO$_2$ regeneration in chemical absorption process, a single-use absorbent has been developed, in which the acid gases can be absorbed and fixed by the renewable absorbent without regeneration[13]. Lots of chemicals can be used as the single-use absorbents, such as KOH, aqueous ammonia solution and even biomass ash[14]. Aqueous ammonia solution is the most promising absorbent because it can be easily recovered from the ammonium nitrogen-rich waste streams like wastewater and anaerobic digestate[15–17]. After saturated with acid gas, the ammonium contained solution can be used safely as the nitrogen fertilizer in agriculture[18,19]. Therefore, ammonia can be an environmentally-friendly absorbent for biogas upgrading. However, unlike the industrial ammonia aqueous solution, the recovered renewable aqueous ammonia (RAA) solution always features with a low concentration of total ammonium nitrogen (TAN)[20,21]. Therefore, the gas-liquid reactor applied for biogas upgrading by using low TAN concentration RAA should be selected deliberately[15].

Hydrophobic hollow fiber membrane contactors (HFMC) have been successfully used for CO$_2$ and H$_2$S absorption from biogas or natural gas[22]. Membrane absorption has the merits of large gas-liquid contact area, fast mass transfer rate, small equipment size and good operational flexibility in comparison of the current absorption technologies. Current absorbents like amine solutions, KOH, NaOH, amino acid salts have been investigated extensively for acid gases removal in the membrane contactor[23,24]. Ammonia was also explored in membrane contactor for CO$_2$ removal from biogas[15]. However, when TAN concentration of aqueous ammonia solution is above 2 mol·L^{-1}, the ammonium salt crystal may be generated on the membrane surface or even in the membrane pores, which would trigger the plugging problem of membrane and then the reduction of mass transfer. Importantly, this aqueous ammonia solution with a low TAN concentration is much easy to acquire[21,25]. Therefore, using the aqueous ammonia solution with a low TAN concentration in membrane contactor for biogas upgrading might be reasonable. In addition, previous studies have given ample consideration to CO$_2$ separation[17,20,26], but few have focused on simultaneous CO$_2$ and H$_2$S removal using ammonia solution in HFMC.

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In this study, we aimed to investigate the simultaneous H_2S and CO_2 removal performance by using HFMC and RAA with a low TAN concentration. We first investigated the effects of TAN concentration on H_2S and CO_2 removal performance. Then, the effects of trace components in RAA on the removal performance were studied. Also, the operating parameters influencing the H_2S and CO_2 removal performance were investigated.

2   MATERIALS AND METHODS

2.1   Materials

In the experiments, the standard gas (Shenkai Gases Technology Co., Ltd., Shanghai, China) was used as the simulated biogas, in which 5 vol‰ H_2S, 40 vol% CO_2 balanced by N_2 were contained. Potassium hydroxide (99.8% purity), aqueous ammonia solution (with a mass concentration range from 25% to 28%), ethanol (99.7% purity), aqueous acetic acid solution (36% mass fraction), propionic acid (99.5% purity), butyric acid (99% purity), and ammonium bicarbonate (99.9% purity) were purchased from Macklin Biochemical Co., Ltd., Shanghai, China. The RAA used in this study was simulated by directly mixing the aqueous ammonia solution and the typical impurities including ethanol, acetic acid, propionic acid, butyric acid or ammonium bicarbonate[26]. The experiments on the impacts of the impurities were conducted with impurity concentrations of 0.01, 0.03 and 0.05 mol·L^{-1} in the RAA solution.

2.2   Experiments

Figure 1 presents a schematic diagram of the experimental setup, in which the most important component is the commercial polypropylene hollow fiber membrane contactor (Ningbo Moersen Membrane Technology Co., Ltd., Zhejiang, China), and its characteristic parameters are shown in Table S1 in the supplementary materials. Before each experiment, deionized water was used to clean the system for at least 5 min to eliminate the influence of prior use. The gas components were tested before membrane absorption through a bypass flow, with the valve 2 on and valves 1 and 3 off. Then, the gas flowed to the shell side of the HFMC, with value 2 off, valves 1 and 3 on. The acid gases could be absorbed by the absorbent in the lumen of the hollow fiber membrane. The gas concentrations in the outlet of the HFMC were determined by an infrared biogas analyzer (Gas-board 3200 L, Wuhan Cubic Optoelectronics Co., Ltd., Hubei, China), and the data was automatically recorded by the analyzer every 10 s. Since H_2S might be contained in the outlet gas stream, the outlet gas was further treated by the desulfurization agent (i.e., Fe_2O_3) to totally remove the H_2S before the exhaust gas discharged into the atmosphere.

During the single pass absorption process, the absorbent solution flowed from tank 1 to tank 2. In the cycle absorption process, the absorbent solution cyclically flowed between tank 1 and the membrane contactor. The temperature and the flow rate of the absorbent solution were controlled by a water bath (SYC, Gongyi Yuhua instrument Co., Ltd., Henan, China) and
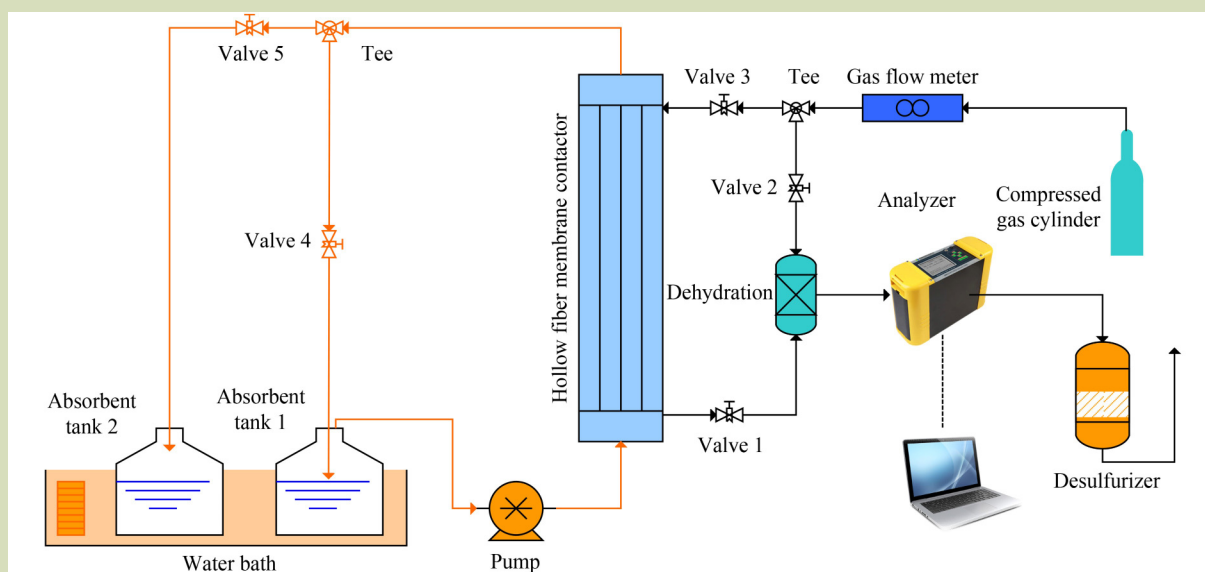

Fig. 1   Experimental setup for biogas upgrading using a hollow fiber membrane contactor.

a peristaltic pump (BT 1000-2J, Baoding Lange Constant Flow Pump Co., Ltd., Hebei, China), respectively. The gas flow rate was adjusted by the valve on the gas flow meter (LZB(J)-4~100(F), Changzhou Shuanghuan Thermal Instrument Co., Ltd., Jiangsu, China).

2.3 Data analysis

The absorption performance mainly includes gas transfer flux (or absorption rate), gas removal efficiency and gas loading in absorbent. The gas transfer flux was as[27]:

$$J_{CO_2} = \frac{(Q_{in}\varphi_{CO_2,in} - Q_{out}\varphi_{CO_2,out}) \times T_0}{V_m \times T_g \times A} \qquad (1)$$

$$J_{H_2S} = \frac{(Q_{in}\varphi_{H_2S,in} - Q_{out}\varphi_{H_2S,out}) \times T_0 \times \rho_{H_2S}}{T_g \times A} \qquad (2)$$

where J_{CO_2} (mol·m^{-2}·h^{-1}) and J_{H_2S} (mg·m^{-2}·h^{-1}) are the CO$_2$ and H$_2$S transfer flux during absorption, respectively, $\varphi_{CO_2/H_2S,in}$ and $\varphi_{CO_2/H_2S,out}$ are the measured CO$_2$ or H$_2$S volume fractions in the inlet and outlet of HFMC by the biogas analyzer, respectively; Q_{in} and Q_{out} are the gas flow rates (L·h^{-1}) in the inlet and outlet of the HFMC, respectively, ρH_2S is the density of H$_2$S (i.e., 1.52 × 10^3 mg·L^{-1}), T_0 and V_m are the temperature (i.e., 273.15 K) and molar volume (i.e., 22.4 L·mol^{-1}) of the gas at the standard conditions, respectively, T_g is the real gas temperature (K) and A is the mass transfer area (m^2).

At any given moment, the gas (CO$_2$ or H$_2$S) removal efficiency (η_{gas}, %) could be determined as[27]:

$$\eta_{gas} = \left(1 - \frac{Q_{out}\varphi_{gas,out}}{Q_{in}\varphi_{gas,in}}\right) \times 100\% \qquad (3)$$

The gas (CO$_2$ or H$_2$S) loading (α_{gas}, CO$_2$: mol·L^{-1} and H$_2$S: mg·L^{-1}) in the liquid phase could be calculated as:

$$\alpha_{gas} = \frac{\int_0^t S J_{gas} dt}{N} \qquad (4)$$

where N (L) is the total volume of the cycle absorbent solution and t is the experimental time (min).

3 RESULTS AND DISCUSSION

3.1 Comparison of chemical and physical absorption

A comparison of physical and chemical absorption of H$_2$S and CO$_2$ from the biogas was studied using pure water, 0.1 mol·L^{-1} KOH solution and renewable aqueous ammonia (RAA, TAN 0.1 mol·L^{-1}) solution. The absorbent was cycled in the lumen

of the hollow fiber membrane contactor (HFMC) with a flow rate of 50 mL·min^{-1}. The results are shown in Fig. 2(a) and Fig. 2(b), in which the acid gas (H$_2$S and CO$_2$) concentration decreases to the lowest point in 2 min. The highest CO$_2$ and H$_2$S absorption fluxes are achieved in the initial stage of the experiment, then the CO$_2$ and H$_2$S fluxes decline with the increase of CO$_2$ and H$_2$S loading (Fig. 2(c) and Fig. 2(d)). It was apparent that the lowest outlet CO$_2$ concentration was acquired using KOH as the absorbent, while using pure water had the lowest acid gas absorption performance. Although using RAA had a relatively low CO$_2$ absorption flux in the first 10 min, it had a higher CO$_2$ absorption flux than that of KOH solution at a high CO$_2$ loading (Fig. 2(c)). This was attributed to the high CO$_2$ absorption rate of ammonia under a relative high CO$_2$ loading[28]. Therefore, with chemical absorption for acid gas removal the performance was superior to using physical absorption, and RAA might be an improvement on KOH for H$_2$S removal.

H$_2$S removal efficiency was much higher than CO$_2$ removal efficiency (Fig. 2(a) and Fig. 2(b)). However, H$_2$S concentration (~0.5 vol%) was lower than that of CO$_2$. The Henry constant is the vital parameter for evaluating acid gas solubility in the absorbent. The greater the Henry constant, the solubility of the gas is the stronger for the same solvent at the same temperature and pressure. Table 1 summarizes the Henry constants of CO$_2$ and H$_2$S in pure water, RAA and KOH solution, respectively. The Henry constants of H$_2$S are about three times greater than these of CO$_2$ in all three absorbents. Hence, H$_2$S can be more efficiently absorbed by the absorbents than carbon dioxide under the same conditions. More than 90% of the H$_2$S was removed by KOH and RAA solution in the first 25 min. After running the experiment for 30 min, almost no H$_2$S could be removed by pure water, and the outlet H$_2$S concentration is 3.5 vol‰. Importantly, we found that the H$_2$S concentration in outlet was higher than that in the feed stream after running the experiment for 37 min for KOH solution and 69 min for RAA solution. This phenomenon could be due to the H$_2$S desorption under a higher CO$_2$ loading. The conditions for H$_2$S desorption from the absorbent in this experiment were: H$_2$S and CO$_2$ loading for 0.1 mol·L^{-1} KOH solution are 80 mg·L^{-1} and 0.077 mol·L^{-1}, and the values for 0.1 mol·L^{-1} RAA solution are 109 mg·L^{-1} and 0.123 mol·L^{-1}.

Taking the absorption of CO$_2$ and H$_2$S by RAA solution as an example, the typical absorption reactions are shown in Table 2[20,23]. Physical absorption cannot be ignored because of the relatively low TAN concentration in the RAA solution (0.1 mol·L^{-1}). In Fig. 2(c), the RAA solution was basically
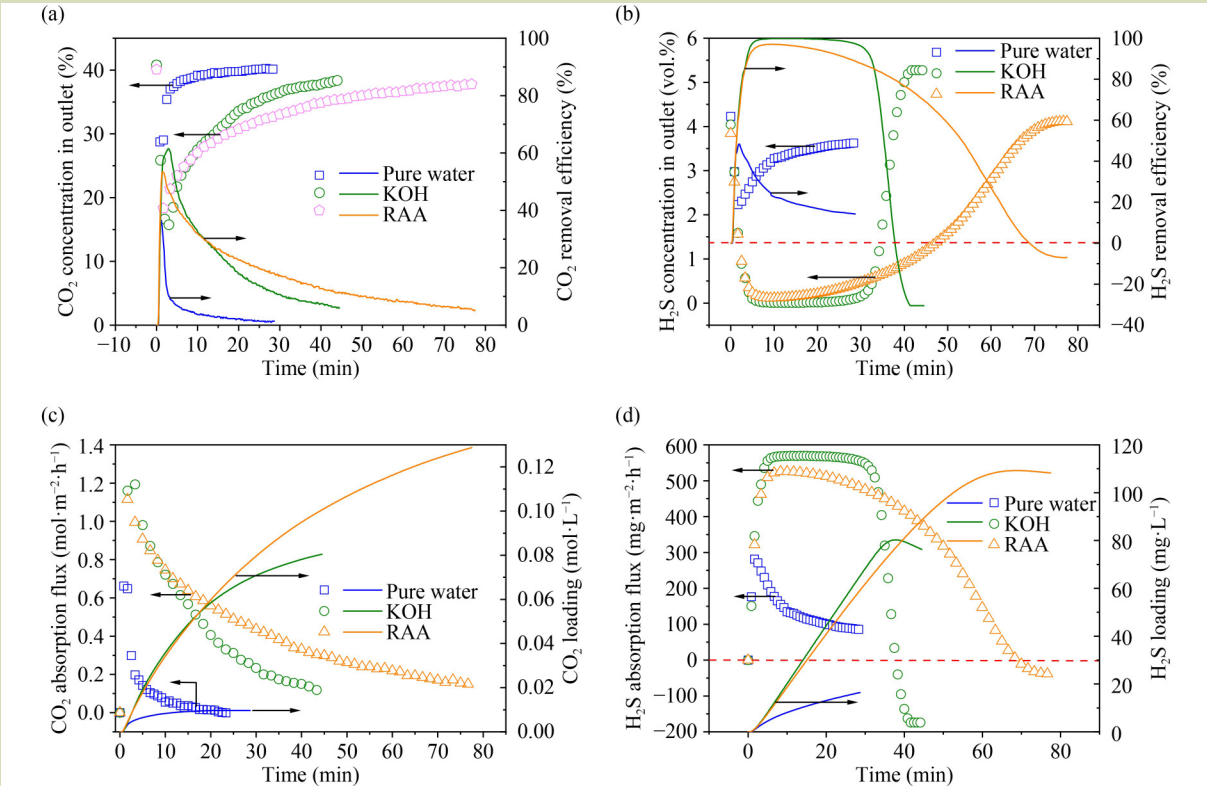
Fig. 2 CO_2 and H_2S absorption flux profile using pure water, 0.1 mol·L^{-1} RAA solution and 0.1 mol·L^{-1} KOH solution in hollow fiber membrane contactor. Experimental conditions: absorbent feed temperature and flow rate were 20 °C and 50 mL·min^{-1}, feed gas flow rate was 400 mL·min^{-1}.

Table 1   Henry constants of CO_2 and H_2S in the different solutions

Acid gas	Henry constants in the different absorbents (mol·m^{-3}·kPa^{-1})		
	Pure water	0.1 mol·L^{-1} RAA	0.1 mol·L^{-1} KOH(aq)
CO_2	0.33[29]	0.39[30,31]	0.33[30,32]
H_2S	1.00[29]	1.20[30,31]	0.97[30,32]

Table 2   Reactions of CO_2 and H_2S absorption with aqueous ammonia solution

CO_2-$NH_3 \cdot H_2O$ reaction	H_2S-$NH_3 \cdot H_2O$ reaction
$NH_3(aq) + H_2O \rightleftharpoons NH_4^+ + OH^-$	$NH_3(aq) + H_2O \rightleftharpoons NH_4^+ + OH^-$
$CO_2(g) \rightleftharpoons CO_2(aq)$	$H_2S(g) \rightleftharpoons H_2S(aq)$
$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3$	$H_2S(aq) \rightleftharpoons HS^- + H^+$
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	$HS^- \rightleftharpoons H^+ + S^{2-}$
$CO_2(aq) + OH^- \rightleftharpoons HCO_3^-$	$H_2S(aq) + OH^- \rightleftharpoons HS^- + H_2O$
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$HS^- + OH^- \rightleftharpoons S^{2-} + H_2O$
$NH_3(aq) + HCO_3^- \rightleftharpoons NH_2COO^- + H_2O$	$NH_3(aq) + HS^- \rightleftharpoons NH_4^+ + S^{2-}$

saturated with CO_2 at about 69 min. Theoretically, only physical absorption weakly existed at this time. Substantial amounts of H_2S gas were absorbed by RAA solution before 69 min, and most of this gas was in the solvent as HS^-. With the injecting of biogas into HFMC, H_2CO_3 and HS^- are generated at the gas-liquid contact interface, and the basic reaction was:

$$H_2CO_3(aq) + HS^- \xrightleftharpoons{K_t} HCO_3^- + H_2S(g) \qquad (5)$$

With an absorption temperature of 25 °C, the chemical equilibrium constant (K_t) of the reaction (Eq. (5)) is about 4.7, and the initial reaction quotient (R) of this reaction is about 0.02 (calculation details are given in the Eqs. (S1)–(S5) in the supplementary materials). Given that R is much smaller than K_t, the reaction (Eq. (5)) proceeds in the positive direction. This results in that the H_2S from the simulated biogas cannot be absorbed by RAA solution. More importantly, the absorbed H_2S was regenerated from the solvent. It was the reason why the H_2S concentration in the outlet was higher than that in the feed stream (Fig. 2(b,d)). Therefore, the operating parameters should be well controlled when using RAA for simultaneous H_2S and CO_2 removal.

3.2 Effect of absorbent concentration

The TAN concentration in RAA solution is always controlled by the ammonia recovery technology and operating time[16,21]. Although the TAN concentration of RAA can reach up to above 1 mol·L⁻¹, the membrane absorption process using RAA with a high concentration may result in a membrane blockage because of the generation of ammonium bicarbonate crystal[17,25]. In the present study, the RAA concentration ranged from 0.1 to 0.5 mol·L⁻¹ (Fig. 3). The CO_2 absorption

flux increased sharply from 0.97 to 1.72 mol·m⁻²·h⁻¹ when the TAN concentration increases from 0.1 to 0.5 mol·L⁻¹. The outlet CO_2 concentration decreased from 40% to 2.4% when adopting 0.5 mol·L⁻¹ RAA. The outlet H_2S concentration was kept at 0 vol‰ when the TAN concentration in RAA solution varies from 0.1 to 0.5 mol·L⁻¹. Apparently, the RAA solution with a TAN concentration above 0.1 mol·L⁻¹ is sufficient to remove H_2S from biogas. However, a high TAN concentration may be still required to upgrade biogas into biomethane.

3.3 Effect of impurities

The impurities from biogas slurry such as ethanol, acetic acid, propionic acid, butyric acid and even CO_2 are dissolved in RAA solution during the ammonia recovery process[21]. Their existences in RAA may have some influences on the acid gas absorption rate. Their effects on CO_2 absorption rate in a wetted wall column were examined in a previous study[26], and the results showed that the butyric acid and acetic acid have the greatest influence on the CO_2 absorption rate, while the CO_2 and ethanol have less influence. In the present study, we tested the CO_2 and H_2S absorption flux of 0.1 mol·L⁻¹ RAA containing different types of impurities (Fig. 4). In the radar chart, the data points in the central location have the low values, which means a negative effect on acid gas removal. It is evident that the ethanol had a lower impact on CO_2 absorption, in which the CO_2 absorption flux was kept at 0.93 mol·m⁻²·h⁻¹, and the CO_2 removal efficiency was also kept at 39%. However, the CO_2 and acetic acid contained in the RAA solution had significant negative influence on CO_2 absorption flux. The CO_2 absorption flux decreased to 0.48 mol·m⁻²·h⁻¹, when the CO_2 or acetic acid concentration in RAA solution increased to
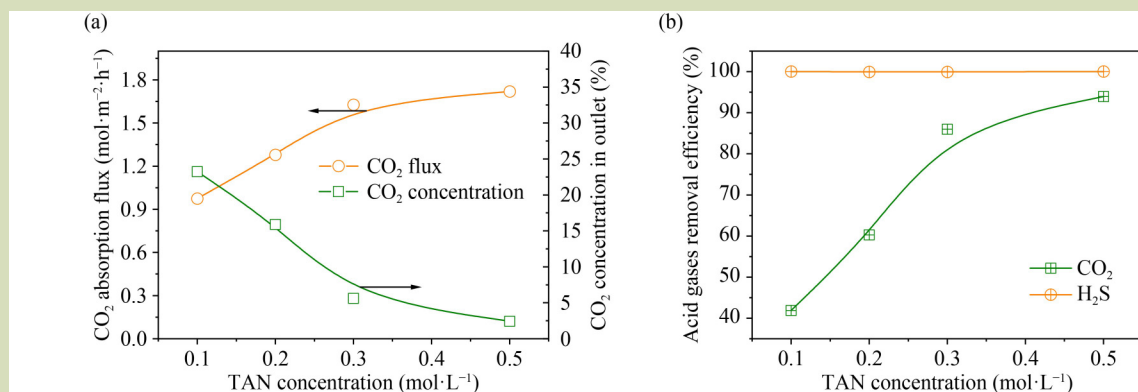

Fig. 3 CO_2 and H_2S absorption performance using RAA solution as the absorbent with TAN concentration varied from 0.1 to 0.5 mol·L⁻¹. (a) CO_2 absorption flux and CO_2 concentration in outlet. (b) Acid gas removal efficiency. Experimental conditions: absorbent feed temperature and flow rate were 20 °C and 50 mL·min⁻¹, feed gas flow rate was 400 mL·min⁻¹.
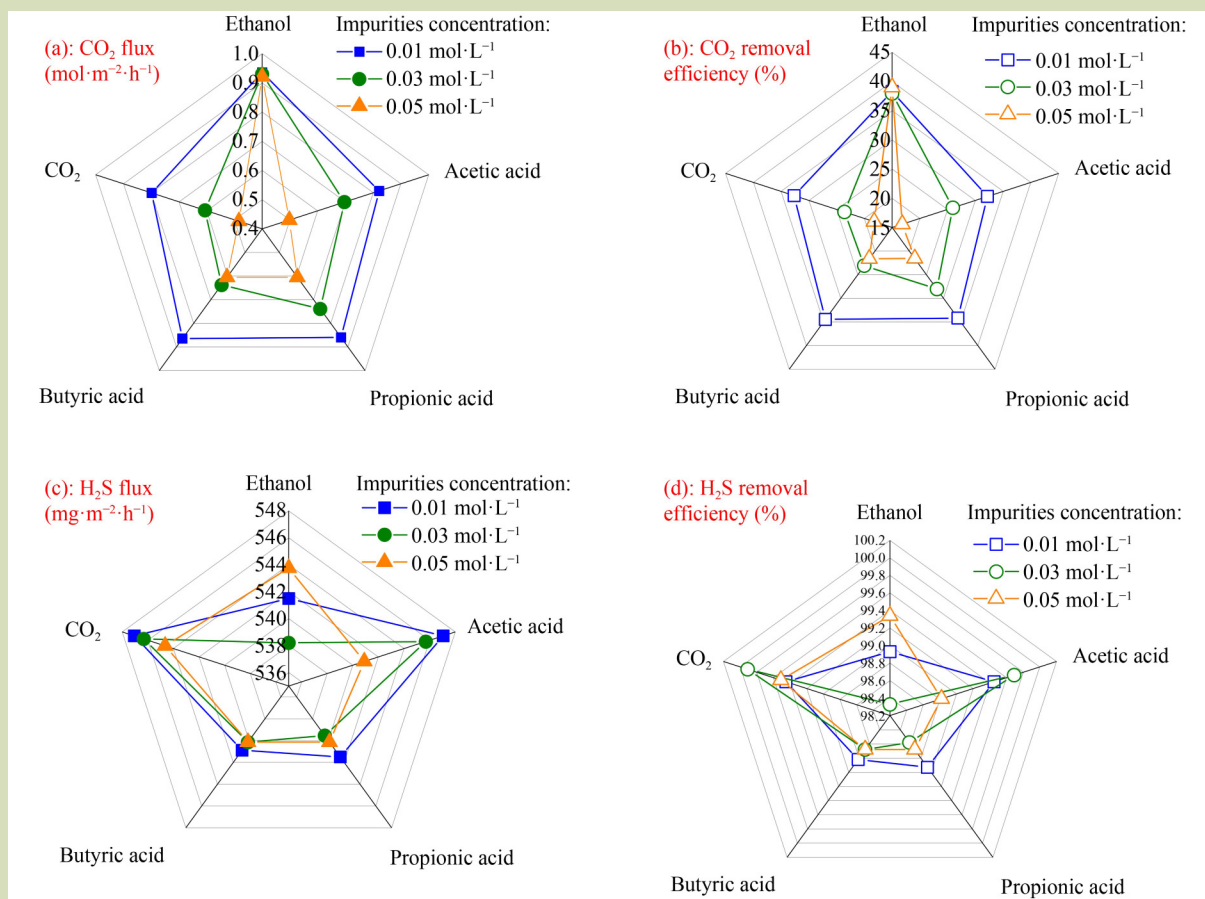
Fig. 4 Effect of impurities in RAA solution on the CO_2 and H_2S absorption performance. Effect of impurity types and their concentration (0.01, 0.03 and 0.05 mol·L^{-1}) on CO_2 absorption flux (a), CO_2 removal efficiency (b), H_2S removal flux (c), and H_2S removal efficiency (d). Experimental conditions: 0.1 mol·L^{-1} RAA, absorbent feed temperature and flow rate were 20 °C and 50 mL·min^{-1}, feed gas flow rate was 400 mL·min^{-1}.

0.05 mol·L^{-1} (Fig. 4(a)). Clearly, the high concentration impurities had negative influence with the CO_2 removal efficiency decreasing from 39% to 16% (Fig. 4(b)). However, the impurities had less influence on H_2S removal efficiency (Fig. 4(c,d), where more than 98% of the H_2S was removed by RAA with 0.05 mol·L^{-1} impurities. Overall, to achieve optimal biogas upgrading performance, the impurities need to be removed or kept to a low level.

3.4 Effect of CO_2 loading

As shown in Fig. 2(c), the CO_2 loading in the RAA, produced by absorbing CO_2 from biogas, increased with time during the cyclic absorption experiment. However, the CO_2 absorption flux decreased lineally with increasing CO_2 loading (Fig. 5(a)). Notably, CO_2 loading had little impact on the H_2S absorption flux and H_2S removal efficiency. The H_2S absorption flux and H_2S removal efficiency were kept at 546 mg·m^{-2}·h^{-1} and 99.8%

when the CO_2 loading is lower than 0.09 mol·L^{-1}. The H_2S absorption flux and H_2S removal efficiency decreased sharply to 491 mg·m^{-2}·h^{-1} and 89% when the CO_2 loading reached 0.1 mol·L^{-1} (Fig. 5(b)). Consequently, the CO_2 loading might have no influence on H_2S removal performance when its concentration is below 0.09 mol·L^{-1}. However, H_2S loading in the RAA needs to be considered because the H_2S content is accumulated gradually during the absorption process. Figure 5(c) shows the effects of the CO_2 and H_2S loading on H_2S absorption flux. Clearly, both H_2S and CO_2 loading had negative impacts on H_2S removal. Further study is needed to determine if H_2S and CO_2 loading have interactions on acid gas removal.

3.5 Effect of temperature

It is expected that temperature will influence the acid gas absorption rate and the final acid gas equilibrium
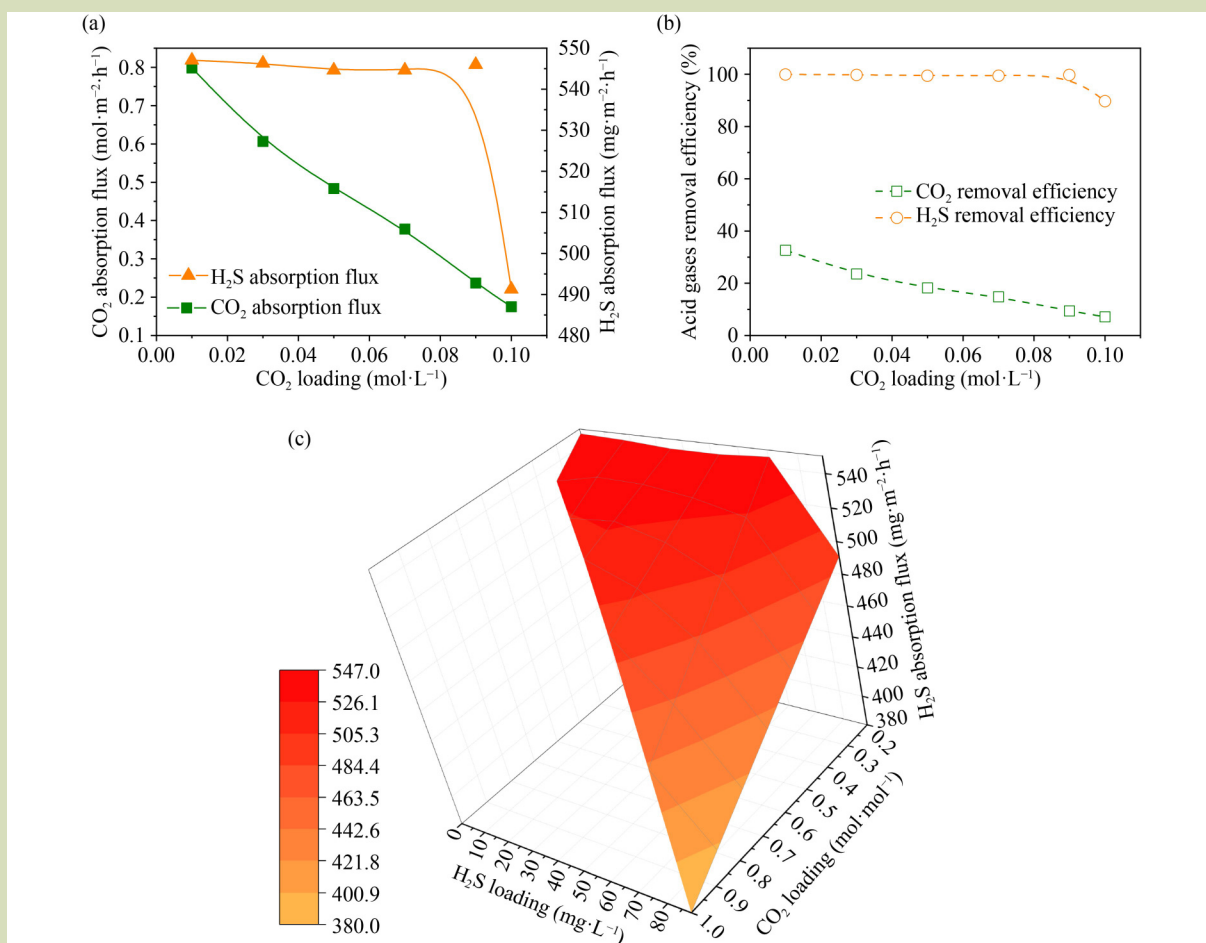
Fig. 5 Effect of CO$_2$ loading on CO$_2$ and H$_2$S absorption performance. (a) Effect of CO$_2$ loading on CO$_2$ and H$_2$S absorption flux. (b) Effect of CO$_2$ loading on acid gas removal efficiency. (c) Effect of CO$_2$ and H$_2$S loading on H$_2$S absorption flux using 0.1 mol·L^{-1} RAA solution. Experimental conditions: absorbent feed temperature and flow rate were 20 °C and 50 mL·min^{-1}, feed gas flow rate was 400 mL·min^{-1}.

concentration. However, it was previously shown that the temperature has little impact on CO$_2$ absorption flux due to the low absorbent concentration. Therefore, the acid gas absorption performance was studied by the RAA solution cycling in the tube side of HFMC (Fig. 6). First, in the initial stage, both the CO$_2$ and H$_2$S absorption flux climb to a high point within 5 min and there was minimal difference between the temperatures tested. This result was consistent with a previous study[20]. However, the acid gas absorption flux decreased with the increment of running time and acid gas loading. Especially, the highest acid gas absorption flux was acquired at 25 °C. In addition, the highest CO$_2$ loading and H$_2$S loading were also obtained at 25 °C. Under each temperature using 0.1 mol·L^{-1} RAA as the absorbent, the CO$_2$ loading with above 0.1 mol·L^{-1} can be achieved. Obviously, a lower absorption temperature (e.g., room temperature) might be suitable for acid gases removal from biogas.

3.6 Effect of absorbent and biogas feed flow rate

Figure 7 shows the effects of the feed absorbent and biogas flow rate on biogas upgrading performance. The CO$_2$ absorption flux increased with the elevation of the biogas feed flow rate, while the CO$_2$ removal efficiency decreased with the biogas feed flow rate. The increased gas feed flow rate could reduce the gas phase mass transfer resistance greatly, thereby promoting acid gas absorption flux. Nonetheless, it is noted that the increased biogas flow rate decreased the biogas residence time in HFMC, thus resulting in a low CO$_2$ removal efficiency. Typically, the mass transfer resistance in the liquid or membrane is higher than that in gas phase[20]. Therefore, low biogas flow rate may be beneficial to acidic gases removal, and some previous studies gave the same conclusion[20,23]. As evident in Fig. 7(a), more than 99% of the CO$_2$ can be removed from the biogas when the system is operated under a biogas feed flow rate of 0.1 L·min^{-1}. Also, more than 99% of the H$_2$S
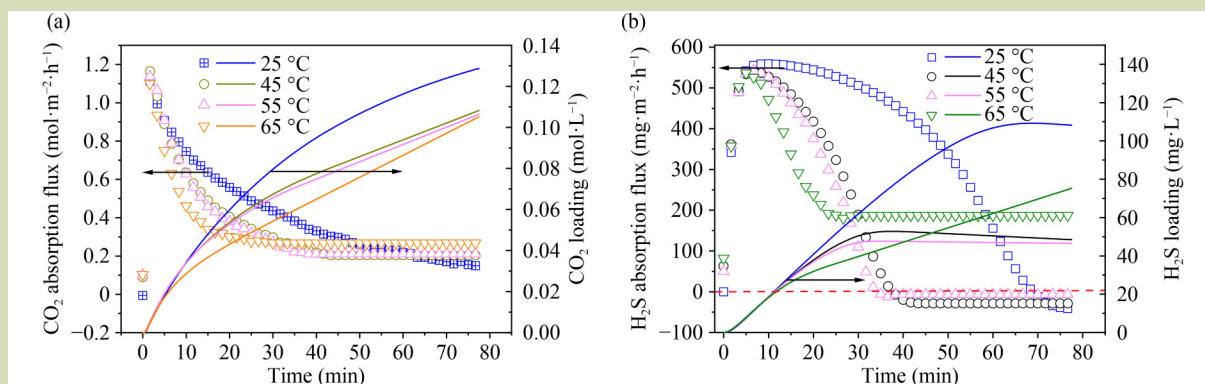
Fig. 6 Effect of absorbent temperature (25, 45, 55 and 65 °C) on CO_2 (a) and H_2S (b) removal performance using 0.1 mol·L^{-1} RAA solution cycling in the tube side of hollow fiber membrane contactor. Experimental conditions: absorbent feed flow rate was 50 mL·min^{-1}, feed gas flow rate was 400 mL·min^{-1}.
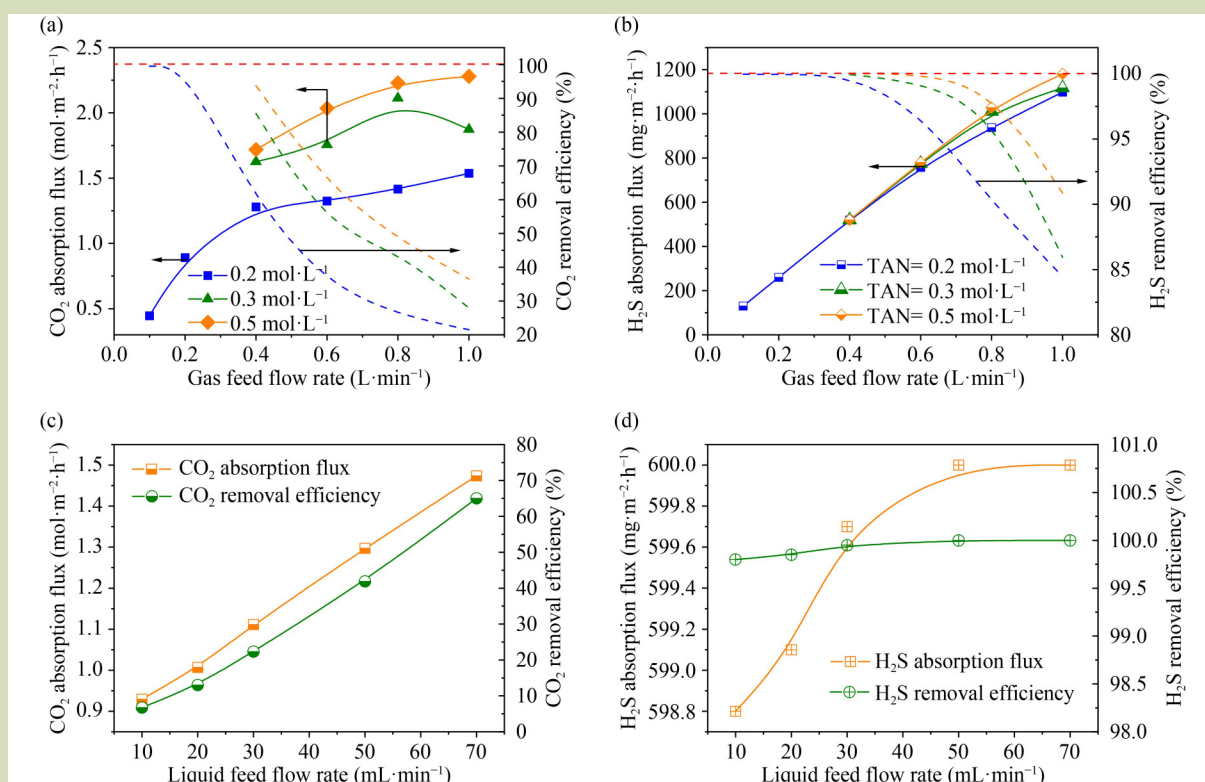

Fig. 7 Effect of biogas feed flow rate on CO_2 (a) and H_2S (b) removal performance using RAA solution with TAN concentration of 0.2, 0.3 and 0.5 mol·L^{-1}. Experimental conditions: absorbent feed temperature and flow rate were 20 °C and 50 mL·min^{-1}, without cycling. Effect of absorbent feed flow rate on CO_2 (c) and H_2S (d) removal performance using RAA solution with TAN concentration of 0.1 mol·L^{-1} without absorbent cycling. Experimental conditions: absorbent feed temperature was 20 °C, feed biogas flow rate was 400 mL·min^{-1}.

can be removed from biogas when the biogas flow rate is less than 0.4 L·min^{-1} (Fig. 7(b)). Consequently, we conclude that a low biogas flow rate to satisfy the requirement or both the CO_2 and H_2S removal.

A high liquid feed flow rate on the tube side is beneficial to reduce the thickness of liquid phase boundary layer, thus to promote the whole mass transfer efficiency. In the present study, the CO_2 absorption flux increased linearly with

increased liquid feed flow rate, in which the CO_2 absorption flux was increased from 0.93 to 1.47 mol·m^{-2}·h^{-1} and the CO_2 removal efficiency also increased from 6.72% to 65%. Given the relatively low biogas flow rate, more than 99.8% of the H_2S in the lumen side is removed by the RAA solution. Consequently, it was found that an absorbent feed flow rate of above 50 mL·min^{-1} could be suitable for H_2S removal.

4   CONCLUSIONS

Membrane absorption is one of the most important ways for upgrading biogas. In this study, a novel, economical and environmentally-friendly solution for simultaneous H_2S and CO_2 removal from biogas using membrane contactor was demonstrated. This solution could reduce the hazard caused by acid gases (CO_2 and H_2S) in biogas, and also provide a simple carbon negative emission technology for the future green energy engineering. RAA recovered from the waste streams or the biogas slurry could effectively solve the high energy consumption problem. In addition, RAA solution saturated with acid gases from biogas could be used for fertigation in agriculture.

Compared with the typical physical absorption using pure water as the absorbent, chemical absorption using a 0.1 mol·L^{-1} NH_3 RAA solution achieved a H_2S removal efficiency of above 97%. In addition, the CO_2 removal efficiency increased from 42% to 91%, when the TAN concentration in RAA solution increased from 0.1 to 0.5 mol·L^{-1}. Also, the impurities had a less influence on H_2S removal efficiency, with more than 98% of the H_2S removed by the RAA. The operating parameters component of this study demonstrated that, a low temperature is beneficial to enhance the acid gas absorption flux and also increase the acid gas absorption capacity. When absorption flux increased the removal efficiency decreased with the rise in the biogas feed flow rate for both CO_2 and H_2S. However, increasing the feed absorbent flow rate could promote both CO_2 and H_2S removal efficiency and flux.

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