Developing aqueous porous carbons for biogas upgrading

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A B S T R A C T

Developing novel sorbents is essential for biogas upgrading. In this study, mixed sorbents of aqueous porous carbons were developed to separate CO₂ from the biogas, where the porous carbon with the developed micropore structure was identified as the most desirable constituent. Both thermodynamics and kinetics were studied experimentally, and Henry’s constant (K_H) and the liquid-side mass-transfer coefficient (k_L) of CO₂ in the mixed sorbent as well as the selectivity of CO₂/CH₄ were obtained accordingly. Furthermore, the CO₂ separation performance was evaluated with a proposed index, and the cost of biogas upgrading using the mixed sorbent was estimated and compared. The results showed that the porous carbon with the developed micropore structure led to better performance on K_H and k_L of CO₂ in the mixed sorbent, and the mixed sorbent with 3.03 wt% porous carbon exhibited the best CO₂ separation performance, reducing 36.2% in cost compared to the current technologies.

1. Introduction

Biogas is considered as an efficient renewable energy to substitute the utilization of conventional fossil fuels [11], and methane (CH₄, 53–70 vol%), carbon dioxide (CO₂, 30–47 vol%), and other trace compounds, such as water (H₂O) and hydrogen sulfide (H₂S), exist in a typical raw biogas [2,3]. The presence of CO₂ (up to 47 vol%) reduces its calorific value, burning velocity, and flammability limit [4,5], and cost-effective and environment-friendly technologies for biogas upgrading, i.e., CO₂ removal, need to be developed.

Several technologies have been developed and commercialized for CO₂ separation or removal from raw biogas, such as adsorption, absorption, membrane, and cryogenic separation [6,7]. Among them, amine scrubbing is a mature technology with the advantages of high CO₂ absorption capacity and rate as well as high CO₂/CH₄ selectivity in biogas upgrading [8,9], while it has many deficiencies like high energy demand for regeneration, corrosion of facility, amine degradation, and so on [10]. Meanwhile, high-pressure water scrubbing (HPWS) is also a widely used technology for biogas upgrading with high efficiency and low CH₄ loss [11]. However, HPWS usually suffers from the deficiencies of huge amounts of H₂O circulation and large-scale equipment, mainly owing to the low CO₂ solubility as well as slow absorption rate in H₂O [12]. Therefore, developing novel absorbents or proposing new strategies is urgent.

Recently, the mixed sorbent, consisting of the porous material and liquid absorbent, has been proposed for CO₂ separation owing to its dual advantages of absorption and adsorption [13,14], which is similar to the porous liquid [15,16]. Previously, the mixed sorbent exhibited better separation performance on CO₂ sorption capacity and rate as well as the selectivity than that of the pure solvent, and the mixed sorbent can be also circulated by pumping [17,18]. For example, the mixed sorbent of metal–organic frameworks (MOFs), 2-methylimidazolide, glycol, and H₂O displayed better CO₂ separation performance than that of 30 wt% aqueous monoethanolamine, i.e., an energy usage reduction to 0.61–0.85 GJ·ton⁻¹ CO₂ [17]. Meanwhile, the superb ideal CO₂/N₂ selectivity of 11,545 was achieved in the mixed sorbent of tetraethylammonium glycinate/molecular sieve (SBA-15), which was 288 times of SBA-15 [19]. In our previous study [18], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Hmin][NTf₂])/titanium dioxide (TiO₂)/H₂O was developed for CO₂ separation in biogas upgrading, and the average cost was 16.6% lower than that of HPWS. However, the
high price and low stability of porous materials, such as MOFs and molecular sieves, usually hinder the long-term industrial applications of such mixed sorbents.

Porous carbons have been recognized as promising materials in developing mixed sorbents because of their large surface area, highly porous structure, good thermal stability, and low cost [20,21]. A lot of efforts have been applied to develop novel porous carbons to achieve desirable CO₂ separation performance [22–24]. Generally, CO₂ separation performance of porous carbon is dominated by the pore distribution and surface property, where the effect of the pore structure is more significant. For example, porous carbon with a large surface area (~2380 m²·g⁻¹) and high micropore volume (~0.896 m³·g⁻¹) synthesized from the cork dust waste showed superior high CO₂ capacities of 7.82 and 4.27 mol·kg⁻¹ at 273.2 and 298.2 K (0.1 MPa), respectively [25]. When porous carbons are used as the porous materials in developing mixed sorbents, the dispersion phase, i.e., solvent, is also a crucial issue. H₂O, as a cheap, stable and green solvent, has been applied in the CO₂ separation as the absorbent [26,27]. On the other hand, H₂O is also an important impurity in raw biogas [28]. Therefore, developing a promising mixed sorbent and performing its technical potential evaluation for biogas upgrading using a desirable liquid absorbent of H₂O and cheap and stable material of porous carbon should be an interesting endeavor. However, to the best of our knowledge, the mixed sorbent consists of porous carbon and H₂O has never been reported for biogas upgrading.

To develop mixed sorbents, the Henry’s constant (K_H) and the liquid-side mass-transfer coefficient (k_L) of CO₂ in the mixed sorbent as well as the selectivity of CO₂/CH₄ (S_CO₂/CH₄) are three important properties featuring the CO₂ separation performance in biogas upgrading [29,30]. Normally, the values of K_H and S_CO₂/CH₄ are closely related to the solubilities of CO₂ and CH₄, which are also the prerequisite for calculating k_L [30,31]. However, it is worth noting that the presence of the porous material in liquid absorbent usually results in complex changes in both thermodynamic and kinetic properties [32]. For example, the addition of MOFs into 2-methylimidazole/glycol was observed to enhance CO₂ solubility and CO₂/CH₄ selectivity and lower CO₂ desorption enthalpy [14]. Additionally, the k_L value of CO₂ in [Hmin][NTf₂]/TiO₂/H₂O increased 31.6 % when the solid mass fraction was 3.07 wt% [18]. Therefore, studying both the thermodynamic and kinetic properties of CO₂ in the mixed sorbent is essential in technology development.

Once the properties of the mixed sorbent are obtained, the CO₂ separation performance and the cost of biogas upgrading can be calculated accordingly. One option is to conduct process simulation and cost estimation, where many theoretical models and parameters, as well as complex facilities and operations, are usually needed [33,34]. In our previous study [26], a new index named “comparative absorption factor” (CAF) was proposed to estimate the cost of CO₂ separation in biogas upgrading from the thermodynamic and kinetic properties, being convenient to estimate the cost for a newly developed technology.

This study was to develop mixed sorbents (aqueous porous carbons) to effectively separate CO₂ from biogas. To achieve this, the CO₂ separation performance of the mixed sorbents with five types of porous carbons was evaluated, and the one with the best performance was identified. The solubilities of CO₂ and CH₄ as well as the CO₂ sorption rate in this optimal mixed sorbent were measured experimentally, and K_H and k_L of CO₂ in the mixed sorbent as well as S_CO₂/CH₄ were calculated. Furthermore, the CO₂ separation performance was evaluated using the CAF index, and the cost of biogas upgrading was estimated and compared with other technologies. Additionally, the recyclability of the mixed sorbent was studied.

2. Experiment and theory

2.1. Materials

CO₂, CH₄, and N₂ (>99.99 vol%) were purchased from Nanjing Max Nan Fen Special Gas Co., Ltd. Deionized H₂O with the conductivity lower than 0.25 µS·cm⁻¹ was obtained by a reverse osmosis membrane in the laboratory. Five types of porous carbons with different pore distributions were obtained from Mulinsen Activated Carbon Jiangsu Co., LTD. Before use, the porous carbon was smashed into 200 mesh, and then dried in an air blast drying oven at 423.2 K for 5.0 h.

2.2. Characterization

N₂ adsorption isotherms of five porous carbons at 78.15 K were measured with the Micromeritics ASAP 2460 analyzer. In this study, the specific surface area (S₆₆₅) of porous carbon was calculated using the method of Brunauer-Emmett-Teller, and the pore volume and pore-size distribution were determined by the method of non-localized density functional theory (NLDF).

2.3. Gas solubilities and sorption kinetics measurements

The schematic diagram for measuring CO₂ and CH₄ solubilities as well as CO₂ sorption rate was illustrated in Fig. 1, which is the same as described in our previous studies [31,35]. An equilibrium cell, a storage tank, and a magnetic stirrer were placed into a water bath with a temperature control system (accuracy: ± 0.1 K). The pressure of the equilibrium cell was recorded with a sensor (Rosemount 2088G, accuracy: ± 0.001 MPa). The parameters of the equilibrium cell and magnetic stirrer are showed in Table 1. During the gas solubility and sorption rate measurements, a specific amount of mixed sorbent (~10.0 cm³) was added into the equilibrium cell, and the cell was degassed with a vacuum pump (~0.012 MPa). Afterwards, a specific amount of CO₂ or CH₄ was injected into the equilibrium cell quickly (~5 s), and the magnetic stirrer...
was switched on immediately. The partial pressure of CO$_2$ or CH$_4$ was recorded with the data collection system every five seconds. Normally, it could be considered that the dissolution equilibrium of CO$_2$ or CH$_4$ in the mixed sorbent was reached when the pressure of the equilibrium cell was kept constant for 2 h. The molar concentration ($c_i$) of CO$_2$ or CH$_4$ in the mixed sorbent was calculated using the following Eqs. (1)-(2):

$$n_i = \frac{P_i(V_i - V_e)}{Z_iRT} - \frac{P_e(V_e - V_i)}{Z_eRT}$$  

(1)

$$c_i = \frac{n_i}{V_e}$$  

(2)

where $n_i$ is the mole of CO$_2$ or CH$_4$, $P_i$ and $P_e$ are the CO$_2$ or CH$_4$ partial pressures at the states of initial and equilibrium, respectively. $Z_0$ and $Z_e$ are the gas compressibility factors at the states of initial and equilibrium, respectively, which were calculated by the second virial coefficients [36]. $T$ is the temperature in Kelvin, and $R$ is the universal gas constant (8.314 J·mol$^{-1}$·K$^{-1}$).

The combined standard uncertainties of CO$_2$ or CH$_4$ solubility ($u(c)$) were calculated using the following Eqs. (3)-(4), where the uncertainties of pressure ($u(P)$), temperature ($u(T)$), and volume ($u(V)$) are 0.001 MPa, 0.1 K, and 0.1 mL, respectively.

$$u(c) = \sqrt{\left(\frac{\sum u(n_i)^2}{n_i^2}\right) + \left(\frac{u(V)}{V^2}\right)^2}$$  

(3)

$$u(n_i) = \frac{n_i}{R} \sqrt{\left(\frac{u(P_i)^2}{P_i}\right) + \left(\frac{u(V_i)}{V_i}\right)^2 + \left(\frac{u(T_i)}{T_i}\right)^2}$$  

(4)

where $n_i$ represents the amount of CO$_2$ or CH$_4$ in the gas phase at the states of initial and equilibrium, and $n_i$ is the amount of CO$_2$ or CH$_4$ dissolved in the mixed sorbent.

### Table 1

Dimensions of the equilibrium cell and magnetic stirrer.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of equilibrium cell</td>
<td>$V_e$</td>
<td>$0.75 \times 10^{-4} \pm 10^{-7}$</td>
<td>m$^3$</td>
</tr>
<tr>
<td>Volume of mixed sorbent</td>
<td>$V_i$</td>
<td>$-10^{-5} \pm 0.7$</td>
<td>m$^3$</td>
</tr>
<tr>
<td>Cross-sectional area</td>
<td>$A_s$</td>
<td>$0.000071 \pm 0.000009$</td>
<td>m$^2$</td>
</tr>
<tr>
<td>Length of magnetic stirrer</td>
<td>$l$</td>
<td>$0.02 \pm 0.001$</td>
<td>m</td>
</tr>
</tbody>
</table>

2.4. Recycling experiment

During the recycling experiment, the mixed sorbent after CO$_2$ sorption was placed into a three-necked flask with a magnetic stirrer. At 308.2 K, N$_2$ was bubbled into the mixed sorbent for 30 min. Then, the mixed sorbent after the regeneration was used for the CO$_2$ sorption again.

2.5. Theory

2.5.1. Henry’s constant

The $K_H$ value of CO$_2$ or CH$_4$ in the mixed sorbent was calculated using Eq. (5):

$$K_H = \lim_{\epsilon \to 0} \frac{P_{\varphi}}{c_i^{\epsilon}}$$  

(5)

where $\varphi$ is the fugacity coefficient of CO$_2$ or CH$_4$ in the vapor phase.

The $\varphi$ value was calculated using the Redlich-Kwong equation of state that was described in Eqs. (6)-(7):

$$\ln\varphi = Z - 1 - \ln(Z - bP/RT) - \left(\frac{a}{P^{2.5}}\right)\ln(1 + bP/RT)$$  

(6)

$$p = \frac{RT}{V - b} \left(\frac{T}{V_m}\right)^{\frac{a}{P^{2.5}}} Z = \frac{PV}{RT}$$  

(7)

where $V_m$ represents the molar volume of CO$_2$ or CH$_4$, $a$ and $b$ are the constants applied for correcting the attractive potential and volume of gas molecules, respectively. The critical pressure ($P_c$) and temperature ($T_c$) of CO$_2$ (CH$_4$) are 7.38 (4.61) MPa and 304.2 (190.6) K, respectively.

2.5.2. Selectivity

The selectivity of CO$_2$ to CH$_4$ ($S_{\text{CO}_2/\text{CH}_4}$) in the mixed sorbent can be obtained using the ratio of Henry’s constant of CH$_4$ over that of CO$_2$ [37], which is described in Eq. (8):

$$S_{\text{CO}_2/\text{CH}_4} = \frac{K_{\text{H,CO}_2\text{-mixed}}}{K_{\text{H,CH}_4\text{-mixed}}}$$  

(8)

2.5.3. The liquid-side mass-transfer coefficient

Based on the mass balance in the gas phase, the overall CO$_2$ mass flux ($N_{\text{CO}_2}$) in the mixed sorbent was expressed in Eq. (9):

$$N_{\text{CO}_2} = \frac{V_G}{ZRT} \left(\frac{dP_{\text{CO}_2}}{dt}\right) = k_aA_i\left(\frac{P_{\text{CO}_2}}{K_H} - C_{\text{CO}_2}\right)$$  

(9)

where $V_G$ is the volume of CO$_2$ in the equilibrium cell, and $P_{\text{CO}_2}$ is CO$_2$ partial pressure at different dissolution times.

According to the mass balance in the equilibrium cell, $C_{\text{CO}_2}$ could be calculated with Eq. (10):

$$C_{\text{CO}_2} = \left(\frac{P_{\text{CO}_2} - P_{\text{CO}_2}}{ZRTV_i}\right)\frac{V_G}{\epsilon}$$  

(10)

After the integration of Eqs. (9) and (10), $k_a$ can be calculated using Eq. (11) with the linear fitting method in the time interval of [0, $t$].

$$\frac{1}{\beta + 1} \ln\left(\frac{P_{\text{CO}_2}}{P_{\text{CO}_2} - \beta P_{\text{CO}_2}}\right) = k_a t$$  

(11)

where the parameters of $\alpha$ and $\beta$ were depicted in Eq. (12).
\[
\alpha = \frac{A_0}{V_L} = \frac{V_0 K_0(T)}{Z R T V_L}
\]  
(12)

In order to use the cross-sectional area of equilibrium cell as the value of \(A_0\), the stirring rate in this study was set at 200 rpm to obtain a smooth and flat gas–liquid interface.

2.5.4. CAF and cost estimation

According to the viscosity (\(\mu\)), molecular weight (\(M\)), selectivity, and Henry’s constant with the unit of Pascal (\(H_s\)), the CAF index was proposed to estimate the cost of CO₂ separation in biogas upgrading [26], where \(H_2O\) was used as the reference solvent. The definition of CAF is shown in Eq. (13):

\[
CAF = \left( \frac{\mu_{H_2O}}{\mu_{mixed}} \right)^{1.00} \left( \frac{M_{mixed}}{M_{H_2O}} \right)^{0.00} \left( \frac{S_{CO₂/H_2O,mixed}}{S_{CO₂/H_2O,H_2O}} \right) \left( \frac{K_{HCO₂,H₂O}}{K_{HCO₂,mixed}} \right)
\]  
(13)

In practice, viscosity is mainly used to describe the effect of the liquid-side mass-transfer coefficient, and Henry’s constant in pascal and the molecular weight are used to describe the Henry’s constant in Pa·m³·mol⁻¹. Therefore, Eq. (13) can be converted into Eq. (14).

\[
CAF = \left( \frac{K_{HCO₂,mixed}}{K_{HCO₂,H₂O}} \right) \left( \frac{S_{CO₂/H_2O,mixed}}{S_{CO₂/H_2O,H_2O}} \right) \left( \frac{K_{HCO₂,H₂O}}{K_{HCO₂,mixed}} \right)
\]  
(14)

3. Results and discussion

3.1. Characteristics of porous carbons

The \(N₂\) adsorption isotherms and pore-size distributions of five types of porous carbons (PCs) are depicted in Fig. 2 and Figs. S1-S4, and the corresponding textural properties are listed in Table 2. It can be seen that the results of \(S_{BET}\) and total pore volume of PC-1, PC-2, PC-3, and PC-4 are larger than that of PC-5, owing to the micro- and mesopore structures. While for PC-5, as shown in Fig. 2, most pore sizes are smaller than 1.0 nm, demonstrating its micropore structure. Generally, micropores with a size smaller than 1.0 nm are considered favorable for improving the CO₂ sorption capacity [38], which was further discussed in the following section.

3.2. Experimental measurement validation

Before measuring the CO₂ and CH₄ solubilities as well as CO₂ sorption rate in the mixed sorbents using the gas–liquid equilibrium set-up, the CO₂ solubility (308.2 K) and CH₄ solubility (313.2 K) in H₂O were measured using the same set-up and compared with the data points reported in the literature [39–41]. As depicted in Fig. 3, the consistent results of gas solubility in H₂O indicate the reliability of the experimental measurements in this study.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Abbreviation</th>
<th>(S_{BET}) (m²·g⁻¹)</th>
<th>(V_t) (cm³·g⁻¹)</th>
<th>(V_{t, 0&lt;1.0 \text{ nm}}) (cm³·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous carbon-1</td>
<td>PC-1</td>
<td>1522.85</td>
<td>0.690</td>
<td>0.223</td>
</tr>
<tr>
<td>Porous carbon-2</td>
<td>PC-2</td>
<td>2357.70</td>
<td>1.169</td>
<td>0.174</td>
</tr>
<tr>
<td>Porous carbon-3</td>
<td>PC-3</td>
<td>2724.08</td>
<td>1.344</td>
<td>0.143</td>
</tr>
<tr>
<td>Porous carbon-4</td>
<td>PC-4</td>
<td>2523.70</td>
<td>1.429</td>
<td>0.138</td>
</tr>
<tr>
<td>Porous carbon-5</td>
<td>PC-5</td>
<td>885.70</td>
<td>0.332</td>
<td>0.242</td>
</tr>
</tbody>
</table>

\(a\) \(V_t\), total pore volume.

3.3. Developing and identifying the mixed sorbent

The pore distribution, especially the amount of micropore of the porous carbon, plays an important role in the CO₂ sorption capacity [42,43]. In this study, the CO₂ sorption capacities in the mixed sorbents with five kinds of porous carbons (PC-1 to PC-5) were measured, where the mass fraction of porous carbon was set at 7.0 wt%. As depicted in Fig. 4, the mixed sorbent with PC-5 exhibits the highest CO₂ capacity, while the mixed sorbent with PC-1 has the lowest CO₂ capacity that is mainly owing to their micropore distributions [25]. The total pore volume with the pore size smaller than 1.0 nm are 0.223, 0.174, 0.143, 0.138, and 0.242 cm³·g⁻¹ for PC-1, PC-2, PC-3, PC-4, and PC-5, respectively. A positive correlation between the CO₂ capacity and the total pore volume with a pore size smaller than 1.0 nm can be inferred in the mixed sorbent, which is described in Fig S5. Therefore, the mixed sorbent of PC-5 and H₂O with better CO₂ separation performance was selected for further biogas upgrading evaluation.

3.4. \(K_S\) values of CO₂ and CH₄ in the mixed sorbent

The solubilities of CO₂ and CH₄ in the mixed sorbents with different PC-5 mass fractions (\(w_{PC} = 0, 1.01, 3.03, 5.02, \text{ and } 6.97\) wt%) at 308.2 K and pressures ranging from 0 to 1.85 MPa were measured experimentally. All the CO₂ and CH₄ solubility data points combined with the deviations are listed in Table S1 and depicted in Fig. 5. It can be seen that both CO₂ and CH₄ solubilities increase linearly with the increasing partial pressures, indicating their physical sorption features. Meanwhile, the increased mass fractions of PC-5 also enhance CO₂ and CH₄ sorption.

![Fig. 2. The curves of N₂ adsorption isotherm (a) and pore-size distribution (b) of PC-5.](image-url)
capacities, which is owing to the higher CO\textsubscript{2} and CH\textsubscript{4} capacities in PC-5 compared to that of H\textsubscript{2}O \cite{44}. However, the increase of CH\textsubscript{4} solubility is inferior for biogas upgrading owing to the possible decrease in the CO\textsubscript{2}/CH\textsubscript{4} selectivity.

Based on all measured CO\textsubscript{2} and CH\textsubscript{4} solubility data points, the $K_H$ values of CO\textsubscript{2} and CH\textsubscript{4} in the mixed sorbents at 308.2 K were calculated using Eq. (5). The results are depicted in Fig. 6. In this study, the $K_H$ value of CO\textsubscript{2} in H\textsubscript{2}O at 308.2 K is 3653.8 Pa·m\textsuperscript{3}·mol\textsuperscript{-1}, which is similar to that reported in the literature \cite{45}. The $K_H$ values of CO\textsubscript{2} and CH\textsubscript{4} in the mixed sorbent decrease with the increasing PC-5 mass fractions, indicating the higher CO\textsubscript{2} and CH\textsubscript{4} sorption capacities in PC-5 than those in H\textsubscript{2}O, as evidenced by the measured solubilities (Fig. 5). For example, the $K_H$ values of CO\textsubscript{2} in the mixed sorbent are 3290.4 and 2354.9 Pa·m\textsuperscript{3}·mol\textsuperscript{-1} when the mass fractions of PC-5 are 1.01 and 6.97 wt\%, respectively, demonstrating the intensification ratio of 39.7 % on the CO\textsubscript{2} solubility. While for CH\textsubscript{4}, its solubility in the mixed sorbent increases 128.2 % when the PC-5 mass fractions increase from 1.01 to 6.97 wt\%. Therefore, the higher increase rate of CH\textsubscript{4} solubility in the mixed sorbent compared to that of CO\textsubscript{2} may be harmful to biogas upgrading owing to the worse CO\textsubscript{2}/CH\textsubscript{4} selectivity at the high PC-5 concentration.
3.5. Selectivity of CO$_2$/CH$_4$ in the mixed sorbent

The selectivity is also an important factor in evaluating the performance of physical sorbents. The selectivity of CO$_2$/CH$_4$ in the mixed sorbent was calculated based on Eq. (8). The results are depicted in Fig. 7. With the increasing mass fractions of PC-5, the $S_{\text{CO}_2/\text{CH}_4}$ values decrease, which is unfavorable for biogas upgrading. When the mass fraction increases from 0 to 6.97 wt%, the $S_{\text{CO}_2/\text{CH}_4}$ value reduces 43.63%. The reason for this phenomenon is that CH$_4$ is slightly soluble in H$_2$O [46,47], while the porous carbon has relatively high sorption capacities both for CO$_2$ and CH$_4$.

However, it should be mentioned that the $S_{\text{CO}_2/\text{CH}_4}$ values in the aqueous PCs are still higher than those of commercialized solvents (i.e., methanol and polyethylene glycol) as well as other mixed sorbents. For example, the $S_{\text{CO}_2/\text{CH}_4}$ values of methanol and polyethylene glycol are 8.62 and 9.26, respectively [48]. For the other mixed sorbents, such as 2-methylimidazole/activated carbon [49], 1-n-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$])/zeolitic imidazolate framework (ZIF-8) [50], and 1-n-butyl-3-methylimidazolium hexafluorophosphat ([Bmim][PF$_6$])/ZIF-8 [51], the $S_{\text{CO}_2/\text{CH}_4}$ values of 2-methylimidazole/activated carbon, [Bmim][BF$_4$]/ZIF-8, and [Bmim][PF$_6$]/ZIF-8 are 4.9–15.4, 2.2–4.0, and 2.5–7.5, respectively. Thus, $S_{\text{CO}_2/\text{CH}_4}$ of the mixed sorbent developed in this study is acceptable.

3.6. $k_L$ value of CO$_2$ in the mixed sorbent

The $k_L$ value is an important engineering parameter for designing sorption/desorption towers, which is strongly related to the viscosity of the mixed sorbent and the hydrodynamics of the separation equipment [30,52]. In this study, to obtain $k_L$, the CO$_2$ sorption rates in the mixed sorbents at 308.2 K with different mass fractions of PC-5 ($w_{\text{PC-5}} = 0, 1.01, 3.03, 5.02,$ and 6.97 wt%) were measured experimentally. Typically, $P_{\text{CO}_2}$-t curves for CO$_2$ dissolution in the mixed sorbents determined in the stirred equilibrium cell are depicted in Fig. 8 (a). The CO$_2$ sorption rate in the mixed sorbent significantly increases with the increasing mass fractions of PC-5, while a drop in the sorption rate is observed when the mass fraction increases from 3.03 to 5.02 wt%. It can be explained that the CO$_2$ sorption rate is dominated by the solubility and the liquid-side mass-transfer coefficient of CO$_2$ in the mixed sorbent, affected by the different PC-5 mass fractions simultaneously.

As shown in Fig. 8 (b), the typical $P_{\text{CO}_2}$-t curves of CO$_2$ in the mixed sorbents were further converted using Eq. (11), where the data points of CO$_2$ sorption rate in the first period ($t < 200$ s) were selected for the $k_L$ calculation. An excellent linear relationship through the point of (0,0) between $\frac{\rho_{\text{CO}_2} \cdot \alpha_{\text{CO}_2}}{\rho_{L} \cdot \alpha_{\text{CO}_2} \cdot \beta_{\text{CO}_2} \cdot \beta_{\text{CO}_2}}$ and $t$ is found, where the slopes represent the $k_L$ values of CO$_2$ in the mixed sorbent.

The calculated $k_L$ values combined with the uncertainties of CO$_2$ in the mixed sorbents are shown in Fig. 9. The $k_L$ value of CO$_2$ in H$_2$O is also obtained for comparison. The $k_L$ value of CO$_2$ in H$_2$O has been widely reported, while an obvious difference can be observed, which is owing to that the $k_L$ value is determined by the diffusion coefficient and the thickness of liquid film [53], where the liquid film thickness is significantly varied for the different equipment and operating conditions [54]. For example, Lu et al. [45] reported that the $k_L$ value of CO$_2$ in H$_2$O at 303.2 K was $4.19 \times 10^{-5}$ m$^2$ s$^{-1}$, while Zhang et al. [55] and Bishnoi et al. [56] reported that the $k_L$ values were $2.1 \times 10^{-5}$ and $2.8 \times 10^{-5}$ m$^2$ s$^{-1}$ at 313.2 K, respectively. In this study, the $k_L$ value of CO$_2$ in H$_2$O determined is $3.94 \times 10^{-5}$ m$^2$ s$^{-1}$ at 308.2 K, indicating the obtained $k_L$ value is reasonable. With the increasing PC-5 mass fractions, the $k_L$ values of CO$_2$ in the mixed sorbent increases first and then falls, and the highest $k_L$ value is observed at the PC-5 mass fraction of 3.03 wt%. The better $k_L$ value with the increasing concentration of PC-5 can be explained as the following two aspects. According to the mechanism of Brownian motion [57–59], an increased concentration of PC-5 is expected to enhance the micro convection, resulting in an intensified CO$_2$ mass transfer rate, i.e., a higher $k_L$ value. On the other hand, a larger CO$_2$ diffusion coefficient in H$_2$O that is confined in the micropore of PC might be achieved owing to that the porous material usually results in a larger CO$_2$ diffusion coefficient in a confined fluid via the interaction [60,61]. However, it has been reported that the agglomeration of porous material in the mixed sorbent could occur when the concentration of porous material was a little bit high [62], which is consistent with a low $k_L$ value for the mixed sorbents at a high-content of PC-5.

3.7. CO$_2$ desorption enthalpy in the mixed sorbent

In addition to Henry’s constant, liquid-side mass-transfer coefficient, and selectivity, CO$_2$ desorption enthalpy in the mixed sorbent is also an important factor featuring its performance. In this study, CO$_2$ solubility data points in the mixed sorbents ($w_{\text{PC-5}} = 6.97$ wt%) at 308.2 K, 323.2 K, and 338.2 K were measured, and the result was depicted in Fig. S5. Furthermore, the Van’t Hoff equation was applied to calculate the CO$_2$ desorption enthalpy in the mixed sorbent [65]. The result shows the CO$_2$ desorption enthalpy in the mixed sorbent is only $-12.95 \pm 3.90$ kJ mol$^{-1}$, indicating its nature of physical dissolution.

Overall, the effect of PC-5 concentration on the CO$_2$ separation performance in the mixed sorbent can be summarized as follows: 1)
higher CO₂ solubility; 2) initial higher and then lower liquid-side mass-transfer coefficient; and 3) lower selectivity. Among them, the high CO₂ solubility and high liquid-side mass-transfer coefficient are beneficial for CO₂ separation, while the low CO₂/CH₄ selectivity will hinder its application for biogas upgrading.

3.8. CAF and cost estimation for CO₂ separation in biogas upgrading

In this study, CO₂ separation performance of the mixed sorbent was evaluated using the CAF index, where H₂O was selected as the reference owing to being a typical solvent for HPWS. The result is depicted in Fig. 10. It can be seen that the mixed sorbent with the PC-5 mass fraction of 3.03 wt% exhibits the highest CAF value, i.e., the best CO₂ separation performance with the considerations of thermodynamic and kinetic properties, which is 1.57 times that of H₂O. Based on the results of Sections 3.4, 3.5, and 3.6, it can be concluded that the performance intensification (i.e., the higher CAF value) of CO₂ separation in biogas upgrading mainly comes from the increases of the CO₂ solubility and the mass transfer coefficient owing to the existence of PC-5.

On the other hand, the cost of CO₂ separation in biogas upgrading was estimated and compared to one typical and widely applied technology, i.e., HPWS [1]. The process flow of aqueous porous carbons for biogas upgrading is depicted in Fig S6, which is the same as that of the typical HPWS process described in our previous studies [18,26]. Raw biogas compression, absorption, flash, and desorption units are included in this process, where the parameters of the packed absorption and desorption towers are listed in Table S2. The economic estimation was followed our previous study [18], where the methodology was illustrated in supporting information. Two assumptions were made: 1) biogas upgrading requirements, facilities size, and operating conditions were the same as those described in our previous study [18,26], and the only change was the biogas production capacity according to the calculation of CAF value; 2) the cost of mixed sorbent was ignored owing to its small contribution on the investment capital as well as the good stability. The calculation results are depicted in Fig. 11. On the other hand, the CO₂ separation cost in biogas upgrading will decrease significantly when the mixed sorbent is applied. Compared to the HPWS technology, the cost of CO₂ separation will decrease by 32.4 %, 36.2 %, 12.8 %, and 7.8 % when the mass fractions of PC-5 in the mixed sorbent are 1.01, 3.03, 5.02, and 6.97 wt%, respectively. Therefore, the mixed sorbents are promising in CO₂ separation for biogas upgrading.
3.9. Recyclability of the mixed sorbent

In addition to the thermodynamic and kinetic properties as well as the cost, the recyclability of the mixed sorbent is also important for its industrial application. The regeneration performance of the mixed sorbent is illustrated in Fig. 12. The regeneration of the mixed sorbent can be realized by the N₂ blowing, which is consistent with the result of CO₂ desorption enthalpy, i.e., it belongs to the physical dissolution. Additionally, the mixed sorbent (w_PC = 3.03 wt%) exhibits a relatively stable ability for CO₂ sorption/desorption after seven cycles, demonstrating its usability for long-term industrial application.

Overall, the mixed sorbent of aqueous porous carbons shows better CO₂ separation performance in biogas upgrading than that of the commercialized HPWS technology. However, the CH₄ purity and CH₄ loss are also important indexes for evaluating the merits of the developed technology, and the requirements are also varied for different countries and regions [8,10], which needs to be further considered. In our future work, a detailed process simulation and economic analysis for using the mixed sorbent to separate CO₂ in biogas upgrading will be conducted. Furthermore, the effect of CO₂/CH₄ mixture on the performance of the mixed sorbent (CH₄ purity, CH₄ loss, and cost) should be determined extensively, and the long-term operational stability as well as the degradation, such as H₂S effect, also needs to be investigated. Additionally, the intensification mechanism on both the gas solubility and mass transfer with the existence of PC should be elaborated deeply, and the quantitative relationship between the pore distributions with the CO₂ capacity, CO₂ sorption rate, and CO₂/CH₄ selectivity will also be established.

4. Conclusion

The mixed sorbent of aqueous porous carbons was developed for CO₂ separation in biogas upgrading. The Henry’s constant (K_H) and the liquid-side mass-transfer coefficient (k_l) of CO₂ in the mixed sorbent as well as the selectivity of CO₂/CH₄ (S_CO₂/CH₄) were measured experimentally. Furthermore, the CO₂ separation performance was evaluated with a previously proposed index named “comparative absorption factor” (CAF), and the cost of biogas upgrading using the mixed sorbent was also estimated.

The presence of porous carbon with the developed micropore structure resulted in better performance in K_H and k_l of CO₂ for the mixed sorbent but worse S_CO₂/CH₄ value. The highest CAF value of 1.57 was achieved at the porous carbon mass fraction of 3.03 wt% compared to that of the widely used absorbents for biogas upgrading. Correspondingly, the estimated cost of CO₂ separation in biogas upgrading using the mixed sorbent could reduce 36.2% compared to the current technologies. The detailed analysis in this study will facilitate the development of aqueous porous carbons applied for practical biogas upgrading.

CRediT authorship contribution statement

Yifeng Chen: Conceptualization, Methodology, Visualization, Investigation, Writing – original draft, Writing – review & editing. Bei Li: Methodology, Writing – review & editing. Ao Wang: Methodology, Writing – review & editing. Kui Wang: Writing – review & editing. Jingcong Xie: Writing – review & editing. Kang Sun: Conceptualization, Writing – review & editing, Funding acquisition. Jianchun Jiang: Supervision, Conceptualization, Funding acquisition. Xiaoyan Ji: Supervision, Conceptualization, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

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