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Humidity sensitivity reducing of moisture swing adsorbents by hydrophobic carrier doping for CO₂ direct air capture

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ABSTRACT

The application of quaternary ammonium-based moisture-swing adsorbent provides an effective strategy for direct air capture (DAC) with low energy consumption of regeneration. This study optimized a fabrication method of shaped adsorbents and a hydrophobicity regulation method by doping polyvinylidene difluoride (PVDF). Characterization of the shaped adsorbents showed a desirable surface area and pore structure. Experiments of CO₂ adsorption revealed that the adsorbents exhibited excellent CO₂ adsorption capacity (~0.90 mmol/ g) in relative humidity (RH) range of $20 \sim 85\%$ was enhanced by 160% of that before doping. Meanwhile, a high CO_2 adsorption rate (with a half-time of 3.6 \sim 3.82 min) at 84.7% RH was displayed. The optimal doping ratio of PVDF was found to be 25% (QAR-25% PVDF). It can effectively release CO2 with 100% RH, and heat assistance (<60 °C) can be considered for optimal results. QAR-25% PVDF exhibited a cyclic capacity of 0.90 mmol/g after ten cycles, demonstrating its stability and reusability. DFT and microscopic characterization revealed the key role of C-F bond in promoting the hydrophobicity of adsorbents. Meanwhile, the isotherm of H₂O/CO₂ adsorption illustrated that doping PVDF could effectively reduce the humidity sensitivity of shaped adsorbents and improve CO₂ adsorption rate significantly. Among DAC adsorbents reported previously, the adsorbents developed in this study showed higher functional group efficiency ($\eta_{OA} = 0.89$) at high humidity conditions. The fabrication method of shaped adsorbent provides a viable strategy for its large-scale deployment. Doping hydrophobic carriers into the adsorbent material is a simple yet effective way to reduce its humidity sensitivity, enabling it to better adapt to complex environmental conditions.

1. Introduction

Numerous severe issues caused by global warming have generated enormous concern in the worldwide community about carbon dioxide emissions [1]. To limit global temperature rise to 1.5 °C, the Intergovernmental Panel on Climate Change (IPCC, 2018) report states that negative CO₂ emissions need to be achieved between 2030 and 2050 [2]. Negative Emission Technologies (NETs) can be classified into two main categories: engineered solutions, such as bioenergy with carbon capture and storage (BECCS) and direct air capture (DAC); and natural climate solutions, such as reforestation and biochar [3]. According to a 2019 joint report on Negative Emission Technologies by the National Academies of Sciences and Engineering, the potential for CO_2 emissions reduction through NETs is significant, with the potential to reduce emissions by 1 billion tons per year by the middle of this century [4]. DAC is a critical component of the NETs portfolio due to its small land and water footprint, ability to handle distributed CO_2 emission sources, and flexible deployment with CO_2 utilization and storage.

The ultra-low CO_2 partial pressure (~40 Pa) in the atmosphere creates main challenge to the effective capture and regeneration of adsorbents. Since the DAC concept was presented by Lackner in 1999 [5], there are three main categories materials for DAC, namely, alkaline metal-based absorbents, adsorbents based on solid amine, and moisture swing adsorbents. Alkaline metal-based absorbents have been

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implemented in commercial applications. However, further research is necessary on the high temperature required for absorbent regeneration [6]. Recent studies have shown that solid amines can be used for adsorption with lower exergy consumption [7,8]. Meanwhile, it is important to prevent oxidative degradation of solid amine adsorbents [9,10]. Both alkaline metal-based absorbents and solid amine adsorbents demonstrate high require for heat.

Moisture-swing adsorption (MSA) process based on quaternary ammonium (QA) adsorbents offers a promising solution to the difficulties encountered with high heat demand and material instability [11,12]. CO_2 adsorption occurs under low humidity, whereas desorption occurs in high humidity environments, typically at 100% RH [13]. The adsorption/desorption cycle is driven by the heat of H2O evaporation, which is freely taken from the environment and has a reported value of approximately 44 KJ/mol [13,14]. The utilization efficiency of the quaternary ammonium functional group (η_{QA}) is close to 100% in a dry condition, generally higher than the amine efficiency (η_{amine}) of solid amine adsorbent (two amines bounded to one CO₂ molecule) [15]. Meanwhile, DAC can couple with renewable energy [11,13]. For instance, MSA can use the electricity generated from renewable energy sources to driven the wind turbines and enhance the CO₂ capture process. However, the large scale deployment of materials and the high impact of humidity become issues that limit the development of MSA.

In the engineering application of DAC, previous moisture swing adsorbents were primarily in powder or particle form, including ion exchange resin [16], quaternized cellulose [17,18] and quaternized chitosan [18,19], which are unlikely to be suitable for large-scale deployment of DAC. In order to prepare adsorbents for large scale deployment, Liu *et al.* developed a molding method that combines quaternary ammonium resin as CO_2 -reactive components and polyether sulfone (PES) as inert binders. However, the high cost of PES and potential environmental hazards make the widespread utilization of such adsorbent a significant challenge [20,21]. Recently, we found cellulose acetate (CA) as a proper alternative option of inert carrier due to its low cost, high flexibility, and porosity [22].

Previous studies have confirmed the essential role of moisture or H₂O in direct air capture, particularly in the moisture swing adsorption process [14,23]. Interfacial H₂O serves as a source of proton transfer and catalyst to enhance CO₂ adsorption. However, excessive H₂O can hinder the dissociation probability of hydrated H₂O molecules and increase CO₂ diffusion resistance and surface reaction resistance, especially in high relative humidity conditions. The main focus of research in MSA has been on regulating the hydrophobic characteristics of adsorbents to increase their activity. Hou et al. utilized reversible addition fragmentation chain-transfer (RAFT) polymerization to synthesize a hydrophobic adsorbent with fluorinated blocks, which exhibited a CO2 adsorption capacity of approximately 2 mmol/g at medium humidity (40% RH). Although the adsorption capacity initially showed promise, it was observed to significantly decay at higher humidity levels. This highlights the need for further improvement in CO2 adsorption performance of adsorbents when operating under high humidity conditions, typically at 60% RH or higher. Alternatively, it may be necessary to explore alternative methods to enhance the hydrophobicity of adsorbents. Polyvinylidene difluoride (PVDF) is a hydrophobic material with low surface energy (typically considered hydrophobic with a surface energy of less than 29 dynes/cm). It also possesses mechanical strength and can be dissolved in a solvent of phase inversion system in a certain proportion, making it an ideal material to add for hydrophobicity purposes.

Based on above challenges, this study proposed a fabrication method of shaped adsorbents and a hydrophobicity regulation method for quaternary ammonium based adsorbent. The doping effect of the hydrophobic carrier (PVDF) was investigated and the optimal doping ratio was determined. The shaped adsorbents are characterized using Fourier transform infrared spectrometer (FTIR), scanning electron microscope (SEM), and N₂ adsorption–desorption (BET). Meanwhile, H₂O static contact angles, Mathers hydrophobicity parameter (MHP) and water



Fig. 1. Fabrication process of QAR and inert carriers (CA and PVDF) shaped adsorbents.

isothermal adsorption were investigated to analyze the hydrophobicity improvement of shaped adsorbents. CO_2 (400 ppm) and H_2O adsorption capacity were tested at different relative humidity conditions. Additionally, the relationship between pore structure, surface characteristics and kinetic behavior of shaped adsorbents was analyzed based on the H_2O/CO_2 kinetic data. Finally, desorption performance and reusability of the shaped adsorbent with optimal doping ratio (PVDF) were investigated. This study presents a potential strategy for mass production, large-scale deployment, and enhancing the tolerance for complex environments of moisture-swing adsorbents.

2. Experimental

2.1. Materials

Cellulose acetate (CA), polyvinylidene difluoride (PVDF) were purchased from Macklin. Polyethylene glycol 400 (PEG-400), N-Methylpyrrolidone (NMP) were purchased from Sinopharm group Chemical Reagent Co., Ltd. Quaternary ammonium cross-linked polystyrene resins (hereinafter referred to as QAR) were purchased from Dongli Chemicals. The QAR were pre-purified according to the standard process, and dried at 70 °C for 8 h. High purity N₂ and CO₂ were purchased from Jingong Special Gas Company. DI water was homemade.

2.2. Fabrication of shaped adsorbents

The shaped adsorbents were prepared by the phase inversion method (Fig. 1) [21]. The pretreated QAR particles were pulverized by mechanical stirring, and sorted by a 200-mesh (d = 75 μ m) sieve tray. 10 g of pre-dried inert carriers (CA and PVDF) and 15 g of PEG-400 were added to the flask, and stirred before the addition of NMP. Then a certain amount of QAR powder was added and stirred for 3 h to obtain a viscous slurry (the proportion of active material is about 60%). The slurry was poured on a clean glass plate, pulled to a long strip with a metal film casting device, and placed in a ventilated desiccator for 24 h. The adsorbents were immersed in DI water for 24 h to remove residual NMP and PEG-400. To activate the sorbents by ion exchange, these composites were immersed in 1 mol/L Na2CO3 aqueous solution for 2 days. The adsorbents were washed with lots of DI water for \sim 4 times to remove residual Na₂CO₃ and stored in DI water [23]. The doping ratios of PVDF to CA were chosen at 0, 1:3, 2:3, and 1:1 (i.e., 0%, 25%, 40%, and 50%. For convenience, hereinafter referred to as "QAR-CA/25% PVDF/40% PVDF/50% PVDF"). The average density of our shaped adsorbent is 0.51 g/cm³. More information about shaped adsorbents can be seen in Table 1.

2.3. Characterization methods

SEM images of the shaped adsorbents were obtained on a Hitachi SU8010. The distribution of the adsorbents was analyzed on Energy Dispersive Spectrometer (EDS) of X-max80 (Oxford Diffraction, Co, Ltd, England). N₂ physisorption experiments were conducted on a Micrometrics ASAP2460 at 77 K. Surface areas were performed using the BET method on a Quantachrome Autosorb IQ3, and data was obtained at partial pressures (P/P_0) ranging from 0.05 to 0.3. Pore volumes were estimated by the total N₂ sorption at a partial pressure of 0.99. A Thermo Nicolet iS50 FTIR spectrometer equipped with ATR accessories was used

Table 1

Characteristics of the shaped adsorbents.

	Carrier composition	$q_{\rm N} ~({\rm mmol/g})^{\rm a}$	$q_{\rm CO_2} \ (\rm mmol/g)^b$	$\eta_{\rm QA}$	$S_{BET} (m^2/g)$	Pore volume (cm ³ /g)	Average pore diameter (nm)
QAR-CA	100 % CA	2.08	0.56	0.54	5.48	0.028	14.23
QAR-25% PVDF	$25\%\ PVDF+75\%\ CA$	2.02	0.90	0.89	10.88	0.022	8.10
QAR-40% PVDF	40 % PVDF + 60% CA	2.05	0.89	0.87	10.16	0.020	7.92
QAR-50% PVDF	50%~PVDF + 50%~CA	2.09	0.87	0.83	11.25	0.022	7.72

^a $q_{\rm N}$ is the ion density determined by conductometric titration.

^b $q_{\rm CO_2}$ is measured at 20 °C and 84.7% RH.

to estimate FTIR spectra. The H_2O static contact angles of the materials were measured using Dataphysics OCA20, and the test was repeated 3 times to obtain the average contact angle. The H_2O equilibrium adsorption capacity was measured by Quantachrome Aquadyne DVS based on gravimetric analysis.

2.4. CO₂ adsorption/desorption measurements

The CO₂ adsorption at 400 ppm of the shaped adsorbents was performed by the volumetric method. As shown in Fig. S1a, the fixed bed reactor is placed in a thermostat (\pm 0.1 °C), with a fan inside to simulate airflow disturbance (2 m/s) and weaken the influence of air film diffusion resistance. The CO₂ and H₂O concentrations of the recirculating gas were measured by an infrared gas analyzer (Li-840A). With H₂O in ppt (parts per thousand), we chose 5 ppt, 10 ppt, 15 ppt, and 20 ppt as the experimental conditions at 20 °C, which correspond to the relative humidity of 21.2% RH, 42.3% RH, 63.5% RH, and 84.7% RH. With a 400 ppm difference in CO₂ concentration between the interior and the ambient, the CO₂ leakage rate was determined as 3.21×10^{-3} ppm/s, and leakage induced errors could be neglected.

At the beginning of experiment, a certain amount of the adsorbent was placed in the sample holder, and the system was purged with dry high-purity N₂ for 1 h at 20 °C to remove H₂O and CO₂. After purging, the gas circulation pump was turned on and a fixed amount of high-purity CO₂ was manually injected through the syringe. Once the CO₂ concentration is stable, the abovementioned steps were repeated until



Fig. 2. (a) SEM image of QAR-CA, (b) SEM image of QAR-25% PVDF, (c) the photograph of the shaped adsorbent, (d) FT-IR spectra of QAR particle, QAR-CA, PVDF particle and QAR-25% PVDF.



Fig. 3. (a) N₂ physisorption isotherms at 77 K of shaped adsorbents, (b) pore volume of different pore size ranges.

no decrease in CO₂ concentration induced by adsorption was observed. The recirculating gas flow was 1.0 L/min. The humidity was precisely controlled by a homemade humidity control device (more details seen in Fig. S2) during the experiment with fluctuations of \pm 0.2 ppt. The CO₂ adsorption capacity q_{ad} (mmol/g) is calculated as follows:

$$q_{\rm ad} = \frac{q_{\rm inj} \times 10^{-3} - c_{\rm e} V_0 \times 10^{-6}}{\rm m} V_{\rm m} \times 10^3$$
(1)

where q_{inj} (ml) is the total volume of CO₂ injected, c_e (ppm) is the CO₂ concentration at equilibrium, V_0 (L) is the reactor volume, m (g) is the mass of shaped adsorbent, and V_m (L/mol) is the molar volume.

The desorption experiment process is shown in Fig. S1b. The sample after adsorption was placed in the sample holder. and the system was purged with dry high-purity N₂ for 1 h at a constant temperature to remove H₂O and CO₂. Then use dry air purging for more than 3 h to ensure that the adsorbent is completely saturated. The CO₂ desorption was purged using wet N₂ (100% RH, by bubbler device) in a constant temperature chamber. Finally, the adsorbent was dehydrated by purging with dry N₂ and the dry sample mass was weighed. CO₂ desorption capacity q_{de} (mmol/g) of the adsorbent is shown as follows:

$$q_{de} = \int_0^{t_{de}} \frac{Q_{N_2}c}{60 \times 10^3 m V_m} dt$$
 (2)

where Q_{N_2} (L/min) is the N₂ purge flow rate, c (ppm) is the outlet CO₂ concentration, t_{de} (s) is the desorption time.

For the cyclic experiments, we put the adsorbent sample into DI water (100% RH) after adsorption to allow the adsorbent fully regenerate. Then, the adsorption-regeneration process was repeated.

2.5. Quantum chemistry calculation methods

Mathers Hydrophobicity parameter (MHP), which is $\text{Log } P \text{ SA}^{-1}$, was calculated quantitatively to analyze the improvement of the hydrophobicity of adsorbents [24]. The Octanol-Water Partition Constant (Log *P*) of CA and PVDF monomer molecules were calculated using Chem-Draw [25]. The monomer molecular structures of two carriers were simulated using Gaussian 09 package.

3. Results and discussion

3.1. Chemical characteristics

The SEM images provided a visual representation of the surface geometry of the shaped adsorbents. As shown in Fig. 2a, the fabrication process resulted in a uniform distribution of the active component (QAR) and the inert carrier (CA). The inert carrier exhibited a porous membrane-like structure, which facilitated gas-phase mass transfer. The QAR particles were encapsulated within the inert carrier, leaving the active sites exposed for efficient CO₂ adsorption. After doping hydrophobic carrier (PVDF), the changes in surface geometry became more apparent (Fig. 2b and Fig. S3). PVDF doping was observed to be evenly distributed on the surface of the adsorbent. Additionally, the EDS analysis conducted on QAR-CA did not detect any signal of element F, indicating successful incorporation of PVDF through the doping process. The clustered PVDF particles covered the carrier membrane, while the smaller PVDF blended with CA to form the carrier membrane, reducing the mechanical strength of the carrier due to the better flexibility of CA than PVDF. This resulted in pore expansion and collapse. In Fig. S4, EDS images showed the uniform distribution of the elements after PVDF doping.

The FTIR spectra of the shaped adsorbents and raw QAR/PVDF particle were shown in Fig. 2d. Characteristic bands of CA were observed, such as C-H stretching at 2911 cm⁻¹, C=O stretching at 1728 cm⁻¹, and C-N stretching at 1097 cm⁻¹ [26,27]. After doping PVDF, it can be observed that pure PVDF has three strong peaks at 1405, 1182 and 876 cm⁻¹, which are bending vibration in the plane of CH₂ group, stretching vibration of CF₂ group, and skeleton vibration of C–C bond [28]. The stability of the QA group during the fabrication process was demonstrated by a broad band of skeletal vibration of the quaternary ammonium group at 1455 cm⁻¹ [17,21] found for shaped adsorbents. It indicated that the mechanical action, such as pulverizing and stirring during the fabrication, did not cause the QA group to degrade or fall off. More information can be seen in Fig. S5.

In Table 1, it demonstrated a significant increase in specific surface area of PVDF material after doping, while the average pore diameter slightly decreased. This can be attributed to two factors: the expansion effect on smaller original pores and the collapse of larger original pores, forming micropores due to PVDF doping. Thus, the specific surface area of the material increased and the average pore diameter decreased. The reduction of pore volume resulted from the collapse of partial pore structure and the clustered PVDF covering behavior, which is more obvious in the higher PVDF doping ratio (as shown in Fig. S3). From Fig. 3a, it can be observed that the N₂ adsorption behavior of adsorbents in the low N₂ partial pressure region after doping PVDF. It confirmed the formation of micropores, and this point can be supported further. From Fig. 3b and Fig. S6, the pore volume contributed by micropores of the shaped adsorbent increased to three times of the original one after doping PVDF. Meanwhile, the decrease of pore volume contributed by macropores after doping PVDF indicated the expansion to collapse of macropores.

In order to better analyze the utilization rate of quaternary ammo-

(a)





(d)



Fig. 4. The static contact angle of (a) QAR-CA, (b) QAR-25% PVDF, (c) QAR-40% PVDF, (d) QAR-50% PVDF. (e) The ball and bond type molecular after optimization. (f) The MHP value and specific fragments contribution.

nium functional group, the functional group efficiency is defined as $\eta_{QA} = q_{CO_2}/q_N$, where q_{CO_2} is CO₂ adsorption capacity of adsorbents at a specific humidity level (measured at 20 °C and CO₂ partial pressure of 40 Pa). Upon analyzing the data presented in Table 1, we observed that η_{QA} of QAR-CA at high humidity was only 0.54. However, after doping PVDF, η_{QA} ranged from 0.83 to 0.89. It indicated that PVDF doping can effectively improve η_{QA} at high humidity condition. The accessibilities of the QA functional groups through ionic transport at full hydration or gaseous transport at high hydration were found to be at similar levels.

3.2. The effect of PVDF doping on the hydrophobicity of adsorbents

Static contact angles of adsorbents (with DI water) doped with different ratio were tested in order to better understand the impact of hydrophobicity after doping PVDF. The results were given in Fig. 4a-d. Weak hydrophobicity of QAR-CA was quantified as contact angles, θ_c , of 94.8°. After 25% PVDF doping, $\theta_c = 116.1^\circ$ meant stronger hydrophobicity, and θ_c steadily rose with increasing doping ratio. It suggested that adding hydrophobic carrier to adsorbents can significantly promote their hydrophobicity.

We found that the C-F bond plays a key role in the hydrophobicity improvement. It has been established that Mathers Hydrophobicity



Fig. 5. (a) H_2O adsorption of shaped adsorbents at 20 °C and different relative humidity, (b) H_2O adsorption kinetics of shaped adsorbents at 20 °C and 84.7% RH, (c) CO_2 adsorption capacity and $t_{1/2}$ of shaped adsorbents at 20 °C and 84.7% RH, (d) CO_2 adsorption rate of shaped adsorbents at CO_2 concentration of 20 °C and 84.7% RH.

parameter (MHP) may reflect the broadest range of functional groups and polymer structures among a number of regularly used hydrophobicity models for polymers [29]. Fig. 4e exhibited the monomer ballstick model after optimization. The surface area (SA) of a monomer molecule was calculated using Multiwfn, and the SA contribution of particular fragments was examined [30]. The contribution's results were displayed in VMD. Fig. S7 displayed further simulation details. In Fig. 4f, the MHP calculation results were displayed. After 25% PVDF doping, MHP value significantly changed (MHP > 0.009), indicating that the hydrophobicity was greatly promoted. MHP value slightly rose as the doping ratio changed. As the PVDF doping ratio increased, the contribution of C-F to the SA increased from 4.51% to 11.52%. Additionally, the SA contribution ratio of -COO-, -OH (hydrophilic functional groups) to C-F reduced from 5.80 to 1.93. It indicated that the hydrophobic functional groups play a crucial role in determining the hydrophobicity of adsorbents.

3.3. CO₂ adsorption/desorption performance

 $\rm H_2O$ isothermal adsorption tests were conducted on the adsorbent both before and after PVDF doping (Fig. 5a). The results indicated that the water adsorption capacity of the shaped adsorbents significantly decreased under high humidity conditions after doping PVDF. This suggested that the addition of PVDF effectively reduces the humidity sensitivity of the adsorbents. We defined $t_{1/2}$ (half-time) as the time needed to attain half of the total adsorption capacity, which served as a metric to evaluate the kinetic performance of the shaped adsorbents. The results showed that the adsorption process for H₂O took longer than that of CO₂. Specifically, the shaped adsorbents took over 3 h to complete the H₂O adsorption process at 84.7% RH (Fig. 5b), while CO₂ adsorption processes were all completed within 1 h and CO₂ saturation was more than 50% at 11 min. For QAR-25% PVDF, the CO₂ adsorption process spent 0.5 h, while the water vapor adsorption saturation θ^{i} is only 0.67 simultaneously. The adsorbent had better selectivity for CO₂ due to its higher adsorption rate for CO₂ compared to H₂O. The reason for this phenomenon was not only the high adsorption rate of CO₂ by the adsorbent itself, but also the higher H₂O saturated capacity of the adsorbent, which resulted in longer adsorption time for H₂O.

The sensitivity of the adsorption performance towards humidity change was investigated. After PVDF doping, the sensitivity to humidity was obviously reduced, while the CO₂ adsorption capacity at 400 ppm remained at around 0.9 mmol/g. Additionally, the half time of adsorption, $t_{1/2}$, reached to 3 ~ 4 min, decreased by more than 50% relative to before doping. The adsorbent doped with high ratios (40%/50%) maintained excellent adsorption performance even at high relative humidity (84.7% RH), with only a minor decrease in adsorption capacity (Fig. 5c).

The impact of doping on the kinetics of H₂O/CO₂ adsorption was

Table 2H2O/CO2 adsorption rate in different adsorbents.

	Conditions	H_2O adsorption rate (1/s)	CO ₂ adsorption rate (1/s)
QAR-CA QAR-25% PVDF QAR-40% PVDF QAR-50% PVDF	$T = 20 ^{\circ}\text{C}$ 84.7% RH θ , $\theta' = 0.5$	$\begin{array}{l} 2.3 \times 10^{-3} \\ 5.9 \times 10^{-3} \end{array}$ $7.3 \times 10^{-4} \\ 3.1 \times 10^{-4} \end{array}$	$\begin{array}{l} 5.0 \times 10^{-3} \\ 9.0 \times 10^{-3} \\ 8.5 \times 10^{-3} \\ 7.9 \times 10^{-3} \end{array}$

investigated. Analysis of Fig. 5d revealed that the CO₂ adsorption rate increased for all adsorbents following PVDF doping. CO₂ adsorption rate of these adsorbents at the initial stage of adsorption procedure was twice that of QAR-CA, and it remained about twice before half of the adsorption procedure ($\theta = 0.5$), which was also reflected in the change of $t_{1/2}$. QAR-25% PVDF exhibited an exceptionally fast $t_{1/2}$ of only 3.6 min, surpassing previously reported adsorbents. In Table 2, the H₂O/CO₂ adsorption rates were examined under conditions of 84.7% RH, CO₂ saturation $\theta = 0.5$, and H₂O saturation $\theta' = 0.5$. It can be seen that CO₂ adsorption rate increased by 1.58 ~ 1.80 times, while the H₂O adsorption rates of the adsorbents decreased by one order of magnitude after PVDF doping, only the adsorption rate of QAR-25% PVDF increased slightly ($5.9 \times 10^{-3} \text{ s}^{-1}$).

The lower doping ratio (25%) of QAR-25% PVDF resulted in anomalous performance. The increased specific surface area promoted the gas-phase mass transfer process for both H_2O and CO_2 . However, the lower amount of PVDF also limited its ability to hinder the diffusion process of H_2O . As a result, the rates of both H_2O and CO_2 adsorption increased. Although higher doping ratios (40%/50%) could effectively hinder the entry of H_2O , they caused more damage to the inert carrier layer. The carrier layer was largely covered by clustered PVDF particles, which could potentially prevent some CO_2 active sites from being exposed. This resulted in a slight decrease in adsorption capacity and a slight increase in half-time. Additionally, the mechanical properties of these adsorbents were poor at a macroscopic level. Therefore, a doping ratio of 25% was deemed optimal for PVDF.

To further investigate the effect of humidity on adsorption performance, CO₂ adsorption tests were conducted for QAR-CA and QAR-25% PVDF under varying relative humidity conditions. As illustrated in Fig. 6a, the CO₂ adsorption capacity of QAR-25% PVDF remained constant (~0.9 mmol/g) across all four relative humidity test points. However, the $t_{1/2}$ values fluctuated but remained within a short time frame of 3.6 to 3.8 min. The CO₂ adsorption capacity of QAR-CA decayed gradually as humidity increased from 21.2% RH to 84.7% RH with 35% capacity decay ratio. Additionally, $t_{1/2}$ became longer with increasing humidity (8.0 ~ 11 min).

Comparison of the efficiency of the quaternary ammonium functional group (η_{QA}) and the amine efficiency (η_{amine}) of reported adsorbents under both low and high relative humidity conditions revealed that the quaternary ammonium adsorbents were notably affected by humidity changes, with η_{QA} experiencing a significant decrease in high



Fig. 6. (a) CO₂ adsorption capacity and $t_{1/2}$ of QAR-CA and QAR-25% PVDF at different relative humidity, (b) η_{QA} and η_{amine} comparison at low and high humidity conditions, (c) CO₂ adsorption capacity and $t_{1/2}$ of QAR-25% PVDF at high relative humidity conditions, (d) desorption performance of QAR-25% PVDF.

Table 3

H₂O/CO₂ adsorption rate at different conditions.

	Conditions	H ₂ O adsorption rate (1/s)	CO ₂ adsorption rate (1/s)
QAR-CA	63.5% RH, θ , $\theta' = 0.8$	9.7×10^{-4}	6.2×10^{-4}
QAR-25% PVDF	63.5% RH, θ , $\theta' = 0.8$	1.8×10^{-4}	$1.1 imes 10^{-3}$
	90.2% RH, θ , $\theta' = 0.5$	/	$9.5 imes 10^{-3}$
	94.8% RH, θ , $\theta' = 0.5$	/	9.1×10^{-3}

humidity conditions (Fig. 6b) [31,32]. However, the adsorbents in this paper which were treated with PVDF doping, demonstrated the stable efficiency of η_{QA} . The efficiency of η_{QA} remained consistently high despite changes in humidity levels, while η_{amine} was low due to less utilization of amine. Compared to other DAC adsorbents previously reported, the adsorbents developed in this study showed higher functional group efficiency ($\eta_{QA} = 0.89$) even at high humidity levels. Compared with reported adsorbents previously, the shaped adsorbents in this study had lower humidity sensitivity [20,21,31], as shown in Fig. S8. QCPS-2/PES and I-200 had large capacity decay with increasing humidity, even I-200 decayed to 0 capacity at ~80% RH. While QAR-25% PVDF maintained high CO₂ capacity over a wide range of humidity.

In Table 3, the adsorption rates of QAR-CA and QAR-25% PVDF were investigated when RH = 63.5%, CO₂ saturation $\theta = 0.8$, H₂O saturation $\theta' = 0.8$. For QAR-CA, considering the same saturation, H₂O adsorbed faster than CO₂. In the actual adsorption procedure, θ' was less than 0.8 when $\theta = 0.8$, the adsorption rate of water was greater than 9.7 × 10⁻⁴ s⁻¹. This leaded to inhibition of the CO₂ adsorption process and ultimately caused a decrease in CO₂ adsorption capacity at 63.5% RH. For QAR-25% PVDF, considering the same saturation, the CO₂ adsorption rate is 1 order of magnitude higher than that of water vapor. The adsorption process. Therefore, this adsorbent could maintain excellent adsorption capacity under varying humidity conditions.

Moreover, it was examined whether QAR-25% PVDF retains its ability to regenerate using moisture swing. The CO_2 adsorption performance of QAR-25% PVDF at higher humidity was measured, as showed in Fig. 6c. At relative humidity levels above 90%, the adsorbents showed a higher rate of H₂O adsorption. However, the QAR-25% PVDF adsorbent had limited ability to hinder the water, leading to a decreased CO_2 adsorption capacity. This presented the potential for regeneration through moisture swing of this adsorbent. Consider the desorption effect within 30 min, the results showed that QAR-25% PVDF could only achieve 0.21 mmol/g desorption capacity at room temperature condition. With heating assistance, the CO₂ desorption capacity could reach 0.41 mmol/g at 40 °C and 0.49 mmol/g at 60 °C (Fig. 6d). The adsorbent demonstrated a relatively short time required to reach 80% desorption capacity (17 ~ 24 min), allowing for continuous operation throughout one day. This indicated that QAR-25% PVDF, despite the addition of a hydrophobic inert carrier, retained its ability to regenerate through moisture swing. Additionally, the residual heat of 40 ~ 60 °C could be utilized in practical scenarios to achieve the ideal desorption capacity of the adsorbent.

Based on the CO₂ adsorption capacity and $t_{1/2}$ at 400 ppm as the basis to evaluate whether the adsorbent has excellent adsorption performance. Table S1 showed a comparison between the performance of these adsorbents and previous quaternary ammonium adsorbents. QAR-25% PVDF exhibited a high CO₂ absorption capacity under both low and high humidity conditions, as well as a low half-time, indicating superior performance for DAC.

3.4. Adsorbent reusability

Considering the reusability of this adsorbent, CO₂ adsorption capacity of QAR-25% PVDF was tested in a cycle at 400 ppm, 20 °C, RH = 21.2% and 84.7%, as shown in Fig. 7. The results showed that no obvious attenuation of CO₂ saturation capacity was found in 10 times tests, which meant the cycling stability. The adsorbent did not degrade under high humidity conditions. The degree of regeneration (q_i/q_{1st}) was above 90% in all 10 cycles, indicating that the adsorbent was almost fully regenerated. The cyclic capacity of shaped adsorbent was ~0.9 mmol/g. Moreover, the high elemental dispersion was maintained from the EDS spectrum of Fig. S4, which also indicated the high chemical stability. Shaped adsorbents have the potential for large-scale application in the future DAC circumstances.

4. Conclusion

This study aimed to investigate the fabrication method and hydrophobicity regulation of QA moisture-swing adsorbent. To achieve macro-production of adsorbents, we proposed a fabrication procedure that combined inert carrier and porous quaternary ammonium resin. Additionally, we presented a method to regulate hydrophobicity by doping PVDF. The shaped adsorbents exhibited a desirable surface area



(b) 1.0 (a) 400 ppm q_i (mmol/g) 1.0 0.8 0.8 0.6 $q_i / q_{1 \mathrm{st}}$ q_i/q_{1st} 0.6 0.4 capacity 04 ģ 0.2 0.2

7

0.0

10

9

Fig. 7. Cyclic adsorption performance of QAR-25% PVDF at (a) 20 °C, 21.2% RH, (b) 20 °C, 84.7% RH.

0.0

2

3

4

5 6

Cycle times

and pore structure. The study conducted H₂O static contact angles, MHP and H₂O isothermal adsorption tests on shaped adsorbents. The results indicated that the surface hydrophobicity of the adsorbents was significantly enhanced through PVDF doping. The CO₂ adsorption capacity showed significant decay at high humidity conditions (a 35% decrease was observed at 84.7% RH) prior to doping. After doping, the adsorbents exhibited excellent CO₂ adsorption capacity (~0.90 mmol/g) and a high CO_2 adsorption rate (with a half-time of 3.6 ~ 3.82 min) at 84.7% RH. Meanwhile, the optimal doping ratio of PVDF was found to be 25%. QAR-25% PVDF exhibited excellent CO2 capacity across a wide range of humidity levels. It can effectively release CO2 with 100% RH, and heat assistance (<60 °C) can be considered for optimal results. The QAR-25% PVDF exhibited a cyclic capacity of 0.90 mmol/g after ten cycles, demonstrating its stability and reusability. The fabrication method of shaped adsorbent provides a viable strategy for its large-scale deployment. Doping hydrophobic carriers into the adsorbent material is a simple yet effective way to reduce its humidity sensitivity, enabling it to better adapt to complex environmental conditions.

Much remains to be done. It includes finding a suitable location for adsorbent placement to minimize pressure drop in CO_2 capture device, as well as gathering more data to fully evaluate adsorbent performance. Moving forward, we will focus on these areas to support the development of DAC technology.

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

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2023.143343.

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