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A moisture-driven direct air capture device for low-cost gas fertilizer

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Direct air capture (DAC) is a negative carbon emission technology that faces challenges in scalability and practical deployment due to its exorbitant costs. Hou et al. (2017) integrated DAC technology with fertilization. A multi-bed desorption system driven by water provides a competitive and sustainable carbon source for indoor agriculture.

Global warming has precipitated a lot of challenges, including escalation of extreme weather events, rapid melting of glaciers, and a consequent rise in sea levels. These developments can disrupt the delicate balance of ecosystems, compromise agricultural production, and exacerbate transmission of heat-related diseases. The greenhouse effect is the primary cause of global warming. Long-wave radiation emitted from the ground is absorbed by excessive greenhouse gas emissions, thereby shifting the atmospheric heat balance and leading temperatures to rise. Greenhouse gas emission reduction has become imperative, and carbon capture, utilization, and storage (CCUS) technology is one of the most effective solutions.

Traditional carbon capture methods, e.g. pre-combustion capture, post-combustion capture, and oxygen-enriched combustion, are used to reduce CO_2 emissions from fixed sources in industrial facilities. To further reduce CO_2 concentration in the atmosphere in line with the 1.5 ℃ temperature rise vision of the Paris Agreement, negative emission technologies like direct air capture (DAC) are indispensable.

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Chemical absorption and adsorption driven by the temperature-swing process are two basic DAC methods which are also widely used in flue gas capture. However, in air with extremely low concentrations of CO_2, the working capacity of sorbents is quite limited, leading to considerable regeneration energy consumption. Considering changes in the free energy of ideal mixed gas through capture processes, the theoretical separation work of DAC is close to that of post-combustion capture (Lackner, 2013), which means that DAC technology still has broad development prospects.

Moisture-swing adsorption (MSA) is another carbon capture method proposed by Lackner (2009), which shows the potential to level down costs due to its near-zero regeneration heat consumption. Moisture-swing adsorbents are usually polymer compounds loaded with quaternary ammonium groups (NR_{4+}), such as strongly basic ion-exchange resins, which adsorb CO_2 molecules by means of chemical reactions. Water plays an important role in adsorption reactions. The number of bound water molecules has a significant influence on adsorption enthalpy, so that CO_2 is adsorbed in dry conditions and desorbed in wet conditions (Shi et al., 2018) (Fig. 1a).

Although the MSA method can be implemented at room temperature, using the temperature-swing process in conjunction with it (Fig. 1b) can further improve the desorption rate and thermodynamic efficiency (Xie et al., 2024). During the adsorption stage, air flows over sheet-like adsorbents. After reaching a certain adsorption saturation, the adsorption bed is closed, and heating and humidification processes are carried out to desorb CO_2. Desorption gas can be extracted with an air pump. After desorption, the bed should be cooled and dried. In practice, the drying, cooling, and adsorption processes are implemented simultaneously by means of a centrifugal fan. Com-

pared with temperature-swing adsorption (TSA) using heat sources, which are often higher than 100 ℃, MSA demands lower temperatures for desorbing water (40~60 ℃ is sufficient). This allows MSA to conveniently adopt waste heat, facilitating energy cascade utilization. During the drying process, adsorbents are cooled without an extra cooling source, which further reduces the energy consumption of the MSA process. Considering the pre-drying requirements for adsorption, water-spray operations for desorption, and the potential dehumidification requirements for product gas, a water recovery and management system (Fig. 1c) could be necessary to control water consumption. Since demands for dehumidification and water supply co-exist in the MSA system, it also delivers a high coupling potential with atmospheric water harvesting.

Current MSA research mainly focuses on adsorption mechanisms and materials, with little discussion of practical application scenarios. Unlike the granular adsorbents used in TSA, membrane adsorbents are preferred in MSA, because they offer a larger specific surface area and superior adsorption kinetics. Hot pressing and phase inversion methods are the two most commonly used for membrane shaping. To ensure sufficient desorption and drying of membranes, the packing density is much lower than that of particles. This directly leads to the low desorption purity of MSA, limiting its application scenarios.

Hou et al. (2017) demonstrated the feasibility of MSA technology applied in agricultural gas fertilization. The group proposed a multi-bed desorption system capable of providing a continuous and stable CO_2 supply to a greenhouse (Fig. 1d). Quaternary ammonium-based resin membrane of the carbonate-ion type was used. This type of membrane can easily upgrade CO_2 concentration from 400 parts per million (ppm) to thousands of ppm (Wang et al., 2011). The entire MSA desorption system has a packing density of 250 kg/m^3, a filling volume of 1 m^3, and a feeding capacity of 20 kg CO_2 per day. These parameters are determined by the adsorption and desorption performance of the adsorbent.

A series of desorption experiments in a rotating reactor was also carried out to obtain desorption isotherms and kinetics of the quaternary ammonium-based adsorbent. As water was sprayed into the closed desorption reactor, CO_2 concentrations easily reached 2000 ppm, up to more than 10000 ppm. The desorption rate and cyclic capacity increased with temperature. When the temperature rose from 25 ℃ to 45 ℃, the desorption rate constant increased by an order of magnitude, and the duration for maintaining a specific CO_2 concentration (such as 1000 ppm) was also extended from 57 min to 98 min.

For a single desorption bed to provide a long-lasting supply, the CO_2 in desorption beds needs to be continuously cycled to greenhouses. With a stripping gas flow rate of 10 L/s, CO_2 concentrations can reach 5-10% at the beginning of the desorption process, then sharply drop and stabilize around 1% for several hours at the end. Through a cultivation experiment, the authors have determined that the optimal concentration of CO_2 is about 1000 ppm, and 800 ppm is selected as the lower limit. Under these conditions, MSA system can fertilize a 3000 m^3 greenhouse. The bed operation at different temperatures are investigated and found that increasing the desorption temperature to improve the kinetics can reduce adsorbent costs. A temperature rise of 20 ℃ can increase the cyclic desorption capacity by nearly 80%.

To obtain a more stable CO_2 supply, the system is disassembled into multiple desorption units. When the CO_2 concentration of a desorption unit in the system reaches the lower limit, it will be replaced by a new unit. The old unit is dried and prepared for desorption again (the adsorption process and drying process are synchronous). The optimal system parameters such as the number of units, outlet CO_2 concentration, and desorption temperature are discussed. The number of units consists of two parts (N_1 and N_2), where N_1 is the number of parallel desorption units, and N_2 is the number of adsorption units. Due to the enhanced desorption kinetics at higher temperatures, the system requires more and smaller desorption units to stabilize the concentration fluctuations. Conversely, the activation time interval between various MSA units is extended at high temperatures, which reduces the number of adsorption units. The total number of MSA units needed is smaller at higher temperatures. At a desorption temperature of 45 ℃, when the CO_2 concentration at the outlet increases from 1% to 5%, the total unit number and desorption unit number are both smaller. However, desorption

time and replacement interval time at high outlet concentrations are shorter, leading to a larger number of adsorption units and a decrease in cyclic desorption capacity.

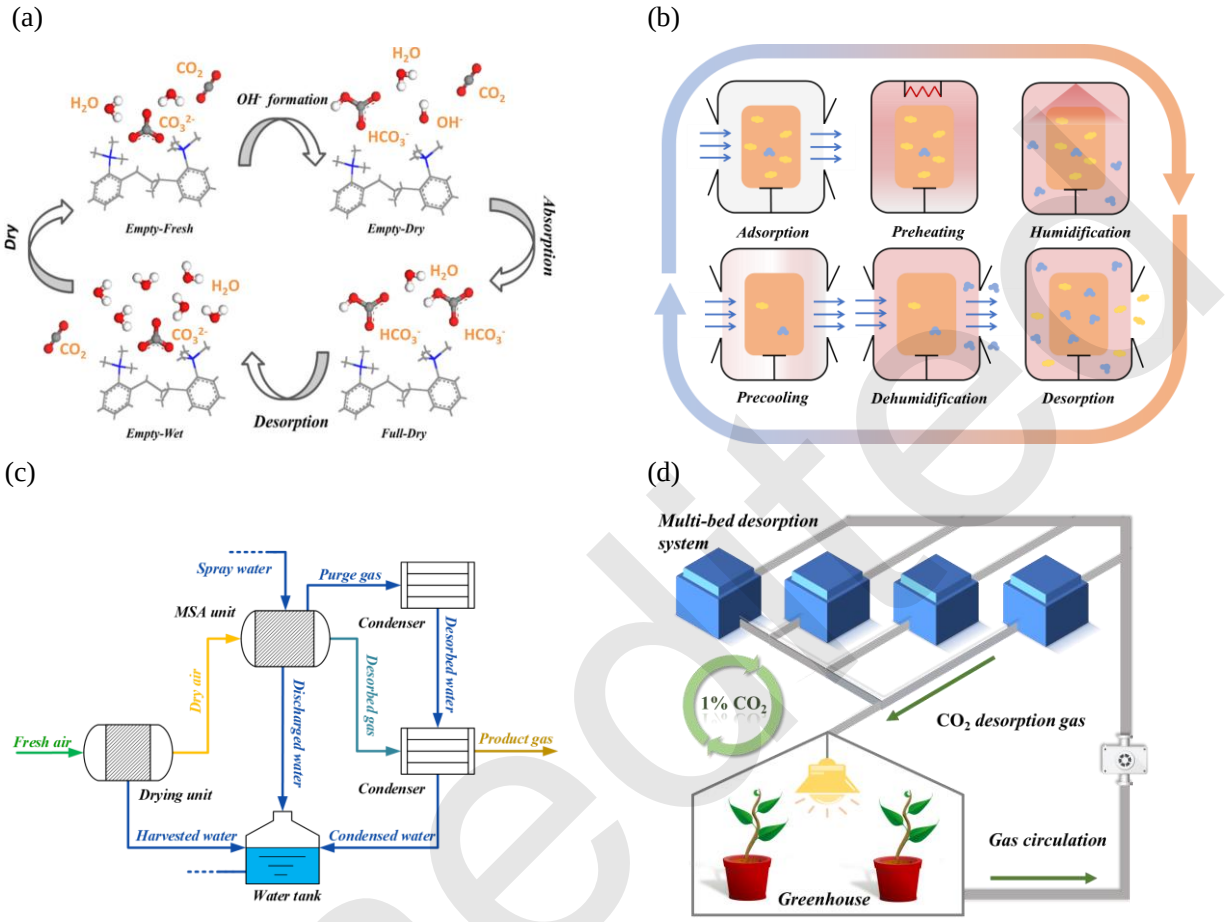

Fig. 1 The mechanism, process and, systems of moisture-driven DAC: (a) Adsorption mechanism of MSA (Shi et al., 2018); (b) 6-step MSA process with temperature swing (Xie et al., 2024); (c) Water recycling system of MSA; (d) A multi-bed MSA desorption system used for gas fertilizer (Hou et al., 2017)

The authors also evaluated the energy consumption and capital costs of the MSA system. Energy consumption includes fan power consumption and water consumption, which is converted from energy consumption of water desalination. Desorption water can be heated by waste heat, and its energy consumption is ignored. The capital costs consist of the expense of sorbent material, DAC unit containers, fans, and other accessories, e.g., piping and valves. Under various conditions, an outlet concentration of 3% and desorption temperature of 45 ℃ are the optimal system parameters. The system offers a minor energy consumption of 35.7 kJ/mol and a cheaper capture cost of 34.68 USD/t compared to flue gas capture (67.6 USD/t) (Knoope et al., 2014).

Through modeling on an optimized multi-bed desorption system, Hou et al. (2017) proved that MSA technology can be a sustainable and economical gas fertilizer source for indoor agriculture. However, energy consumption of water is obtained from water desalination, which could be replaced by a more adaptive technology such as atmospheric water harvesting. Adsorbent degradation should be considered, as it may seriously weaken the actual cyclic desorption performance and operation cost.

Overall, CO_2 gas fertilizer is probably one of the most promising application scenarios for highlighting the low energy consumption characteristics of MSA. When applying MSA in a higher CO_2 concentration application scenario, further purification with a recti-

fication system may be required, which would increase its energy consumption. To address the inferior purity, high capacity absorbents, fast vacuum regeneration methods, and high-density packing techniques should be developed. The latter two points are optimizations at the process level, which need to be improved and perfected in engineering demonstrations.

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Author contributions

Jiang LONG and Renyu XIE initiated the project. Renyu XIE organized the first draft of the manuscript. Shen CHEN helped to draw pictures and revise the first draft. Xuejun ZHANG and Jiang LONG helped to revise and edit the final version. All authors contributed to the discussion.

Conflict of interest

Renyu XIE, Sheng CHEN, Xuejun ZHANG and Long JIANG declare that they have no conflict of interest.

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