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Integrated direct air capture and CO_2 utilization of gas fertilizer based on moisture swing adsorption*

Cheng-long HOU[1], Yu-song WU[1], You-zhou JIAO[2], Jie HUANG[1], Tao WANG[†‡1],
Meng-xiang FANG[1], Hui ZHOU[3]
(*[1]State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China*)
(*[2]Key Laboratory of New Materials and Facilities for Rural Renewable Energy of the Ministry of Agriculture,*
Henan Agricultural University, Zhengzhou 450002, China)
(*[3]Department of Earth and Environmental Engineering, Columbia University, New York 10027, USA*)
[†]E-mail: oatgnaw@zju.edu.cn

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Abstract: A new concept of low-cost direct air capture technology integrated with a fertilization system is proposed, as an alternative to the application of air derived CO_2. A moisture swing sorbent can elevate the CO_2 concentration from 400 parts per million (ppm) to several thousand ppm, and this can be used to cultivate plants. Desorption isotherms were determined and are described well by a Langmuir model. The adsorption rate constant and the desorption rate constant were gained at 25 °C, 35 °C, and 45 °C under 1000 ppm concentration of CO_2. In accelerated cultivation experiments, the effects of CO_2 concentration, light intensity, and spectrum on the CO_2 uptake rate of the plants were investigated. A multi-bed desorption system which is capable of providing a continuous and stable CO_2 supply for a greenhouse is demonstrated based on the desorption characteristic and CO_2 uptake feature of plants. An energy and cost assessment for the integrated system was performed and the results indicated that minimum energy requirements and cost estimate of CO_2 are 35.67 kJ/mol and 34.68 USD/t, respectively. This makes direct air capture a competitive and sustainable carbon source for agriculture.

Key words: Direct air capture; Desorption kinetics; Greenhouse; CO_2 fertilizer; Cost analysis
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1 Introduction

According to the mitigation scenarios given by the Intergovernmental Panel on Climate Change (IPCC), the temperature change caused by anthropogenic greenhouse gas (GHG) emission should be kept to less than 2 °C for sustainable development (IPCC, 2014). So far, carbon capture and storage (CCS) is viewed as an effective means of addressing anthropogenic CO_2 emissions and global warming. Traditional CCS technologies, such as post-combustion capture and oxy-fuel combustion, can capture CO_2 emitted from large point sources, followed by transportation of CO_2 and physical storage or chemical conversion (Benson and Orr, 2008). Alternatively, direct air capture of CO_2 (DAC) presents a promising approach to fix CO_2 emitted from distributed sources (Lackner *et al.*, 1999; Lackner, 2009; Wang *et al.*, 2011), followed by physical storage or chemical conversion without transportation. CO_2 utilization, such as fuel synthesis and algae planting, with DAC and renewable energy (Brilman *et al.*, 2013; Goldberg *et al.*, 2013) would potentially revolutionize the net-zero carbon economy.

[‡] Corresponding author

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ORCID: Tao WANG, http://orcid.org/0000-0002-0535-7821

For the regeneration of sorbent, DAC technologies can be categorized into three types: temperature swing (Kong *et al.*, 2015; Pang *et al.*, 2015), vacuum swing (Gebald *et al.*, 2014; Wurzbacher *et al.*, 2016), and moisture swing (Wang *et al.*, 2011; 2013; Shi *et al.*, 2016a; 2016b). For the first two technologies, strong alkali Ca/K/Na based solvent/sorbent (Bandi *et al.*, 1995), solid amines (Choi *et al.*, 2011; Goeppert *et al.*, 2011), and modified metal-organic frameworks (MOF) (Schell *et al.*, 2012; Lee *et al.*, 2014) have been proposed for direct air capture. Although substantial high-temperature heat (150–850 °C) or electricity would be required for the temperature or vacuum swing process, CO_2 concentration could be elevated directly from 400 parts per million (ppm) to 100% (Wurzbacher *et al.*, 2012). On the other hand, the moisture swing process based on quaternary ammonium functional groups (Wang *et al.*, 2011; He *et al.*, 2013) can separate CO_2 directly from the air with low-grade heat. The partial pressure of CO_2 could be increased by two orders of magnitude by wetting the sorbent (Wang *et al.*, 2011). This moisture-induced cycle utilizes the free energy released by water evaporation and avoids the use of heat for sorbent regeneration (Wang *et al.*, 2013). In addition, various CO_2 utilization processes integrated with air capture technology have been proposed or developed. DAC can provide an *in situ* carbon source for hydrocarbon materials, such as fuel (Goldberg *et al.*, 2013), polymer (Dey *et al.*, 2012), and bio-products (Brilman *et al.*, 2013). Nikulshina *et al.* (2006) employed the high temperature $Ca(OH)_2$-$CaCO_3$ cycle to capture CO_2 from the air. Using concentrated solar heat, the captured CO_2 could be reformed into syngas with an additional methane source. Researchers at the University of Southern California, USA developed a Ru-based catalyst for the production of CH_3OH from *in situ* hydrogenation of CO_2 on a polyamine sorbent (Kothandaraman *et al.*, 2016). Goldberg *et al.* (2013) suggested combining the air capture and CO_2 geological storage at a remote Kerguelen island for long-term carbon sequestration. High-grade energy, such as high-temperature heat, electricity or hydrogen rich fuel, is generally required for regeneration of sorbent during the above process.

An alternative approach to utilize the CO_2 captured from ambient air is the cultivation of plants, such as algae and crops. CO_2 fertilization has been proved to be efficient in greenhouse agriculture, which can be used to cultivate vegetables out of season and boost yields (Qiu *et al.*, 2013; Khoshnevisan *et al.*, 2014). Studies showed that increasing CO_2 concentration can boost the yields for both C3 and C4 plants (Poorter, 1993), promote the rates of leaf photosynthesis of vegetables like chickpea (Saha *et al.*, 2015), Gerbera jamesonii (Xu *et al.*, 2014), and cucumber (Zhou *et al.*, 2004), and enhance the disease-resistant ability of vegetables (Runion *et al.*, 1994; Hibberd *et al.*, 1996; Ferrocino *et al.*, 2013). Traditional CO_2 fertilization methods utilize concentrated CO_2 from flue gas (Wolff *et al.*, 2015) or CO_2 from the reaction between sulfuric acid and ammonium bicarbonate. These methods generally have issues of gas contamination or high cost. The optimum CO_2 concentrations for the cultivation of plant and natural algae are found to be 0.1%–0.2% and 1%–3%, respectively (Chiu *et al.*, 2008; Park *et al.*, 2013), which are only 1–2 orders of magnitude higher than those in ambient air. Therefore, CO_2 fertilization from air capture can take advantage of the thermodynamically low energy requirement for gas separation. Brilman *et al.* (2013) cultivated microalgae using the solid amine based air capture technology under a regeneration temperature of 70–80 °C rather than over 100 °C. Moisture swing technology based on the quaternary ammonium sorbent could be another candidate for gas fertilization. The concentration of desorbed CO_2 (1%–5%) (Wang *et al.*, 2011) matches with that of CO_2 fertilization. In order to efficiently integrate the moisture swing-based DAC technology to CO_2 fertilization, one needs to explicitly understand the kinetics of CO_2 fixation during cultivation, as well as the desorption kinetics of the CO_2 sorbent.

In this study, moisture swing technology based on a quaternary ammonium sorbent is proposed to provide CO_2 fertilization for greenhouse agriculture. Lettuce is selected for studying the CO_2 fixation kinetics at different CO_2 concentrations and growth stages. The desorption kinetics of the sorbent are measured experimentally and fitted to the Langmuir model. The kinetic parameters under different temperatures are obtained. Then a zero dimensional mass transfer model is built to simulate the CO_2 desorption rate in a fix bed reactor. For the continuous and stable supply of CO_2, a multi-bed desorption system is designed and the operation strategy is discussed. Finally, the requirements of energy, water, and capital cost are analyzed for the optimization of the integrated system.

2 Experiments and models

2.1 Desorption performances

2.1.1 Materials

A quaternary ammonium-based anion exchange resin is employed in this study for the air capture sorbent. The material was supplied in the form of a heterogeneous sheet with Cl^- as the exchangeable ion (Wang *et al.*, 2011). By introducing carbonate ions (CO_3^{2-}) into the material, the sorbent can directly capture the CO_2 from the air at relatively low humidity. When it is wet, the sorbent can be regenerated with the release of CO_2.

2.1.2 Desorption isotherms

The desorption reactor set-up consists of a 1.05 L chamber equipped with a rotating sample holder and a water sprayer as shown in Fig. 1. Dry samples were initially saturated in the chamber by being exposed to standard gas with CO_2 concentration of 400 ppm at 1 L/min for 2 h. Over 99% of full saturation could be reached according to isotherms (Wang *et al.*, 2011). Deionized water was then sprayed into the chamber from the top to initiate the desorption process. The rotation of samples could not only accelerate the wetting of the sample, but also strengthen the diffusion of desorbed CO_2 to the environment. The water was drained out of the reactor immediately to reduce the dissolution of CO_2 in water. During the desorption process, the gas was cycled with a peristaltic pump (BT300-2J, Longer, China) and the concentration of CO_2 in the chamber was logged every second by an infrared gas analyzer (LI-840A, LI-COR, USA). The chamber temperature was controlled and kept constant by a water bath system with a fluctuation of ±0.5 °C.

Desorption isotherms were obtained by plotting the relationship between sorbent saturation and CO_2 equilibrium partial pressure at a certain temperature. In the closed system, the wet sample reached a certain equilibrium state after a period of time, at which point its saturation can be calculated as

$$\theta = 1 - 1000(C_1 - C_2)V_0/(22.4mq_0), \tag{1}$$

where θ is defined as the saturation of sorbent, m (kg) is the mass of sorbent, q_0 (mol/kg) is the CO_2 capacity for sorbent in carbonate form (Wang *et al.*, 2011), C_1 is the equilibrium CO_2 concentration and C_2 is the initial CO_2 concentration inside the chamber which were both measured by infrared gas analyzer (IRGA), and V_0 (m^3) is the volume of the reactor. For the CO_2 sorbent, the relationship between θ and the CO_2 concentration in equilibrium (C_e) can be described by the classic Langmuir equation (Wang *et al.*, 2013):

$$\frac{\theta}{1-\theta} = K_d C_e, \tag{2}$$

where K_d is the equilibrium constant of desorption.

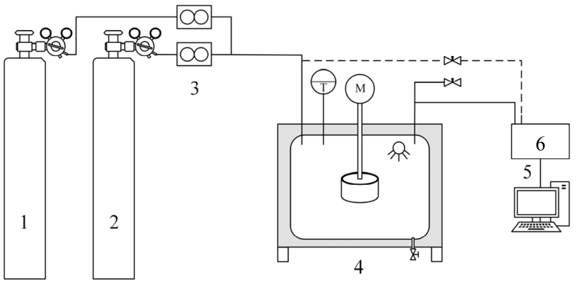

Fig. 1 Layout of the desorption equilibrium measurement system

1: N_2; 2: CO_2; 3: flow meter; 4: desorption reactor; 5: peristaltic pump; 6: IRGA. Parts 4, 5, and 6 form a closed cycle (with dashed line) for desorption isotherm measurement

2.1.3 Desorption kinetics

Desorption kinetic experiments were conducted in the desorption reactor as mentioned above. Similar to isothermal experiments, dry samples were fully loaded with CO_2 under a concentration of 400 ppm and then were wetted for desorption. For a closed reactor, the gaseous CO_2 concentration increased during desorption and the rate could be determined by the slope of the desorption curve. When the CO_2 concentration inside the reactor exceeded the upper limit (e.g., 2000 ppm), wet N_2 (>95% relative humidity) was then introduced to flush the reactor with a flow rate of 1 L/min. The purge process stopped when the CO_2 concentration at the outlet reaches a lower limit (e.g., 1000 ppm) and the desorption system was closed again for a second around kinetics measurement. The total amount of desorbed CO_2, Q_d (mol), under a certain CO_2 concentration, C, can be calculated by

$$Q_{\mathrm{d}} = Q_{\mathrm{off}} + \frac{P^0 V_0 C}{RT}, \tag{3}$$

where Q_{off} (mol) is the accumulated amount of CO_2 flushed off the reactor before each test and is zero for the first round measurement; P^0 is the atmospheric pressure which is 1.01×10^5 Pa; R is the universal gas constant which is 8.314 J/(mol·K) and T is the temperature of the experimental system. CO_2 saturation of the sample can be calculated by

$$\theta = 1 - Q_{\mathrm{d}}/(mq_0). \tag{4}$$

The apparent desorption rate defined by $\mathrm{d}\theta/\mathrm{d}t$ could be determined from the slope of the curve of θ against time t, $\mathrm{d}\theta/\mathrm{d}t$. According to the Langmuir equation, the desorption kinetics can be expressed as

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = k_{\mathrm{a}}(1-\theta)C - k_{\mathrm{d}}\theta, \tag{5}$$

where k_a is the adsorption rate constant, and k_d is the desorption rate constant. The rate constants are temperature-dependent and can be obtained by linear fitting of Eq. (5) at a constant temperature.

2.2 CO_2 fertilization experiments

Seeds of lettuce were buried in a piece of sponge with 1 cm^3 volume. By keeping the sponge wet, the seeds germinated in a week and then were transplanted into a vessel used for soilless cultivation. The nutrient solution was replaced every three days. The germination and initial cultivation processes were performed in a curing room to ensure stability of temperature, humidity, and light intensity. All the relevant parameters of cultivation conditions are given in Table 1. Two weeks after germination, lettuce samples of similar size were selected for the accelerated cultivation experiment with different CO_2 concentrations.

The accelerated cultivation experiments were conducted in a closed chamber which can hold 30–50 lettuce vessels. The atmospheric temperature and humidity were controlled. Illumination devices were employed to provide two modes of the spectrum: white and a mixture of red and blue (4:1). The gas tight measurement was tested and the CO_2 leakage rate was lower than 0.5 ppm/h under a CO_2 concentration of 2000 ppm. When a given amount of CO_2 was injected into the chamber, the CO_2 concentration in the reactor would quickly reach a maximum value and then gradually drop because of the CO_2 uptake during photosynthesis. The instantaneous rate of CO_2 uptake (mol/(s·m^2)) can be determined from the curve of concentration against time.

Table 1 Atmospheric parameters for cultivation

Parameter	Value	
	Germination and initial cultivation	Accelerated cultivation
Temperature (°C)	25.0	25.0
Humidity (%)	60.0–65.0	60.0–65.0
Light intensity (lux)	48 000	18 000–98 000
CO_2 concentration (ppm)	480	400–3000

3 Results and discussion

3.1 CO_2 desorption performance

Desorption isotherms under different temperature are illustrated in Fig. 2. The desorption data is a good fit to the Langmuir model. Through moisture swing desorption, the CO_2 concentration could be easily increased from 400 ppm (ambient) to the level of 2000 ppm which is favorable for accelerated cultivation of the green plant. The desorption ratio, $1-\theta$, can be significantly enhanced by increasing the desorption temperature from 25 °C to 45 °C. This indicates the potential of utilizing low-grade heat.

Desorption kinetic parameters were obtained through linear fitting of Eq. (5). The desorption rates under CO_2 concentrations of 1000, 2000, and 3000 ppm were employed for curve fitting, as seen in Fig. 3a. As the kinetic parameters should be independent of CO_2 concentration, the results of kinetic parameters in Table 2 were the average value of the corresponding parameter under the three different

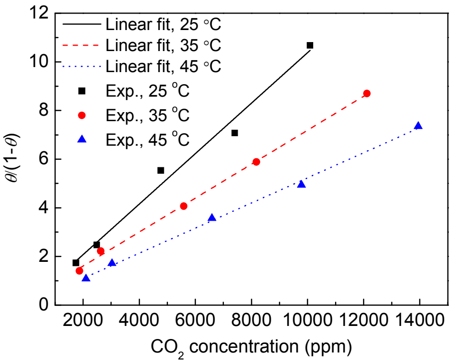

Fig. 2 CO_2 desorption isotherms at different temperatures

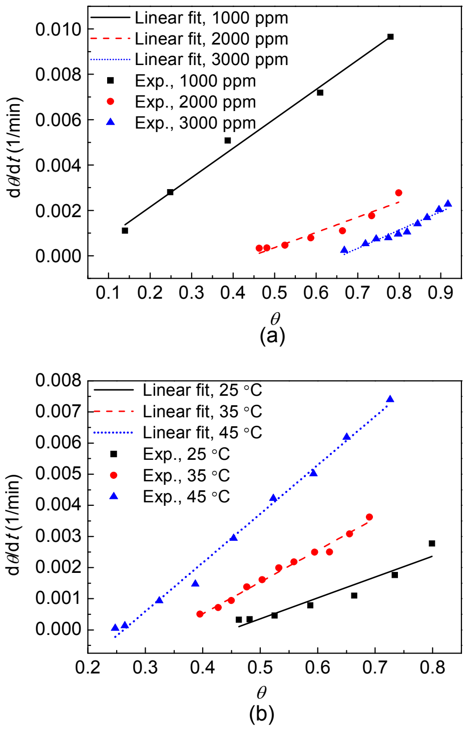

Fig. 3 Performance of desorption kinetics under different conditions: (a) 25 °C, different CO_2 partial pressures; (b) CO_2 concentration of 2000 ppm, different temperatures

CO_2 concentrations. The rate constants increase significantly with increased temperature, as shown in Fig. 3b and Table 2.

3.2 Accelerated cultivation by CO_2 fertilization

The effect of CO_2 concentration on the CO_2 uptake rate of lettuce was measured and is plotted in Fig. 4. For lettuce under two different growth stages, CO_2 uptake rates both increase dramatically as the CO_2 concentration increases from 400 ppm to 1000 ppm and then reach a plateau (Fig. 4a). Although the lettuces in the mature state (21 d after germination) have larger leaf area compared to those at the early stage of growth (14 d after germination), the CO_2 uptake rate per unit leaf area is relatively low. The CO_2 uptake rate also increases with increased light intensity and then reaches a plateau. It is interesting to find that the CO_2 concentration has a significant effect on the light saturation point. As shown in Fig. 4b, the light saturation point can be extended from 60 000 lux to 80 000 lux by elevating the CO_2 concentration from 400 ppm to 1000 ppm.

Table 2 Thermodynamic and kinetic parameters during desorption

Parameter	Value		
	25 °C	35 °C	45 °C
K_d ($\times10^{-4}$) (r)	10.43 (0.98)	7.23 (0.99)	5.29 (0.99)
$(1-\theta)$ (%)	67.1	59.1	51.4
k_a (1/(Pa·s))	8.90×10^{-6}	1.25×10^{-5}	2.00×10^{-5}
k_d (1/(Pa·s))	8.50×10^{-4}	1.72×10^{-3}	3.78×10^{-3}
T_d (min)	57.1	76.8	97.6
q_{cyc} (%)	10.5	14.6	19.0

r is correlation coefficient; $(1-\theta)$ is the calculated desorption ratio of sorbent under a CO_2 concentration of 2000 ppm; T_d is the desorption time for maintaining CO_2 concentration at 1%; q_{cyc} is the cycling capacity of the sorbent for a single DAC unit

Fig. 5 shows the effect of the light spectrum on CO_2 uptake rate under 1000 ppm CO_2. Compared to the white spectrum, the spectrum of red & blue can enhance the CO_2 uptake rate by 18.2% and 42.8% for lettuces of 14 d and 21 d after germination, respectively. This is consistent with the results of previous studies under CO_2 concentrations of 300–400 ppm (Wang *et al.*, 2014). Therefore, a CO_2 concentration of 1000 ppm and light spectrum of red & blue with 80 000 lux intensity could be considered as optimal planting conditions.

3.3 Optimization of CO_2 fertilization system

3.3.1 Desorption model for DAC unit

An integrated system which combines moisture swing adsorption-based DAC and greenhouse agriculture is proposed. To maintain a stable gas pressure inside the greenhouse, the stripping gas for the DAC desorption unit is cycled from the greenhouse. According to the above CO_2 fertilization study, the

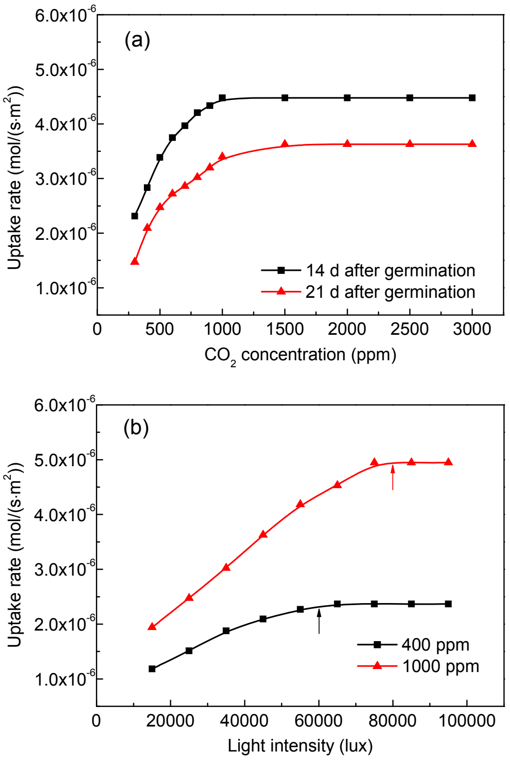

Fig. 4 Effects of CO$_2$ concentration (80 000 lux white light) (a) and white light intensity (14 d after germination) (b) on CO$_2$ uptake rate of the plants (light saturation points are marked by arrows)

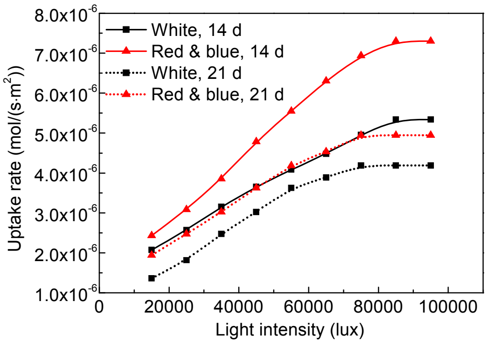

Fig. 5 Effects of light spectrum on CO$_2$ uptake rate of the plants at two different growth stages under 1000 ppm CO$_2$

optimal CO$_2$ concentration is around 1000 ppm. Hence, 800 ppm is selected as the lower limit in the greenhouse, as well as the inlet CO$_2$ concentration of stripping gas for DAC desorption unit. For convenient calculation, the CO$_2$ concentration can be considered as uniform inside the DAC unit at an instantaneous time t. For practical implementation, strong turbulence can be produced to ensure uniform CO$_2$ concentration inside the DAC unit.

A zero dimensional desorption model is developed, as illustrated in Fig. 6. φ (m^3/s), $C_{\text{in-0}}$, and V (m^3) represent gas flow rate, CO$_2$ concentration of inlet gas, and the volume of the DAC unit, respectively. The CO$_2$ concentration at the outlet is governed by the following equations:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = k_{\mathrm{a}}(1-\theta_i)C_i - k_{\mathrm{d}}\theta_i, \tag{6}$$

$$C_{i+1} = C_i + \left[-mq_0\frac{\mathrm{d}\theta}{\mathrm{d}t}\frac{22.4}{1000} + \varphi(C_{\text{in-0}} - C_i)\right]\Delta t/V, \tag{7}$$

$$\theta_{i+1} = \theta_i + \frac{\mathrm{d}\theta}{\mathrm{d}t}\Delta t, \tag{8}$$

where C_i and C_{i+1} represent the outlet CO$_2$ concentration at instantaneous time t_i and t_{i+1} ($t_{i+1}=t_i+\mathrm{d}t$). In the initial state, θ_0 equals 1 and C_0 equals $C_{\text{in-0}}$. The outlet CO$_2$ concentration at any moment can be achieved by discretizing the time derivative and iterative calculation.

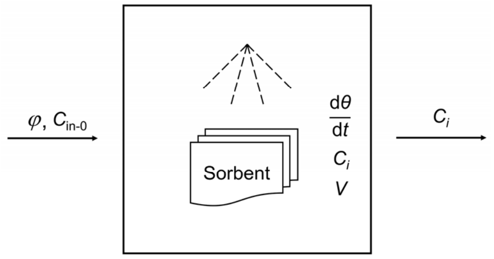

Fig. 6 Zero dimensional model of a DAC desorption unit

By assuming a feeding capacity of 20 kg CO$_2$ per day, which can fertilize a greenhouse with a volume of around 3000 m^3, 0.1 L/s of pure CO$_2$ flow rate or a stripping flow rate of 10 L/s for outlet CO$_2$ concentration of 1% is required. Based on the capacity and adsorption/desorption kinetics of resin sorbent, the requirement of the sorbent is estimated as 250 kg. For a desorption chamber with a packing density of 250 kg/m^3, the CO$_2$ outlet concentration change with time was calculated by employing the above zero dimensional model. As illustrated in Fig. 7, the outlet CO$_2$ concentration is as high as 5%–10% within the first few minutes because of the relatively high desorption kinetics in the initial state. Although the CO$_2$ concentration decreases dramatically, it stabilizes at around 1% for hours. It was also found that under the same CO_2 concentration, a higher desorption rate and cycling capacity of the sorbent can be achieved by increasing the temperature. As listed in Table 2, for an outlet CO_2 concentration of 1%, the cycling CO_2 capacity can be increased from 10.5% to 19% as the desorption temperature increases from 25 °C to 45 °C. This can be realized by utilizing low-grade heat from agricultural process, including fermentation or combustion of biomass (Caton *et al.*, 2010).

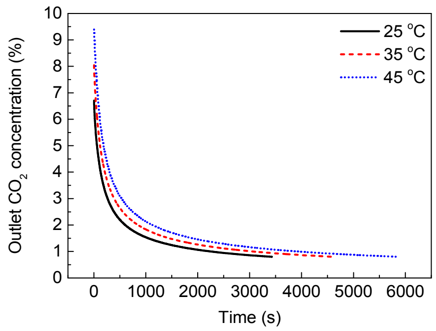

Fig. 7 Outlet CO_2 concentration of DAC sets at three different temperatures (1 m^3 desorption chamber with a packing density of 250 kg/m^3, and a stripping gas flow rate of 10 L/s)

3.3.2 Multi-bed desorption model

In order to obtain stable CO_2 output from the DAC during the CO_2 fertilization process, a multi-bed desorption system is proposed as shown in Fig. 8. For sorbent of a constant total amount of 250 kg, it can be divided uniformly into DAC desorption units of number N_1. The DAC units, from 1 to N_1, were then introduced into the desorption system in sequence. When the CO_2 concentration at the outlet reaches the lower limit, a new DAC unit would be added. The (N_1+1)th unit would be introduced to replace the first DAC unit which has the longest desorption time and lowest loading in the whole desorption system. The replaced DAC unit would then be dried and ready for adsorption. For a desorption system with a constant total sorbent, the increased unit number N_1 could reduce the fluctuation of CO_2 concentration at the outlet, as shown in Fig. 9.

A preliminary study showed that at least 15 units were required in the desorption system to obtain an outlet CO_2 concentration of 1%. The system complexity and capital cost increase with the increase of unit number. Therefore, higher CO_2 concentrations at the outlet, i.e., 2%, 3%, and 5%, were studied as typical conditions for further optimization. Taking 3% CO_2 at the outlet as a representative condition, Fig. 10 demonstrates the fluctuation of CO_2 concentration. The total sorbent amount in the desorption system and total supply of CO_2 are kept constant at different temperatures. The relative fluctuation of CO_2 concentration is controlled to be within ±20%, which is equivalent to a concentration fluctuation of ±3.3 ppm in the greenhouse with the volume of 3000 m^2. N_1 is determined as 5, 6, and 7 for temperatures of 25 °C, 35 °C, and 45 °C, respectively. Because of higher desorption kinetics at higher temperatures, DAC units of smaller size and larger number are required to control the fluctuation. On the other hand, the DAC desorption system would have a longer interval time (t_{int}) between two neighbor units under higher temperature so that a lower adsorption unit number, N_2, would be required. By assuming that every unit leaving desorption system needs 2 h for drying and adsorption, the total DAC unit number (N_1+N_2) required was determined as 19, 16, and 16, for 25 °C, 35 °C, and 45 °C, respectively. Therefore, higher desorption temperature or kinetics can significantly reduce the requirement of sorbent material.

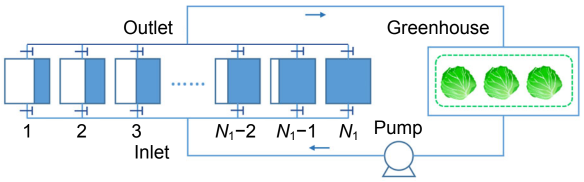

Fig. 8 Multi-bed DAC desorption system for the CO_2 fertilization

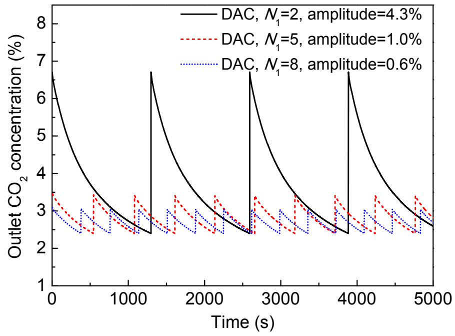

Fig. 9 Output CO_2 concentration of DAC system with different numbers of units at 25 °C

Under constant desorption temperature of 45 °C, the desorption was simulated based on different average CO_2 concentrations at the outlet to seek the required number of DAC units. As shown in Fig. 11, with a flow rate of 0.1 L/s CO_2 and a concentration fluctuation of 20%, the calculated N_1 are 11, 7, and 4 for outlet CO_2 concentrations of 2%, 3%, and 5%, respectively. Although fewer desorption units are required for the CO_2 concentration of 5%, the desorption time for single unit, t_{des}, and interval time, t_{int}, between two neighbor units turn out to be shorter. This would result in a larger DAC unit number for absorption, N_2. Assuming a drying and re-adsorption process taking 2 h, the total number of DAC units is calculated as listed in Table 3. Moreover, the cycling capacity of the sorbent decreases by 48% as outlet CO_2 concentration increases from 2% to 5%, because of shortened t_{des}. The relatively low cycling capacity will result in higher requirements on material and water. Therefore, the energy consumption and material requirement ought to be balanced to seek the minimum cost of direct air capture in this system.

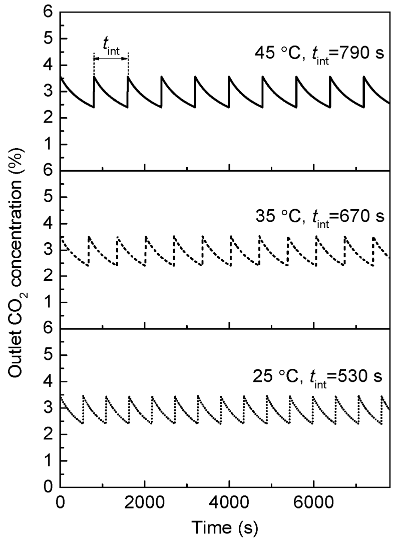

Fig. 10 Outlet CO_2 concentration of DAC sets at 25 °C, 35 °C, and 45 °C

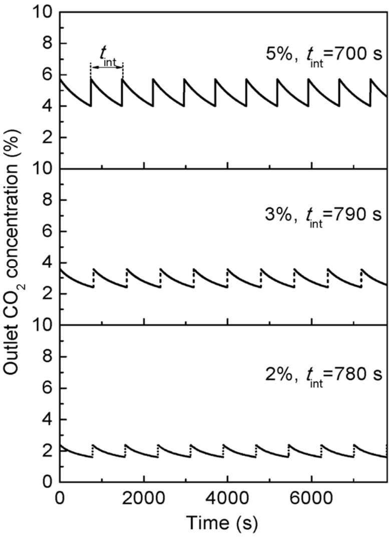

Fig. 11 Outlet CO_2 concentration of DAC sets at 2%, 3%, and 5%

Table 3 Calculation of DAC numbers with different outlet CO_2 concentrations

CO_2 concentration	N_1	N_1+N_2 (weight (kg))	t_{des} (s)	t_{int} (s)
2%	11	20 (454.55)	8580	780
3%	7	16 (571.43)	5530	790
5%	4	14 (875.00)	2800	700

3.3.3 Energy and cost analysis

By considering a passive adsorption of CO_2 from the air without forced convection, the energy and material consumptions of DAC system would be dominated by electricity for pumping CO_2 from the desorption chamber to the greenhouse and water for wetting the sorbent. The desorption temperature, e.g., 45 °C, could be maintained by the waste heat. The electricity for pumping desorbed CO_2 is calculated by

$$E_{pump} = W_p / Q, \tag{9}$$

where W_p (W) is the total power of fans, and Q (mol/s) is the flow rate of desorbed CO_2. With a constant flow rate of desorbed CO_2, the flow rate of stripping gas will decrease with increased concentration of desorbed CO_2. Therefore, both the power for fans and E_{pump} (Fig. 12) will decrease with increased concentration of desorbed CO_2.

As for the hydrophilic property of sorbent, the requirement of water for wetting sorbent should be constant for the same amount of sorbent. Therefore, the water consumption per mole of CO_2 is inversely proportional to the cycling capacity, q_{cyc}. As the cost of water is discrepant regionally, the water is assumed to be supplied by a desalination process. The corresponding energy requirement is

$$E_{\text{water}} = E_{\text{desal}} m_{\text{w}} \, q_0 / q_{\text{cyc}}, \tag{10}$$

where E_{desal} (kJ/mol) is the energy consumption of water desalination, and m_{w} (mol/kg) is the minimum water requirement for wetting sorbent. The values of the above parameters are listed in Table 4. E_{water} would increase with increased concentration of desorbed CO_2, because of the decreased cycling capacity. The total energy consumption shown in Fig. 12 illustrates an optimal condition of 3% CO_2 concentration at 45 °C with the energy consumption of 35.7 kJ/mol.

The capital cost covers the expense of sorbent material, DAC unit containers, fans, and other accessories, e.g., piping and valves. The total material requirement under different CO_2 concentrations is listed in Table 3. The cost of containers is proportional to the total surface area of the DAC units, or to $N_1^{2/3}(N_1+N_2)$. A 20-year economic life for the plant is assumed (APS, 2011). The cost is estimated under different temperatures and outlet CO_2 concentrations as shown in Fig. 13. Compared to the operating cost, the capital cost is much more temperature-dependent. A lower capital cost at 45 °C should be mainly attributed to a higher cycling capacity of sorbent. The cost for fan operation can be drastically cut through increasing outlet CO_2 concentration since a smaller flow rate of stripping gas is required. The cost of water increases due to increased cyclic times and insufficient utilization of the sorbent. Taking all factors into consideration, 3% is calculated as the optimal outlet CO_2 concentration at 45 °C, with a total cost of 34.68 USD/t. Comparing with CO_2 capture from flue gas and transportation (assuming a transport distance of 100 km) whose cost is around 67.6 USD/t (Knoope *et al.*, 2014), DAC is competitive as a carbon source for gas fertilizer.

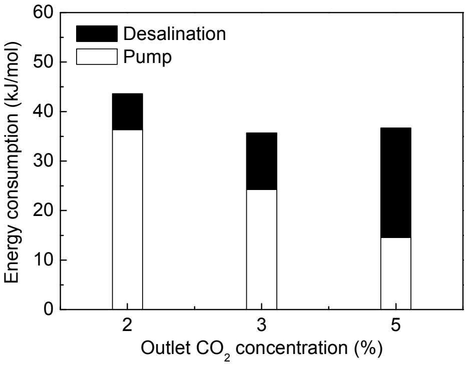

Fig. 12 Energy consumption of DAC with water from desalination

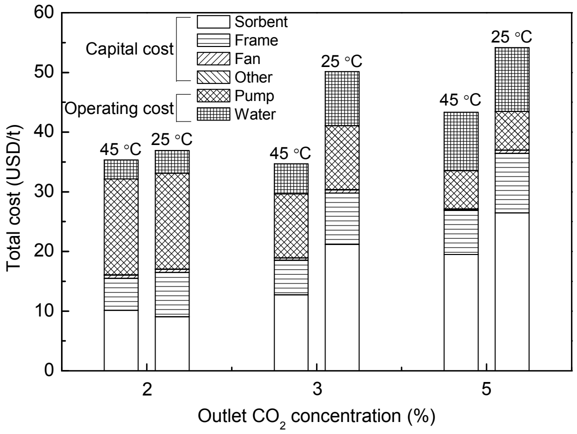

Fig. 13 Operating and capital costs for DAC at different desorption temperatures and outlet CO_2 concentrations

Table 4 Energy consumption of DAC

CO_2 concentration	Temperature (°C)	Flow rate (mol/s)	Energy consumption of pumping (kJ/mol)	q_0/q_{cyc}	Energy consumption of H_2O desalination (kJ/mol)	Total energy consumption (kJ/mol)
2%	25	0.22	36.37	4.70	8.60	44.97
	45	0.22	36.37	5.44	7.24	43.61
3%	25	0.15	24.24	8.77	20.56	44.80
	45	0.15	24.24	6.82	11.43	35.67
5%	25	0.09	14.54	9.43	24.19	35.73
	45	0.09	14.54	8.64	22.15	36.70

4 Conclusions

Atmospheric CO_2 capture with moisture swing can be used to increase the CO_2 concentration to several thousand ppm at a lower cost and energy consumption than other methods. Desorption isotherms are described by the Langmuir model. The equilibrium constant, K_d, decreases from 10.43×10^{-4} to 5.29×10^{-4} as temperature increases from 25 °C to 45 °C. Under 1000 ppm of CO_2 concentration, desorption kinetic parameters were gained at temperatures of 25 °C, 35 °C, and 45 °C. The results showed that the adsorption rate constant (k_a) and the desorption rate constant (k_d) increase with increasing temperature.

For lettuce accelerated cultivation, the effect of CO_2 concentration level on the growth rate was tested and found to be optimal at around 1000 ppm. The effect of light intensity on the growth rate of the lettuce is also found to be optimal at around 8000 lux. Based on these data, an integrated system was proposed, where a set of DAC units circularly provide CO_2 to the plant factory with the volume of 3000 m^3. From the analysis of material utilization and cost, 45 °C of desorption temperature and 3% of outlet CO_2 concentration are chosen as the optimal conditions with minimum energy requirements and an estimate of 35.67 kJ/mol and 34.68 USD/t, respectively. This makes atmospheric CO_2 capture a competitive and sustainable option for a gas fertilizer in agriculture.

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中文概要

题　目：基于变湿吸附的空气 CO_2 捕集与植物利用的耦合研究

目　的： 探究季铵型聚合物 CO_2 解吸附过程温度和 CO_2 浓度等变量对解吸附热力学和动力学的影响；研究空气 CO_2 捕集供给植物增产的耦合方法，降低空气 CO_2 捕集与利用的能耗与成本。

创新点： 1. 基于变湿吸附技术，探究了季铵型聚合物 CO_2 解吸附过程的热力学及动力学特性；2. 获得了 CO_2 作为气肥供给植物增产的关键影响参数；3. 建立并优化了空气 CO_2 捕集与植物利用的耦合模型。

方　法： 1. 通过 CO_2 吸附平衡与动力学实验，获得季铵型聚合物 CO_2 解吸附的平衡常数和动力学常数的影响参数；2. 通过植物 CO_2 吸收实验，获得 CO_2 供给植物增产过程中 CO_2 浓度和光照强度对吸收速率的影响；3. 通过理论推导，构建解吸附 CO_2 浓度与吸附剂质量、温度以及吹扫气流量等的关系，获得空气 CO_2 捕集与植物增产的耦合模型并计算 CO_2 捕集的能耗与成本。

结　论： 1. 季铵型聚合物材料吸附 CO_2 的平衡常数随温度的升高而降低；吸附、解吸附动力学常数随温度的升高而升高。2. CO_2 供给植物增产的最佳浓度和光照强度为 1000 ppm 和 8000 lux。3. 基于优化的空气捕集与植物利用的耦合算法，CO_2 的捕集能耗与成本分别为 35.67 kJ/mol 和 34.68 USD/t。

关键词： 直接空气捕集；解吸附动力学；温室；CO_2 气肥；成本分析