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CO2 fertilization system integrated with a low-cost direct air capture technology

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Abstract

An integrated system combined direct air capture (DAC) and greenhouse agriculture is proposed, in which moisture swing adsorption technology is used to concentrate CO_2 from the atmosphere and then feed CO_2 to the greenhouse. Absorption isotherm study and desorption kinetic study have been achieved in the paper. The results show that the behaviour of membrane conforms to Langmuir model and its capacity reaches to 0.83 mol of CO_2 per kilogram of sorbent. When the output CO_2 concentration of the desorber is around 1000 ppm, desorption efficiency increases from 71.3% to 79.6% when the temperature is changed from 25°C to 40°C. Besides, based on the experiment of the uptake kinetics of plants under different light and different light intensity, energy consumption and techno-economic analysis of the system have been carried out.

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Keywords: Air Capture, moisure swing, kinetics, greenhouse, integrated system

1. Introduction

Preventing climate change is among the greatest environmental challenges facing the world today. [1]Carbon dioxide capture and storage (CCS) technologies have been extensively developed to mitigate the greenhouse effect due to anthropic CO_2 emission. Traditional chain of CCS includes carbon capture, transportation and geological storage, of which each process has very high energy or material requirement. Converting CO_2 into useful products

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could decrease the costs and risks resulted from high-cost carbon capture technologies.[2]Therefore, instead of CCS, the concept of CO_2 capture, utilization and storage (CCUS) emerges recently.

Two basic approaches to CCS are available. In one approach, CO_2 is captured directly from the industrial source and the other is from the atmosphere. [3]Direct air capture for CO_2 was first suggested by Prof. Klaus Lackner in 1999[4], which can be especially environment friendly and economically viable. Based on exchange resin as a medium and moisture regeneration, it could negative global CO_2 emission and reduce the atmospheric CO_2 concentration when applied on both large industrial scale and small mobile scale. As the capacity of exchange resin is limited, the cost and energy consumption will increase with the concentration of CO_2 of the output in a system .Considering the relatively low value for agricultural products compared to industrial products when the same mass of carbon is converted, [5] any process requiring significant energy input during CO_2 capture and supply, such as purification, compression or heating is not acceptable. Therefore, a CO_2 fertilization system for greenhouse farming is introduced. A low-cost direct air capture technology, which only elevates the CO_2 concentration from 400 part per million (ppm) only to several thousand ppm, is integrated with a CO_2 fertilization system to provide a clean, stable and low-cost CO_2 source.

CO_2 fertilization has been proved very efficient in greenhouse agriculture, which can be used to cultivate vegetables out of season and boost yields, such as the cultivation of tomato and cucumber in winter. Studies showed that increasing CO2 concentration can boost the yields [6]and enhance the disease-resistant ability of the plants [7,8], and the optimum CO2 concentration for most plants is in the range of 600 to 1200ppm. CO_2 fertilization is achieved by using some traditional methods including high pressure liquid CO_2, solid CO_2 ice, and chemical reaction etc., such as ammonium bicarbonate reacts with sulfuric acid to produce CO_2. However the cost (including the material cost and the transportation cost) or environment problem are the challenges for above methods.[9] Besides, the CO_2 uptake rate under different temperatures and CO_2 concentrations is unknown yet for different vegetables. Direct air capture (DAC) of CO_2 has attracted much attention as it can complement with traditional carbon capture from concentrated sources, and the capture will not be affected by time and location. However, most of DAC technologies aim to get pure CO_2 and employ thermal swing regeneration at temperature over 100°C. From thermodynamic point of view, it is meaningful to explore CO_2 separation technology at mild environment with dilute CO_2 production for greenhouse farming.

An integrated system combined DAC and greenhouse agriculture is an innovation thought, in which moisture swing adsorption technology is used to capture CO_2 from the atmosphere and an anion exchange resin was used as the adsorbing material. Until now, the adsorption performance of the sorbent material has been studied [10,11], and the adsorption capacity and kinetics have been determined. [12] However, the desorption performance under low CO_2 concentration is unknown yet. Especially for some commercial exchange resin membrane, experiments should be conducted to explore the CO_2 desorption kinetics and the effects of temperature, humidity and gas turbulence. Furthermore, an integrated system is designed by matching the CO_2 supply of air capture units and CO_2 demand of greenhouse farming.

Nomenclature

C_0	Initial concentration of CO_2 in experimental system [ppm]
C_1	Concentration of CO_2 in the equilibrium [ppm]
C_t	Concentration of CO_2 logged by the IRGA [ppm]
K_a	Adsorption equilibrium constant of Langmuir Equation [1/Pa]
P	Pressure of experimental system [Pa]
P_0	Initial pressure of experimental system [Pa]
P_{atm}	Atmospheric pressure [101325 Pa]
q_d	CO_2 desorbed [mol]
q_e	CO_2 absorbed at equilibrium [mol]
q_∞	CO_2 capacity of a sorbent sample [mol]
Q	CO_2 capacity of 1 kg of sorbent [mol/kg]
R	Universal gas constant [8.314 J/mol.K]
T	Temperature of experimental system [K]

V_0	Volume of experimental system [m3]
V_d	Volume of CO_2 desorbed [mL]
V_{inj}	Volume of CO_2 injected [mL]
θ	Saturation of sorbent [-]
θ_e	Saturation of sorbent at equilibrium [-]

2. Experimental methods

2.1 Desorption kinetic study and absorption isotherm study

2.1.1Material preparation

The resin membrane used for experiments was IONSEP-MC-A ion exchange resin membrane made by Hangzhou ei environmental protection technology company, which was cut into 30 sheets with shape of square (6cm*6cm). The total mass of these sheets added up to 60g in a dry environment and the thickness of one sheet was within 1mm.

All the dry resin membrane samples covered with chloride ions was washed 12-14 times in 1 M Na_2CO_3 solution, until all the chloride ions were considered to be replaced by Carbonate ions, while the solution was titrated with 0.1 M standard silver nitrate solution. The sample was then thoroughly washed in DI water stream in order to remove Na_2CO_3 solution residue. In the end, the samples were assumed to reach carbonate form after the treatment.

2.1.2Absorption equilibrium measurement

Selected three sheets of samples and placed them in the reaction chamber (20L) where they were exposed to high purity nitrogen flow to assure no CO_2 and H_2O gas. This would dry the sample without loading it. Then, the system was closed to form inner loop based on a pump. A volume of CO_2 (5ml or 10ml) was injected into the sample chamber by syringe, and the gas was cycled for several hours to allow the system to reach equilibrium. The experimental system was presented in Figure 1.The whole experiment was finished after more than 10 times injection when CO_2 absorbed by resin membrane samples got closed to their capacity. Besides, the humidity was controlled at 10ppt during the process. Every time at equilibrium, the CO_2 absorbed can be calculated by:

$$q_e = \frac{P_{atm}V_{inj}}{RT_{amb}} - \frac{PV_0(C_1 - C_0)}{RT} \tag{1}$$

Where P_{atm} is the atmospheric pressure, V_{inj} is the total amount of CO_2 injected, R is the universal gas constant, T_{amb} is the ambient temperature, P, V_0, T are respectively the pressure, volume and temperature of the system, C_1 is the equilibrium CO_2 concentration and C_0 is the initial CO_2 concentration both measured by Infrared Gas Analyzer (IRGA).

2.1.3 Desorption kinetic study

Resin membrane samples were put in the unsealed chamber to be exposed to a large flow of air without H_2O until the samples were dried and the humidity of the chamber was little. At this time, the sample was assumed to be fully loaded (θ=1) and in bicarbonate form when the CO_2 concentration of output remained the same. Then the nitrogen flow was replaced by a saturated air flow with 420ppm CO_2 at 1.00L/min, while water at a given temperature was sprayed into system through a pump. Discharged the redundant water in the chamber and tighten the pipe orifice rapidly to ensure the tightness. The experimental system was presented in Figure 2.

Main chamber and pipeline were placed in the incubator to create a constant temperature and humidity of the environment. The electric fan installed in the sample chamber was capable of creating a wind velocity of 4 m/s, which was largely sufficient to overcome the boundary layer effect. The CO_2 concentration was logged every second by the IRGA. At an instant t_1, the amount of CO_2 released can be calculated by:

$$q_d = \frac{PQ_0 \int_{t_0}^{t_1} C(t)dt}{RT} - \frac{P_0 V_0 C_0}{RT} \quad (2)$$

Where P_0 , V_0 and C_0 are respectively the pressure, volume and initial CO_2 concentration of the system.Q_0 was the flow of the open system and keep 1.0L/min and C(t) was CO_2 concentration logged by the IRGA changing long with desorption process. The saturation of the sample can be calculated by:

$$\theta = 1 - q_d / q_\infty \quad (3)$$

Where q_∞ is the capacity of the samples used. It can be determined by knowing m the mass of samples.

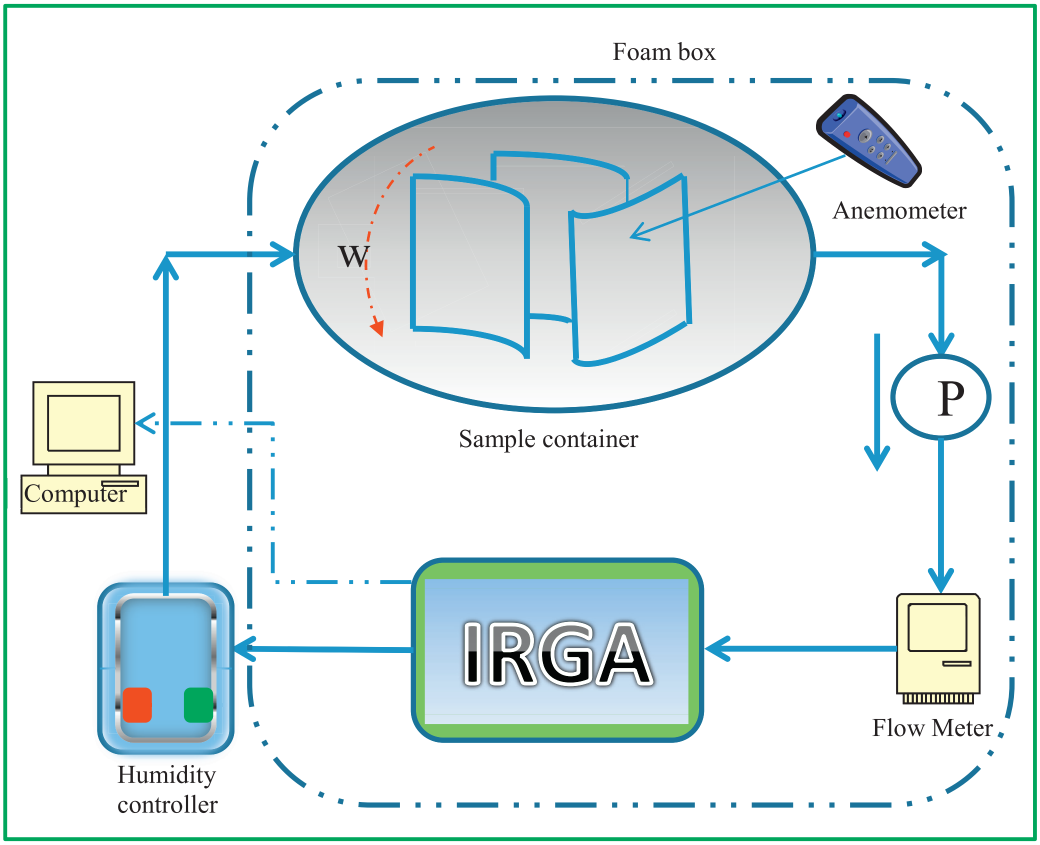

Figure 1. Schematic of experimental system for absorption equilibrium study

2.2 *Uptake kinetics of plants*

A growing Lettuce was put in a culture dish which was full of nutrient solution for Soilless culture. Injected a moderate amount of CO_2 and opened the pump to create a Loop line. As the volume of culture dish was 2L, the concentration of CO_2 could be kept nearly 1000ppm within a few seconds. Infrared Gas Analyzer (IRGA) inserted in the system logged the change of the CO_2 concentration due to the photosynthesis of the lettuce.

Considering the effect nutrient solution for absorbing the CO_2 from ambient air, a blank control group which was the same culture dish without plant was set up to reduce experimental error. Experiment had measured the photosynthesis of the lettuce under the different light and under different light intensity. The experimental system is presented in Figure 3.

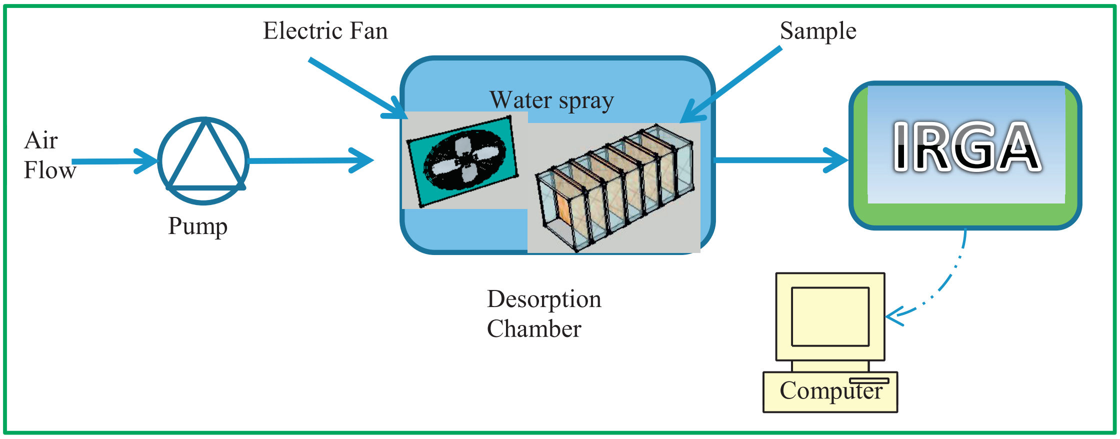

Figure 2. Schematic of experimental system for desorption kinetic study

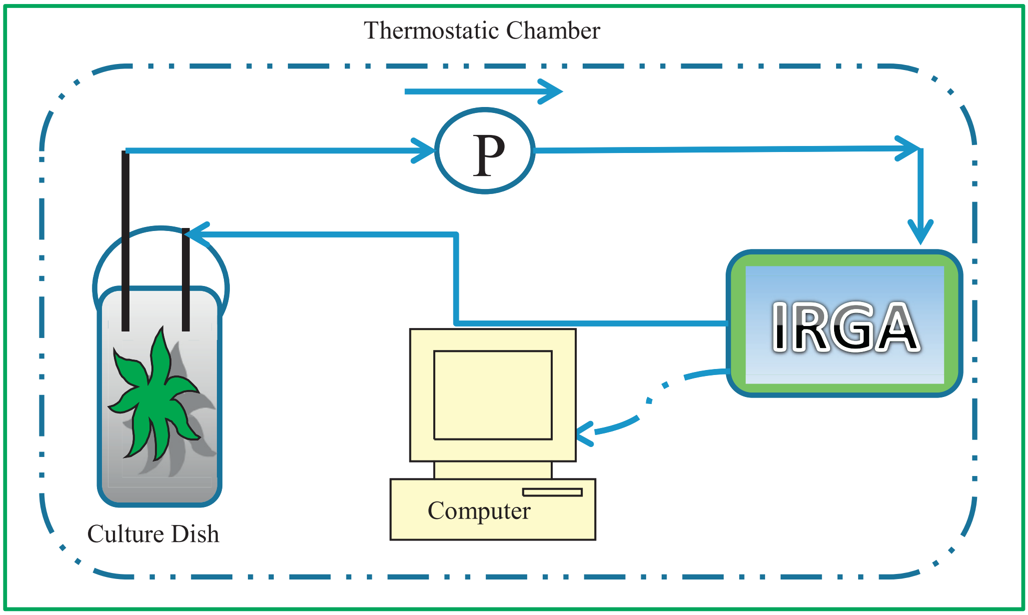

Figure 3. Schematic of experimental system for the study of uptake kinetics

3. Experimental results and discussion

3.1. Absorption isotherm

From the formula (3), θ can be defined as the saturation of a CO_2 sorbent. When it is at equilibrium, θ would change to another form:

$$\theta_e = q_e / q_\infty \tag{4}$$

where q_e is the amount of CO_2 absorbed by the sorbent when the equilibrium is reached and q_∞ is the capacity of the sorbent.

Figure 4 shows that Langmuir model describes well the absorption isotherm at high saturation. Due to the instrument precision and uncertainty closing to saturated state, the data are limited at a range between 0.3 and 9.5. As chloride ions were measured by previous titrating experiment, it can be calculated that for 1 kg of material, nearly 2.0mol of the ion exchangeable functional groups are involved in CO_2 absorption.

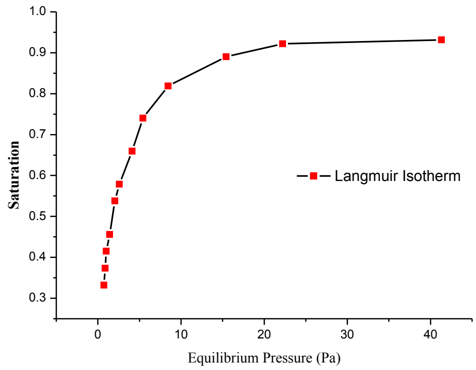

Figure 4. Absorption isotherm described by Langmuir model at 25°C

According to the empirical formula, for an exact Langmuir behavior, $1/q$e is a linear function of *1/P*, which can be expressed as Line weaver -Burk equation:

$$\frac{1}{q_e} = \frac{1}{K_a q_\infty}\frac{1}{P_e} + \frac{1}{q_\infty} \tag{5}$$

In the case of this resin membrane, by tracing the curve of $1/q_e$ against $1/P_e$, it is found that the behavior of the sorbent follows Langmuir's model. Linearity is obtained with a correlation coefficient of 0.99. The CO_2 absorption capacity and absorption equilibrium constant, K_a, which can be determined from the intercepts and slope of the straight line of $1/q_e$ as function 1/P, is 0.81.The result is accountable for the study by Wang.T et al [13], which are all summarized in the following Table 1.

Table 1. Absorption performance at 25 °C

Q (mol CO_2/kg)	K_a (1/Pa)	Correlation Coefficient
0.83	0.81	0.99

It is necessary to understand how the CO_2 concentration varies in the atmosphere. Therefore, we select four locations nearby the campus including the hill top, the library, the road at the campus gate and the tea garden, which are the locations 1 to 4 respectively in Figure 5. Then we logged the data in different time. By statistics, it is found that the CO_2 concentration changes slightly at different times of the day. From the comparison among the different locations, the CO_2 concentration varies slight in distribution of the atmosphere, which is presented in Figure 5.

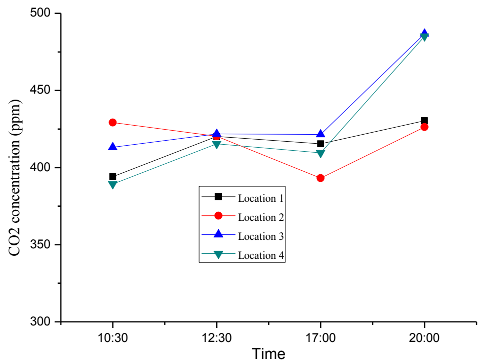

Figure 5. CO_2 varies with location in the atmosphere

3.2. Desorption kinetic study

Temperature is one of the most influencing factors which will affect the desorption performance including desorption rate and total amount. By observing the desorption performance of the samples under 25°C and 40°C for nearly 8 hours, the desorption rate in two cases both decreases over time and the curve under high temperature falls faster, which is showed in Figure 6. The whole desorption process was under the flow of ambient air with 420ppm CO_2, until the concentration of CO_2 reached 1000 ppm in the end. Choose the same span and the total amount of CO_2 desorbed can be calculated based on integration, which is shown in Table 2.

Besides, for a system, analysis of energy consumption and economy evaluation are critical factors to evaluate its superiority .Both the water input and recycled are measured to get the utilization rate for water, which is presented in Table 2.

3.3. Uptake kinetics of plants

The effect of different light and light intensity excitation on photosynthesis of lettuce under the condition of constant temperature (22°C), was studied. Light is the indispensable factors in the process of plant growth and development. Figure 7 shows that by comparing LED lights, where the proportion of red light and blue light is 4:1, and white light, plants are more sensitive to the former, when they are both kept in 5000 Lux (Lumen/m^2).

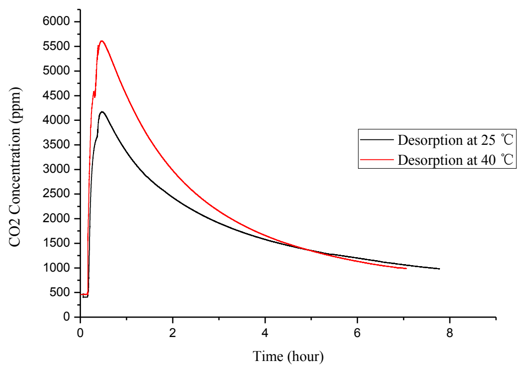

Figure 6. Desorption performance under different temperature

Table 2. Desorption performance under different temperature

Temperature (K)	298	313
Total amount (ml)of V_d	855.4	955.
The Proportion of Desorption	71.3%	79.6%
Recovery of water	65.2%	66.3%

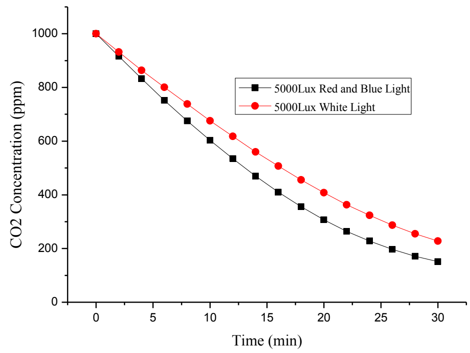

Figure 7. CO_2 uptake in photosynthesis under different light

During the 30 minutes under the photosynthesis, the rate of CO_2 uptake decreases following with decrease of the concentration of CO_2 in ambient air, which is showed in Figure 8.

3.4. Integrated system model

As follows, Figure 9 shows the integrated system is designed by matching the CO_2 supply of air capture units and CO_2 demand of greenhouse farming. The sorbent material is fabricated into a flat sheet for contacting air with small resistance and form compact structure during desorption. The sorbent will be open to atmosphere during adsorption and be closed inside desorption chamber during the moisture swing regeneration. The desorbed CO_2 can be continuously fanned into the greenhouse through three parallel units. A DAC (Direct air capture) unit can supply 1.5kg CO_2 per day for a 60m^2 greenhouse.

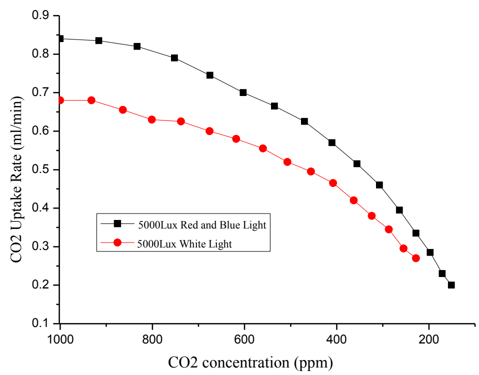

Figure 8. CO_2 uptake rate in photosynthesis under different light

Although the capacity of the samples is 0.83mol CO_2/kg, the amount of CO_2 which can be offered to greenhouse by desorption should only include the part when the concentration of CO_2 is over 1000 ppm which have been calculated in Table 2.

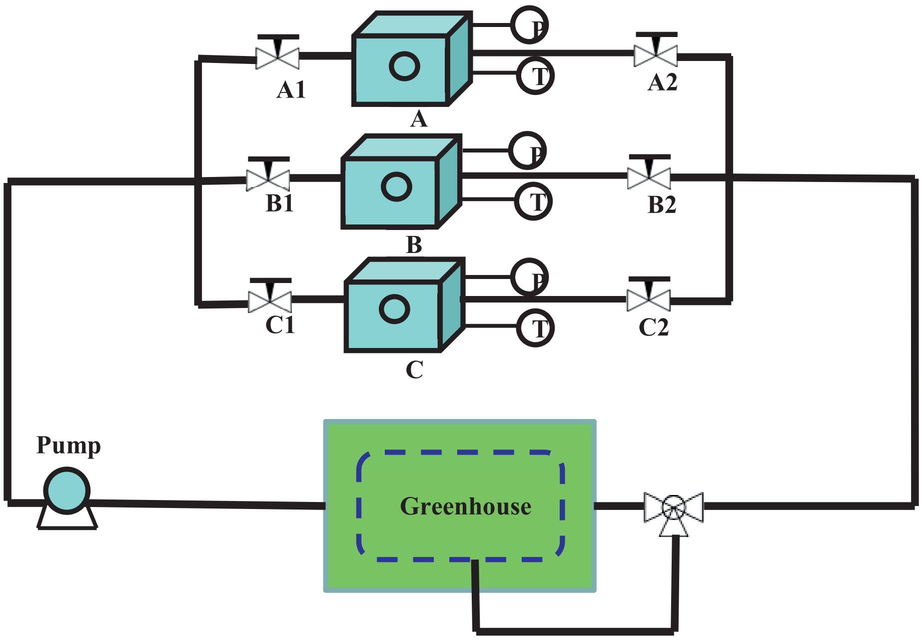

Figure 9. Schematic of integrated system combined with DAC unit and greenhouse

Based on the calculation, each unit (A, B, C) of the DAC which can offer 1.5 kg CO_2 to the greenhouse need 9.6 kg material or 17.3m^2. According to time for the regeneration of the membrane, the total amount of the CO_2 is alternated to provide by the three units. Each unit of the DAC device use 10 floors layout structure and every floor are embedded by the membranes to gain the total area of 17.3m^2. Each unit has a volume of 3.375 cubic meters. To keep the output CO_2 concentration 1000ppm, when the input CO_2 concentration is around 400 ppm, the flow of the pump can be defined. Assuming the pump works 24h every day, the electricity consumption can reach 440 kwh/a. According to Table 2, we can easily estimate that the water consumption is about 0.06 m^3 if spraying water 6 times to the DAC device in a day. As the electric charge is 0.4 RMB/kwh and water rate is 3.5 RMB /m^3 in China, the operating cost for capturing 1 kg CO_2 can be calculated then. In every 100g of the plants (lettuce for example), the proportion of carbohydrates is 2% to 5%. Equivalently, assuming half of the CO_2 input is converted in carbohydrates, the feeding of 1.5 kg CO_2 per day is equivalent to a production of plants around 17 kg every day. Related parameter is presented in Table 3.

Table 3. Energy consumption and economic evaluation on the system

Material (kg)	Electricity consumption (kw • h/a)	Water consumption (m^3/a)	Operating cost (RMB /kg CO_2)	Plant production (t/a)
9.6	440	22	0.5	6.2

4. Conclusion

In summary, an integrated system combined direct air capture (DAC) and greenhouse agriculture is proposed, in which moisture swing adsorption technology is used to capture CO_2 from the atmosphere and provide it to the greenhouse. The absorption isotherm test shows that the capacity of the membrane in carbonate form is 0.83 mol of CO_2 per kilogram and its behaviour defer to Langmuir model at high saturation.

Desorption kinetic study have also been achieved in the paper. When the concentration of CO_2 in the export is beyond 1000 ppm, desorption efficiency increases from 71.3% to 79.6% when the temperature is changed from

25°C to 40°C.

Besides, based on the experiment of the uptake kinetics of plants under different light and different light intensity, energy consumption and techno-economic analysis of the system have been carried out. On the other hand, further experiments are needed to reveal more information about the desorption process under different conditions, and the feasibility scheme of the integrated system should be further refined in future work.

Acknowledgements

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References

[1] Terwel B W, Harinck F, Ellemers N, et al. Competence - Based and Integrity - Based Trust as Predictors of Acceptance of Carbon Dioxide Capture and Storage (CCS)[J]. Risk Analysis, 2009, 29(8): 1129-1140.
[2]. Song, C., Global challenges and strategies for control, conversion and utilization of CO2 for sustainable development involving energy, catalysis, adsorption and chemical processing. Catalysis Today, 2006. 115(1-4): p. 2-32
[3]Benson S M, Orr F M. Carbon dioxide capture and storage[J]. MRS Bull, 2008, 33(4): 303-305.
[4] Lackner, K. S.; Ziock, H.-J.; Grimes, P. Carbon Dioxide Extraction from Air: Is It an Option? 24th Annual Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, 1999.
[5] Ismail, A., et al., Cooling Potentials and CO2 Uptake of Ipomoea Pes-caprae Installed on the Flat Roof of a Single Storey Residential Building in Malaysia. Procedia - Social and Behavioral Sciences, 2012. 35: p. 361-368.
[6] Weigel, H. and R. Manderscheid, Crop growth responses to free air CO2 enrichment and nitrogen fertilization: Rotating barley, ryegrass, sugar beet and wheat. European Journal of Agronomy, 2012. 43: p. 97-107.
[7] Stephen A. Prior, G. Brett Runion, S. Christopher Marble, etc. A Review of Elevated Atmospheric CO2 Effects on Plant Growth and Water Relations: Implications for Horticulture [J]. HORT SCIENCE, 46(2), 158-162.
[8] Anvarkhah, S , Koocheki, A. R and Mahallati, M.N. Effects of elevated CO2 on the competition ability between various C-3 and C-4 crops and weed species in greenhouse condition [J].
[9] Sim, S., et al., A review of the protection strategies against internal corrosion for the safe transport of supercritical CO2 via steel pipelines for CCS purposes. International Journal of Greenhouse Gas
[10] Sunho Choi, Jeffrey H. Drese, Peter M. Eisenberger and Christopher W. Jones. Application of Amine-Tethered Solid Sorbents for Direct CO2 Capture from the Ambient Air[J]. Environmental Science & Technology, 45, 2420–2427.
[11] Hongkun He, Wenwen Li, Mingjiang Zhong, Dominik Konkolewicz, etc. Reversible CO2 capture with porous polymers using the humidity swing [J]. Energy & Environmental Science, 6, 488-493.
[12] Wang T, Liu J, Fang M, et al. A Moisture Swing Sorbent for Direct Air Capture of Carbon Dioxide: Thermodynamic and Kinetic analysis[J]. Energy Procedia, 2013, 37: 6096-6104.
[13] Tao Wang, Klaus S. Lackner and Allen B. Wright. Moisture-swing sorption for carbon dioxide capture from ambient air: a thermodynamic analysis [J]. Phys. Chem. Chem. Phys., 15, 504-514