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Temperature swing adsorption process for CO_2 capture using polyaniline solid sorbent

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Abstract

To capture carbon dioxide from power plant flue gas which consists of 15% CO_2 and 85% N_2, with a temperature swing adsorption (TSA) by using polyaniline solid sorbent as the adsorbent, is explored experimentally and theoretically. First, single component adsorption equilibrium data of carbon dioxide on polyaniline solid sorbent is obtained by using Micro-Balance Thermo D-200. Then isotherm curves and the parameters are obtained by numerical method. The adsorption is expressed by the Langmuir-Freundlich isotherm. After accomplishment of isotherm curves, the breakthrough curve experiment is investigated with single adsorption column. The experiments test the change in adsorbed gas concentration at the outlet by adsorbed gas, CO_2, and non-adsorbed gas, helium. Finally, this study accentuates the TSA experiments on CO_2 purity and recovery by operation variable discussion which includes feed pressure, adsorption temperature and desorption temperature to find optimal operation condition. The results of optimal operation condition are CO_2 purity of 47.65% with a 92.46% recovery.

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Keywords: CO_2 capture; Temperature swing adsorption; polyaniline solid sorbent

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1. Introduction

In recent years, the rapid industrial development makes too great a consumption of fossil fuel, which developed into the so-called "petroleum-based" pollution. Fossil fuel combustion produces waste gas such as SO_2, NO_X, CO_2, and CO, which cause combined pollution. For example, acid rain is caused mainly by SO_2 and NO_X and the excess of CO_2 produced causes greenhouse effect. Therefore, it can reduce the emissions of CO_2 to the atmosphere through the capture and storage of CO_2 in solving the problem of global warming [1,2]. One of the methods for treating this problem is to capture CO_2 from power plant flue gases. The main types of technology for CO_2 capture from flue gases are the following: absorption, adsorption, membrane separation, cryogenic distillation, etc [3]. Adsorption process has played an important role in recovery of CO_2. In the past few years, the process and equipment improved and new types of adsorbents developed make the adsorption method more diversified.

Leal et al. [4] using 3-aminopropyl groups to modify surface of silica gel. This exhibited a CO_2 adsorption capacity as 0.41 and 0.89 mmol/g under an anhydrous and hydrous environment, respectively. Tlili et al. [5] performed the adsorption experiment with 5A zeolite for feed composition 13%CO_2 and 87%N_2. Their experiment tests different generation methods. Their experimental results with desorption by heating only could achieve 99% purity of CO_2 and recovery from 45% to 79% at different temperatures. As adding a N_2 purge the CO_2 recovery increased to more than 98% but CO_2 purity decreased. Su and Lu [6] explored dual-bed TVSA process with 13X zeolite for feed component 15%CO_2 and 85%N_2. The experimental results show that the process could concentrate CO_2 to more than 90%.

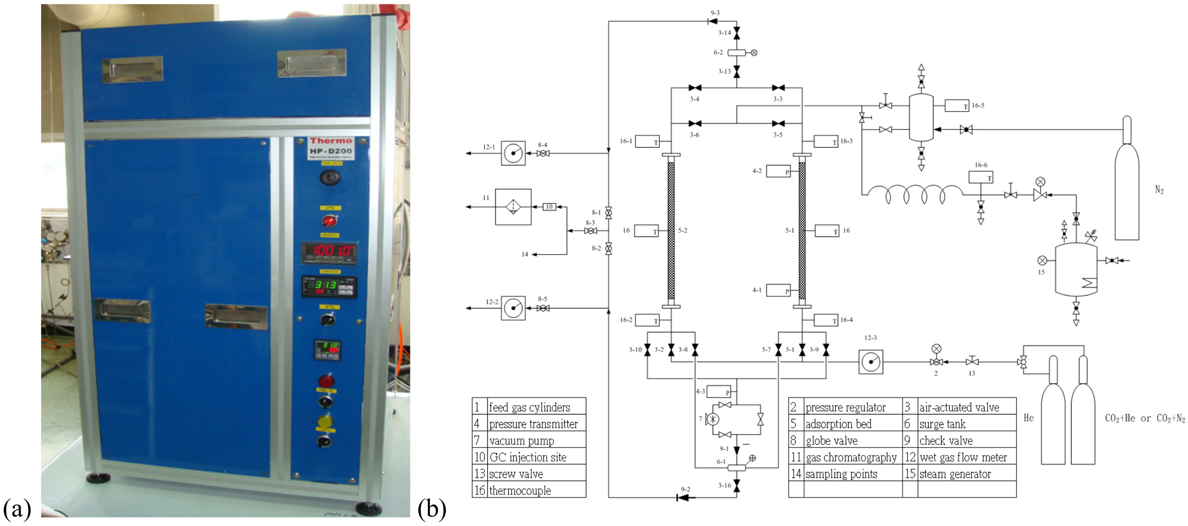
This study uses the polyaniline solid sorbent, which is prepared by the Taiwan Power Research Institute and employed TSA process for recovery and concentration of CO_2 from flue gases. For simplifying experiments in this study, the flue gas is assumed to have removed sulfide and steam so that the content of feed mixtures gas for experiments is made to be 15.03%CO_2 and 84.97%N_2. The effects on experiments are discussed for operation variables to find the optimal operating condition.

2. Experiment

Fig. 1. is the experimental devices in this study. The polyaniline solid sorbent, which is based on silicone and aminated modification on the surface of the sorbents by using 3-aminopropyltriethoxysilane is prepared at the Taiwan Power Research Institute. The adsorbent is heated in the oven at 100°C for 12 hours before experiment. Feed gas is purchased from Jian-Fa Gases Co., Ltd. The valves include check valves, solenoid valves and air-actuated valves. The CO_2 concentration is detected by gas chromatograph, which is manufactured by China Chromatography Co., Ltd. Some other experimental characteristics are described in Table 1.

Table 1. Characteristics of adsorbent and bed

Adsorbent	Weight of adsorbent (g)	Bed length (cm)	Outside diameter of bed (cm)	Inside diameter of bed (cm)	Diameter of adsorbent (mm)	Density of adsorbent (g cm^{-3})	Surrounding temperature (K)
polyaniline solid sorbent	372	98.3	2.75	2.24	1.4~2.8	1.7172	298



1	feed gas cylinders	2	pressure regulator	3	air-actuated valve		
4	pressure transmitter	5	adsorption bed	6	surge tank		
7	vacuum pump	8	globe valve	9	check valve		
10	GC injection site	11	gas chromatography	12	wet gas flow meter		
13	screw valve	14	sampling points	15	steam generator		
16	thermocouple						

Fig. 1. (a) Micro-Balance Thermo D-200; (b) experimental device TSA

This study uses Micro-Balance Thermo D-200 to obtain adsorption equilibrium data of CO_2 on polyaniline solid sorbent and discusses variables of breakthrough curve experiment to obtain the feed time for single-bed five-step TSA experiment. TSA experiments for CO_2 separation are studied. The five-step TSA process includes feed at low temperature (step 1), heating (step 2), counter-current depressurization (step 3), purge (step 4), and cooling (step 5). The flow diagram of five-step TSA process is described in Fig. 2. In TSA experiments, product comes from the outlet of counter-current depressurization step and purge step.

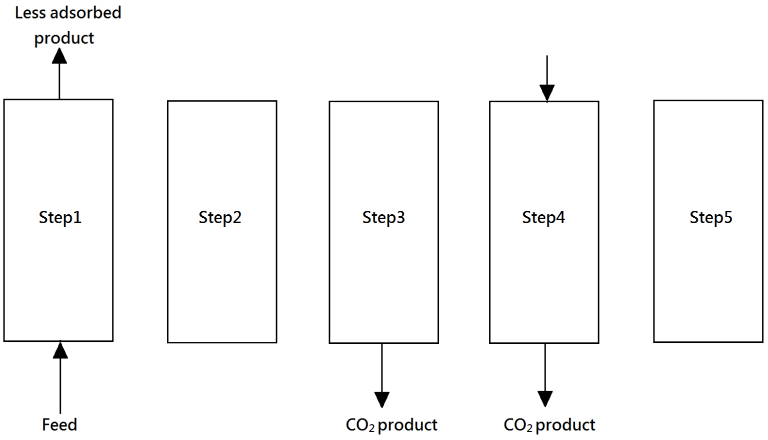


Fig. 2. Single-bed five-step TSA process

3. Results and discussion

3.1. Adsorption equilibrium curve

Because that pressure change has affected buoyant force in the experiments, we have corrected it by the Blank Experiment to improve measurement accuracy in Fig. 3(a). Fig. 3(a) shows when the pressure increases or temperature decreases, the sample weight decreases. From Archimedes' principle, when gas pressure increases or temperature decreases, the gas density increases, which leads to the increasing of buoyant force and the sample weight decreasing. Fig 3(b) shows the adsorption equilibrium data of carbon dioxide which had been measured at three different temperatures, 301K, 311K, and 321K, up to 12 bars in a Micro-Balance Thermo D-200. When temperature increases, the CO_2 adsorbed quantity decreases. The adsorption is expressed by the Langmuir-Freundlich isotherm.

$$n_i^* = \frac{\rho_s q_{m,i} b_i P_i^{ni}}{1 + \sum_{j=1}^{n} b_j P_j^{ni}} \tag{1}$$

$$q_{m,i} = a_{i,1} + a_{i,2} \times T, b_i = b_{i,0} \exp(b_{i,1}/T), n_i = n_{i,1} + n_{i,2}/T$$

where n_i^* is the equilibrium adsorptive quantity, and $q_{m,i}$ is the saturated adsorptive quantity.

Table 2. Parameter of the Langmuir-Freundlich isotherms for CO_2

$a_{i,1}$ (mole/kg)	$a_{i,2}$ (mole/kg)	$b_{i,0}$ (1/bar)	$b_{i,1}$ (K)	$n_{i,1}$ (-)	$n_{i,2}$ (K)
38.59	-3.58×10^{-2}	9.30×10^{-5}	1.69×10^{3}	1.38	-2.29×10^{2}

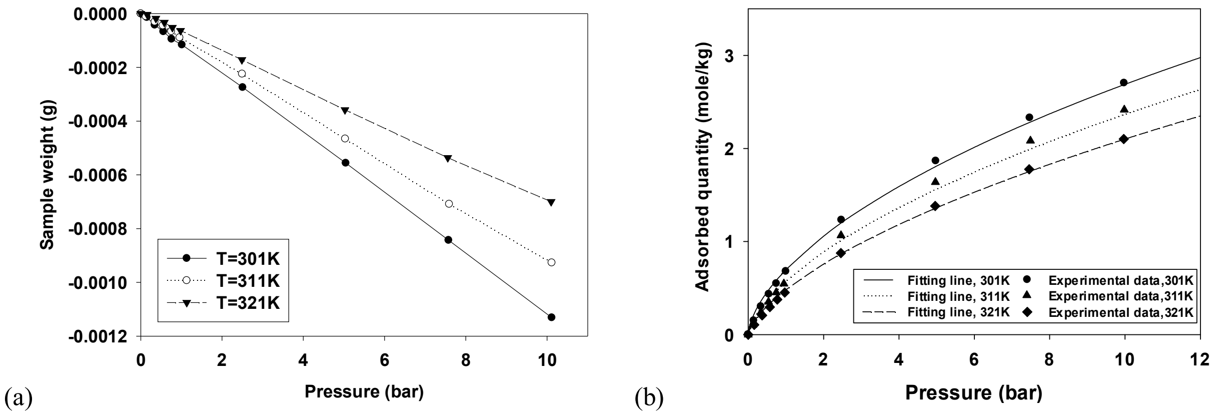


Fig. 3. (a) Buoyancy effect of adsorbent; (b) adsorption equilibrium curve of CO_2

3.2. Breakthrough curve experiment

The experiment tests the change in adsorbed gas concentration at the outlet by adsorbed gas, CO_2, and non-adsorbed gas, helium. This study considers variables for breakthrough time by varying the operating conditions, such as adsorption temperature, feed composition and feed rate and observed the effects on breakthrough curve in Fig. 4. When adsorption temperature increases, the CO_2-adsorbed quantity decreases, so does the breakthrough time decrease. This phenomenon can be observed from the adsorption equilibrium experiment. When feed rate increases or feed composition of CO_2 increases, the amount of CO_2 into the bed increases, which cause the decreasing of breakthrough time, but the effect of feed composition of CO_2 on breakthrough time is small at high temperature. As mentioned above adsorption temperature and feed rate have greater affect on breakthrough time.

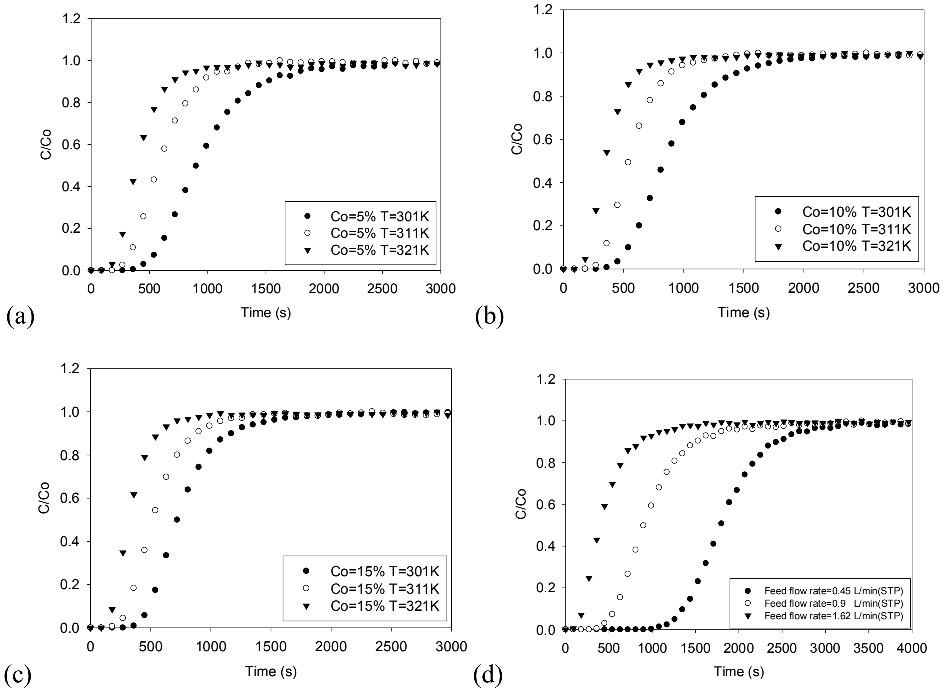


Fig. 4. The effect of adsorption temperature on adsorption breakthrough curve (a) inlet CO_2 mole fraction 0.05; (b) mole fraction 0.1; (c) mole fraction 0.15; (d) the effect of feed rate on inlet CO_2 mole fraction 0.05 and at 301K

The desorption experiments are investigated by helium in Fig. 5. After each adsorption breakthrough experiments, the bed is fed by pure helium to perform desorption without changing other operating conditions. The results show that the desorption time decreases when operating temperature increases from 301K to 321K, because the higher the temperature, the less CO_2 adsorption quantity.

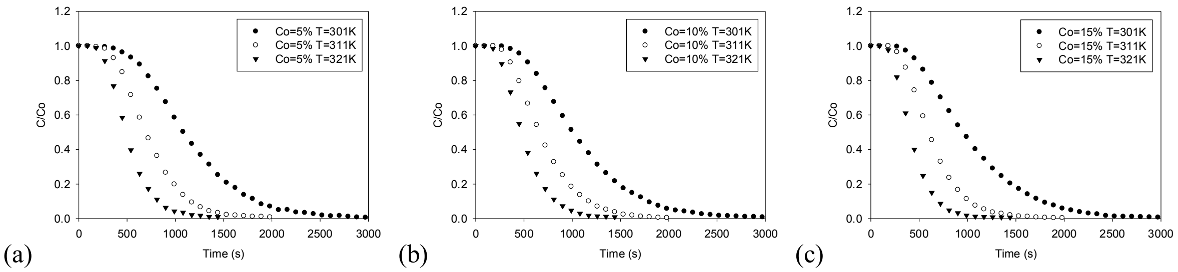


Fig. 5. The effect of temperature on desorption experiments with pure helium (a) inlet CO_2 mole fraction 0.05 at previous adsorption experiment; (b) inlet mole fraction 0.1 at previous adsorption experiment; (c) inlet mole fraction 0.15 at previous adsorption experiment

3.3. Single-bed five-step TSA process

The single-bed five-step TSA is explored in this study. The changes of CO_2 concentration and recovery in desorption step is discussed. The definition of the recovery is:

$$Recovery = \frac{product\ flow\ rate \times product\ concentration}{feed\ flow\ rate \times feed\ concentration} \tag{2}$$

This section discusses operating variable to find the optimum operating condition by TSA process. The TSA process operating conditions are given in Table 3. The variable studied as follows: adsorption temperature, desorption temperature, and feed pressure.

Table 3. TSA operation condition

Adsorbent regeneration time (hrs)	Adsorbent regeneration temperature (K)	Feed time (min)	Feed component	Adsorption temperature (K)	Desorption temperature (K)	Feed pressure (atm)
12	373.14	30	15.03% CO_2, 84.97% N_2	308, 313, 318, 323	353, 363, 373, 383	1.05, 1.10, 1.15

Fig. 6 shows the results of experiments for the TSA process. When adsorption temperature increases, the adsorptive quantity decreases. It can be observed from the previous experiments, so that the CO_2 purity and recovery decrease. When the desorption temperature increases, the CO_2 desorptive quantity increases which causes the increasing of the CO_2 purity and recovery. When feed pressure increases, the adsorptive quantity increases and the feed rate increases. When feed pressure increases from 1.05atm to 1.10atm, CO_2 purity increases but recovery deceases; however, when feed pressure increases further from 1.10atm to 1.15atm, there is no significant increase on CO_2 purity but CO_2 recovery decreases. The following is the optimum condition obtained: adsorption temperature 308K, desorption temperature 383K, and feed pressure 1.10atm. The results of optimal operation condition are CO_2 purity of 47.65% with a 92.46% recovery.

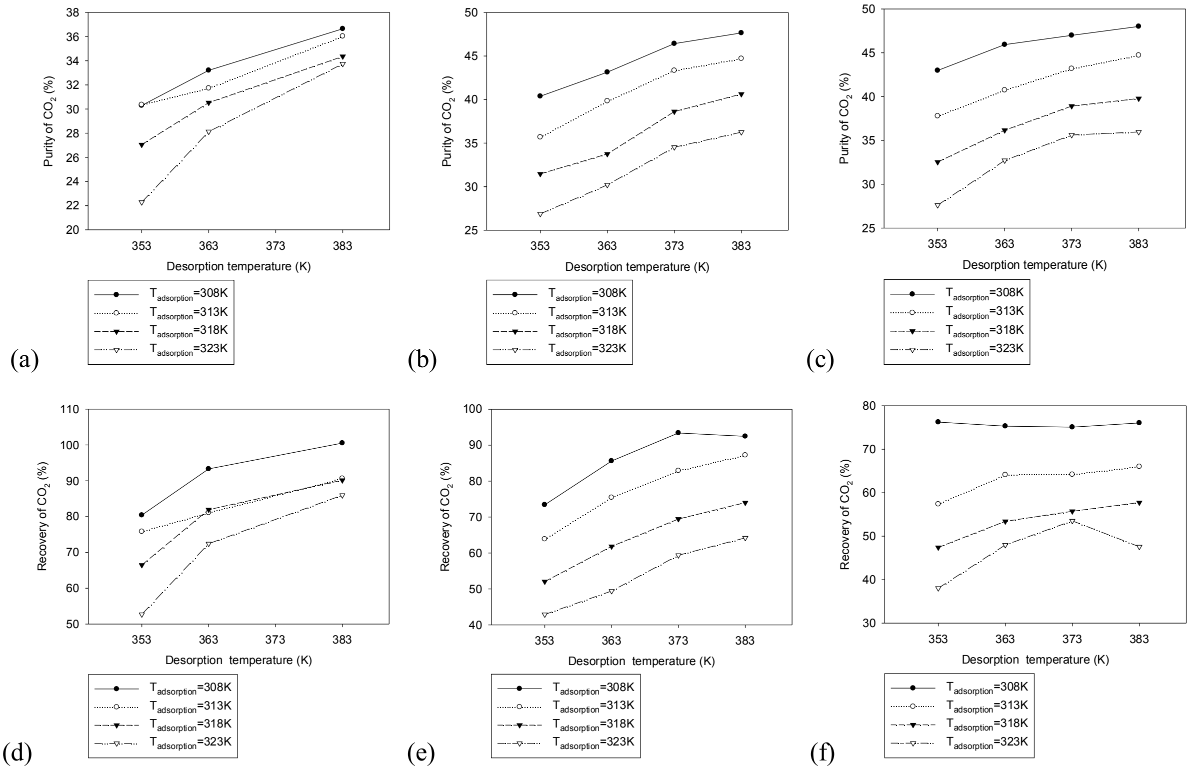


Fig. 6. The effect of desorption temperature on CO_2 purity and recovery at (a) 1.05 atm feed pressure (b) 1.1 atm feed pressure (c) 1.15 atm feed pressure (d) 1.05 atm feed pressure (e) 1.1 atm feed pressure and (f) 1.15 atm feed pressure

4. Conclusions

This study uses the polyaniline solid sorbent to test its performance on CO_2 capture. For adsorption equilibrium experiment, the adsorption capacities at 301K are higher than those at other temperature conditions (311K and 321K). After accomplishment of isotherm curves, the breakthrough curve experiment is investigated with single adsorption column. From the breakthrough experimental results, it is observed that adsorption temperature and feed rate have greater effect on breakthrough time. The TSA experiments discuss operating variable (adsorption temperature, desorption temperature, and feed pressure) to find the optimum operating condition. The optimal operation condition for single-bed five-step TSA process is observed to be: adsorption temperature 308K, desorption temperature 383K, and feed pressure 1.10atm. The results of optimal operation condition are CO_2 purity of 47.65% with a 92.46% recovery.

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