Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Dasgupta, Soumen , Nanoti, Anshu , Gupta, Pushpa , Jena, Dilip , Goswami, Amar N. and Garg, Madhukar O.(2009) 'Carbon Di-Oxide Removal with Mesoporous Adsorbents in a Single Column Pressure Swing Adsorber', Separation Science and Technology, 44: 16, 3973 — 3983

To link to this Article: DOI: 10.1080/01496390903183170

URL: http://dx.doi.org/10.1080/01496390903183170

Separation Science and Technology, 44: 3973–3983, 2009
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903183170

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Abstract: A five-step PSA cycle was studied for CO_2 separation from CO_2-N_2 gas mixture in a single column at elevated temperatures using Poly-ethyleneimine (PEI) impregnated mesoporous silica SBA-15 as adsorbent. The PSA cycle study included a strong adsorptive rinse step in which the strongly adsorbed component, i.e., CO_2 was used for rinsing the adsorbent bed in order to increase the purity of CO_2 product. The study indicates that the adsorbent is regenerable under typical PSA conditions. The productivity of the adsorbent studied for CO_2 separation was found to be comparable with commercial zeolite adsorbents as reported in literature.

Keywords: Adsorbent, CO_2 separation, poly-ethyleneimine, pressure swing adsorption, sba-15

BACKGROUND

Rising levels of atmospheric CO_2 emissions from burning of fossil fuels are now recognized to be the prime contributor to global warming and climatic change (1). The power plant constitutes a major CO_2 emitter and being a stationary source offers the best possible opportunity for application of CO_2 mitigation technology to combat global warming.

Received 19 December 2008; accepted 10 June 2009.

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Accordingly there are concerted research efforts being made worldwide to develop suitable technological solutions to capture CO_2 from power plant emissions (2). There are two possible scenarios where CO_2 can be captured in power plants and these are post-combustion capture and pre-combustion capture. Pre-combustion capture involving IGCC for power generation is still not widely commercialized and of immediate concern is post-combustion capture where CO_2 has to be removed from flue gas at pressures slightly above ambient temperature in the range 55 to 75°C and from levels varying from 5–6% in natural gas fired power plants to 10–15% from coal-based power plants. The challenges in supplying a technological solution to this problem appear daunting due to these constraints and the best available separation technology at present (which is amine absorption based) has been shown to increase the cost of power production by 35 to 40% if applied (3). Accordingly, several alternatives are being actively investigated to provide solutions at lower cost. In this context the adsorptive removal of CO_2 using Pressure Swing or Pressure–Temperature Swing Adsorption is one such alternative showing promise (4a,b,c). Among the adsorbents which have been investigated for such applications, zeolites 4A, 5A, 13X, ZSM-5, and activated carbons have shown high capacity for CO_2 at low temperature ($\sim$25°C) and atmospheric pressure but these capacities fall drastically with moderate increases in temperature (5a,b,c). Accordingly the search has been directed to the development of novel adsorbent materials with high capacity for CO_2 at moderate temperatures and low CO_2 partial pressures.

In an attempt to combine the favorable properties of liquid amine absorbent with those of solid adsorbents, the use of amine- or imine-impregnated mesoporous adsorbents for CO_2 removal is being actively studied. Mesoporous adsorbents of the MCM-41 or SBA-15 type have been chosen as support because of the large well-defined pore channel and pore volumes available which allow easy access of amine molecules into the structure so that significant quantities of amine can be loaded onto the adsorbent. Thus Xu et al. reported that polyethylene imine impregnated Al-MCM-41 has capacities of 126 mg/gm for CO_2 at temperatures of 75°C and in the presence of moisture (6). Similarly, amine impregnated SBA-15 adsorbents also show high capacities for CO_2 at moderate temperatures. Thus Hiyoshi et al. reported an increase in the adsorption capacities of amino silane grafted SBA-15 for CO_2 both under moist as well as dry conditions (7). Typical capacities reported at CO_2 partial pressure of 15 kPa and at 333 K were in the range of 1.51 mmol CO_2 per gm adsorbent. Zheng et al. reported CO_2 uptake by ethylene diamine modified SBA-15 was not affected by moisture and the adsorbent was fully regenerable by thermal treatment (8).

The above studies indicate that there is a possibility of developing an adsorption based (either Pressure Swing or Pressure-temperature swing) process for CO_2 recovery from flue gas at moderate temperatures using such mesoporous adsorbents loaded with amines or imine molecules having specific affinity for CO_2. It may be noted that there have been several studies on vacuum swing adsorption for CO2 recovery using commercial zeolites (9,10) and most of the studies with mesoporous adsorbents have dealt with CO_2 adsorption capacity measurements with some limited reports on adsorbent regenerability. There has been no study reported on the behavior of such mesoporous adsorbents for CO_2 removal under typical PSA conditions. The present paper reports studies on a polyethylene imine modified SBA-15 adsorbent for CO_2 removal at moderate temperatures in a single column PSA. The aim was basically to observe the cyclic steady state behavior of the adsorbent with respect to adsorbent productivity and CO_2 purity in a typical PSA cycle that would be used for recovery of a strong adsorptive like CO_2 from flue gas. SBA-15 was chosen as the mesoporous support for the polyethylene imine because of its higher wall thickness compared to MCM-41, which would offer better attrition resistance required to counter the pressure surges in the PSA cycle (11).

EXPERIMENTAL

Synthesis and Characterization

SBA-15 was synthesized by a modified literature procedure (11). In a typical synthesis 40.6 g of $EO_{20}PO_{70}EO_{20}$ (P123), a tri block copolymer surfactant (Av. Mn. 5800), was dissolved into 1200 ml of 2 M HCl solution by vigorous stirring at 35°C for 3 hours. Into this solution 93 ml TEOS (Aldrich, 98%) was added dropwise over a period of one hour under continuous magnetic stirring at 35°C. After the TEOS addition the stirring was further continued for 24 h at the same temperature. The white slurry obtained was kept at room temperature for 2 days without stirring. The slurry was next kept in a closed Teflon beaker and heated at 100°C for 12 hours. The solid obtained was recovered by filtration, washed thoroughly with hot distilled water, dried, and then calcined at 550°C (1°C/minute heating rate) for 8 hours. An extrudate of the calcined SBA-15 was formed by mixing the solid with γ-alumina (30 wt%) as binder to form a paste which was extruded through a stainless steel hand extruder provided with a die of 1.5 mm i.d. The SBA-15 alumina extrudate was finally calcined at 500°C for 5 hours.

The synthesized SBA-15 material and its alumina extrudate were characterized for their BET surface area, pore volume, and pore size

Table 1. Surface characterisation of mesoporous silica PEI support

Sample	BET S.A. (m^2/g)	BJH cumulative pore volume calculated from he adsorption branch of N_2 isotherm (cm^3/g)	BJH Av. Pore width calculated from the adsorption branch (Å)
Calcined SBA-15	787.07	1.86	123.5
SBA-15-Alumina Extrudate	590.26	1.35	110.2

distribution by measuring their N_2 adsorption-desorption isotherms at liquid nitrogen temperature (−196°C) in a Micromeritics Tristar instrument. These materials were degassed at 120°C for 12 h prior to measurement. Specific surface areas were calculated by using the multiple-point Brunauer–Emmett–Teller (BET) method in the relative pressure range of $P/P_0 = 0.01 - 0.3$. Pore size distribution curves were computed based on the Barrett–Joyner Halenda (BJH) model and the pore sizes were estimated from the peak positions of BJH pore size distribution curves. Total pore volumes were obtained from the volumes of N_2 adsorbed at $P/P_0 = 0.995$. The pore characteristics of these materials are tabulated in Table 1.

For 50 wt% poly-ethyleneimine (PEI) impregnation into this extrudate, 15 g PEI (Aldrich, Av. Mn. 800) was first dissolved into 75 g of methanol. 15 g of the SBA-15-alumina extrudate was poured into this PEI solution and the mixture was mechanically shaken for 10 minutes. Then methanol was then slowly evaporated with the help of a rotavapor instrument. The 50 wt% PEI impregnated SBA-15-alumina extrudate was next dried at 80°C for overnight before loading into the PSA column.

Equilibrium isotherm measurements of CO_2 and N_2 on the adsorbent synthesized were carried out at 55 and 75°C using Micromeritics ASAP 2020 apparatus.

Breakthrough Measurements and PSA Cycle Studies

The breakthrough measurements and single column PSA studies have been carried out in the experimental set-up shown in Fig. 1. It consists of a SS316 made adsorption column of an internal diameter 0.5 cm and a total column height of 65 cm with external electric heaters thermostatically controlled to maintain experimental temperature. 12 gm of the 50 wt% PEI impregnated SBA-15 extrudate was loaded into this column. The unit is PC/PLC based and equipped with five electronically actuated

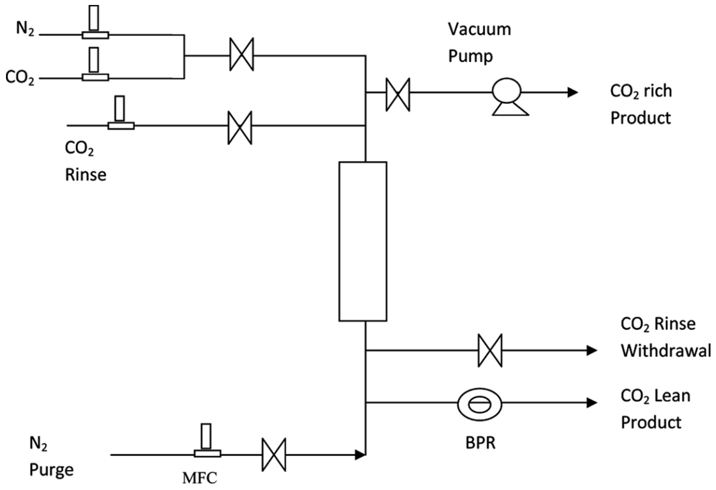

Figure 1. Single column PSA unit.

solenoid valves for the control of the cycle times and gas flow direction. The pressure within the column was monitored by a pressure transducer and controlled by a back pressure regulator. The CO_2 concentration in the various gas streams withdrawn during various steps in the PSA cycle was measured by on-line IR based CO_2 gas analyser. All the experiments were carried out at two temperatures, 55°C and 75°C. The experimental data was gathered after a cyclic steady state was attained in each run, which was usually after 10–15 cycles. Nitrogen purge and CO_2 rinse streams were provided from respective gas cylinders through flow control of respective mass flow controllers.

Process Description

The PSA cycle investigated is based on the strong adsorptive rinse cycle consisting of rinsing of the adsorbent bed with a strongly adsorbed component after completion of the adsorption step. In the present work the strongly adsorbed component is CO_2, which is required in a high purity for sequestration purposes. The five steps PSA cycle investigated consisted of the following steps:-

Feed Pressurization: The PSA cycle starts with pressurization of the adsorption column by introducing the feed mixture at a particular feed rate up to a column pressure of 3.0 bar (a).

Adsorption Step: The feed mixture continues to flow and CO_2 lean nitrogen gas is withdrawn through the product line and subsequently analysed for CO_2 concentration by an on-line gas analyser. Column pressure is maintained at 3.0 bar (a) by the back pressure regulator.

Blow Down: In this step, the column is depressurized co-currently to almost atmospheric level to remove the void gas. The column pressure during the rinse is around 1.2 bar (a).

Rinse Step: This step consists of pressurization of the column with pure CO_2 co-currently from a CO_2 gas cylinder followed by withdrawing rinse effluent while the CO_2 flow is continued. This step is used to replace the remaining nitrogen in the column by CO_2.The column pressure during this step is 1.5 bar (a).

Evacuation + Purge Step: The CO_2 saturated bed is evacuated counter-currently and purged simultaneously with nitrogen gas. The column pressure during this step is 0.5 bar (a).

RESULTS AND DISCUSSION

The single component isotherm data for adsorption of CO_2 and N_2 at 55 and 75°C are plotted in Fig. 2. The breakthrough measurements have been carried out at two different temperatures, 55°C and 75°C and at three different feed concentrations of CO_2 in nitrogen at each temperature. Feed flow rates and column pressures were maintained constant at 0.4 LPM and 3 bar absolute respectively. The breakthrough curves are reported in Figs. 3 and 4.

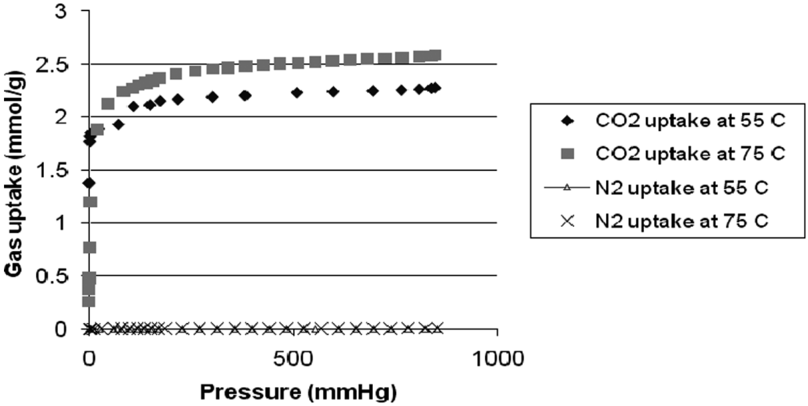

Figure 2. Equilibrium isotherm on CO_2 and N_2 at 55°C and 75°C.

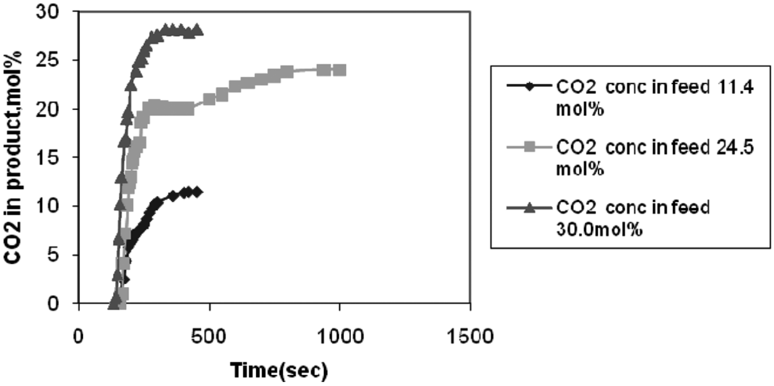

Figure 3. Breakthrough curve with SBA-15 + PEI 50% at 55°C.

The adsorption capacity for CO_2 has been calculated from the breakthrough curves using the following relationship

$$Q = v_f^* \rho_{f*} [\int (1 - c_t/c_0) dt]^* m_f / W_{ad} \qquad (1)$$

The results of these measurements are given in Table 2.

The adsorption capacities calculated from the breakthrough measurements with CO_2 partial pressures in the range of 1 bar are around 3 mmol/gm at temperatures 55 to 75°C. These calculated capacities are slightly higher than the capacities determined from the equilibrium isotherm measurements (Fig. 2). Capacities in this range have also been

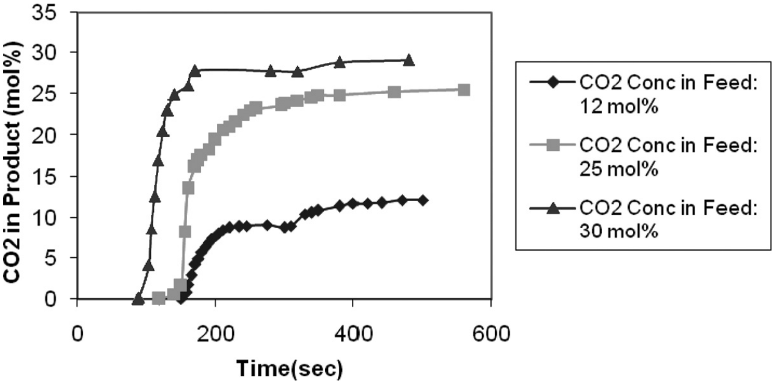

Figure 4. Breakthrough curve with SBA-15 + PEI 50% at 75°C.

Table 2. Adsorption capacities from breakthrough measurements

Temperature [°C]	CO_2 concentration in the feed, [vol %]	Adsorption capacity for CO_2, [mmol/gm adsorbent]
55.0	11.5	1.295
55.0	24.0	2.872
55.0	30.0	2.967
75.0	12.0	1.358
75.0	24.0	2.27
75.0	30.0	3.120

reported by Xu et al. for PEI impregnated MCM 41 adsorbents (6). Son et al. have also recently reported capacities of 2.88 mg/mol for PEI impregnated SBA-15 (12).

At temperatures of 333 K, with 15 kPa of CO_2 partial pressure, Hiyoshi et al. reported adsorption capacities of 1.58 mmol/gm for CO_2 using 3 (trimethoxy silylpropyl) diethylene triamine impregnated SBA-15 adsorbent which is slightly lower than our isotherm data taken with CO_2 pressures in this range at 328 to 348 K (7). The adsorption capacity data both from the isotherm and breakthrough measurements indicate that the increase of temperature does not adversely affect the adsorption of CO_2 in the imine-impregnated mesoporous adsorbent. On the contrary a slight improvement in capacity is noted at the higher temperatures.

Similar to conditions used in the breakthrough experiments, the PSA Experiments in the single column were also carried out at two temperatures 55° and 75°C, at feed gas flow rate of 0.4 LPM. CO_2 concentration in the feed was 11.5 to 12 mol%. The five-step PSA cycle timings used are reported in Table 3. As the breakthrough times observed with this feed mixture were around 120 to 130 secs for both temperatures, the feed pressurization plus the adsorption cycle time was taken as 25% of the

Table 3. Cycle timings used in single column PSA

Cycle step	Time [secs]
Feed Pressurization	5
Adsorption	25
Blowdown	5
CO_2 rinse	10, 15, 20
Evacuation with N_2 purge	25

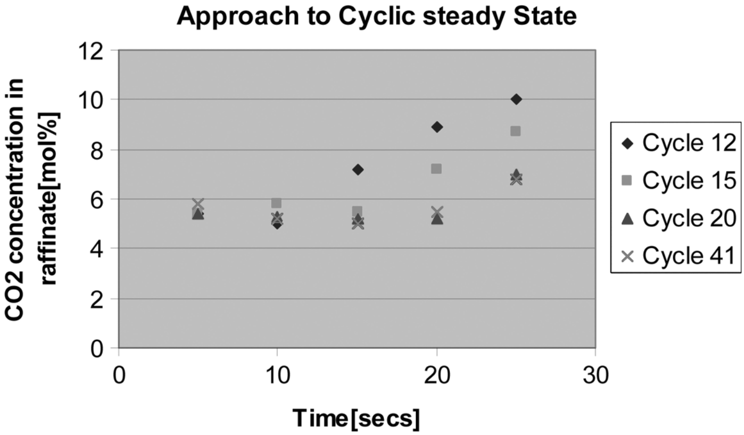

Figure 5. Time dependant CO_2 concentration in Raffinate.

breakthrough time which totalled to 30 secs. The evacuation time was taken as the same as the adsorption time. Adsorption pressure was kept at 3.0 bar (a) while during the evacuation and purge step the column pressure reached 0.5 bar (a). The CO_2 concentrations in the various effluent streams were measured using IR based CO_2 analyser. Figure 5 shows the approach to cyclic steady state for the CO_2 lean effluent stream from the adsorber. The data demonstrate the satisfactory regenerability of the SBA-15 adsorbent with cyclic steady state being readily reached after 15 to 20 cycles.

At each experimental temperature, the parameter varied was the CO_2 rinse time which was varied from 10 to 20 seconds. The effect of variation of this parameter on the purity of the recovered CO_2 and the

Table 4. Single column PSA data for CO_2 recovery with Imine Impregnated SBA-15 adsorbent

Experimental temperature [°C]	CO_2 rinse time [sec]	Recovered CO_2 purity [mol %]	Adsorbent productivity N. L. CO_2/Kg/min.
55.0	10	27.3	3.3
55.0	15	34.7	2.9
55.0	20	42.0	2.7
75.0	10	27.4	3.4
75.0	15	40.0	3.4
75.0	20	45.3	2.9

productivity of the adsorbent was evaluated. Here the productivity was defined in terms of Normal Liter CO_2 recovered per Kg adsorbent per minute. The results are reported in Table 4 below.

The results of the PSA cycle studies indicate that as CO_2 rinse time increases, the recovered CO_2 purity increases. This is expected as increase in the rinse time serves to displace more void nitrogen present in the column. The effect is seen at both experimental temperatures. The CO_2 purity improves slightly at higher temperatures in line with our measurements of capacities from both isotherm and breakthrough data which indicated improvement in capacities at higher temperatures. It is interesting to note the adsorbent productivities observed. These productivities compare very well with the productivity data reported by Chue et al. on a two bed PSA for CO_2 recovery in a similar CO_2 rinse cycle using commercial zeolite adsorbents (13). Their data had been taken at ambient temperatures and the productivities will decrease further at higher temperatures of 55 to 75°C as used in the present study. This suggests that the SBA-15 adsorbent would offer a better performance in PSA than commercial zeolites at the temperatures required for CO_2 recovery from flue gas. However, while the presence of moisture which is present in flue gas is reported (14) to promote the adsorption of CO2 on PEI loaded mesoporous adsorbents, the effect of SO_x and NO_x which are also present in flue gas, is not known and further studies are required.

CONCLUSION

Mesoporous adsorbents of the SBA-15 type impregnated with PEI have been synthesized and evaluated for CO_2 recovery in a single column PSA at typical temperatures expected for a recovery system in a power plant. The adsorption capacities of this adsorbent for CO_2 has been measured and found to compare reasonably well with literature data. The PSA cycle studies demonstrate that in a typical strong adsorptive rinse cycle that would be used for CO_2 recovery, the adsorbent performs satisfactorily with the system reaching a cyclic steady state in a reasonably short period. Adsorbent productivities are better than those reported with commercial zeolite in a similar PSA cycle.

ACKNOWLEDGMENT

The authors would like to thank Dr. R.S.Somani, Central Salt and Marine Chemical Research Institute, for his assistance with the isotherm measurements.

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