Evaluation of pressure-temperature swing adsorption for sulfur hexafluoride (SF$_6$) recovery from SF$_6$ and N$_2$ gas mixture

Wan-Seon Cho[*,‡], **Kwang-Hoon Lee**[*], **Hyang-Ja Chang**[**], **Wansoo Huh**[*], **and Heock-Hoi Kwon**[*,†]

*Department of Chemical Engineering, Soongsil University, Sangdo-5 dong, Dongjak-gu, Seoul 156-743, Korea
**Wonik Materials Corporation, Gakri, Ochang-myun, Chungwon-gun, Chungbuk 363-883, Korea

Abstract–The separation/concentration of SF$_6$, a strong greenhouse gas, of 1.3% in N$_2$ was investigated using pressure-temperature swing adsorption (PTSA) with activated carbon. To screen an effective adsorbent to be used for PTSA, adsorption isotherms on the selected adsorbents were obtained. Among the studied adsorbents, AC-1, a coconut-shell based commercial activated carbon, showed the largest adsorption amount of 3.5 mmol-SF$_6$/g-carbon at 303.65 K and 3 atm and the highest selectivity among the adsorbents tested. Its adsorption isotherm was well fit into Langmuir-Freundlich model. Before feasibility test of PTSA, a series of experiments were performed to investigate the effect of operating parameters including adsorption pressure, feed flow rate, desorption temperature and evacuation time on the PTSA performance using the 3-step PTSA cycle (pressurization, adsorption and regeneration-recovery). As the adsorption pressure, desorption temperature and evacuation time were increased, respectively, purity and recovery increased. Increasing the feed flow rate resulted in low purity and recovery. The maximum purity of 19.5% and recovery of 50.1% were obtained with adsorption pressure of 2.5 atm, desorption temperature of 200 °C and evacuation of 1 hour.

Key words: SF$_6$, PTSA, SF$_6$ Isotherm, Greenhouse Gas

INTRODUCTION

Owing to its high dielectric strength and material characteristics including chemical stability, non-toxicity, and non-flammability, sulfur hexafluoride (SF$_6$) has been widely utilized in electrical power industry as a gaseous dielectric medium for high-voltage circuit breakers and other electrical equipment, and in the semiconductor and electronics industries as a chamber cleaning agent and a dry etchant. The emission amount of SF$_6$ into air, along with the other perfluorinated compounds, however, has been limited by the reason of international concern of global warming since the gas turned out to be a greenhouse gas [1-4].

Although many industrialized countries have tried to reduce the emission of the gas, observing the Kyoto Protocol, monthly averages of SF$_6$ concentration at Mauna Loa, Hawaii, USA, measured by the National Oceanic & Atmospheric Administration, have kept increasing from 4.5 ppt at 2000 to over 7 ppt at 2010 [5]. Even though its concentration in the atmosphere is quite small, it has drawn attention due to its extremely high 100-year global warming potential of 22,200 and long life time of 3200 years; those of CO$_2$, major contributor to global warming due to its high concentration in the atmosphere, are 1 and 200 years [6,7].

Emission reduction of SF$_6$ can be realized by recycling after separation and purification and/or destruction. Among several possible treatment techniques [2-4,8-15], the separation/concentration research with adsorption technique was selected for feasibility study since

purification after concentration can be easily achieved due to its relatively high boiling point through liquefaction compared to other air constituents [12,16]. To screen an effective adsorbent to be used for PTSA, adsorption isotherms were obtained for the employed adsorbents including coconut shell- and coal-based commercial activated carbon samples and a few commercial zeolite samples. The performance test of a lab scale PTSA system was carried out and the results were presented and discussed.

EXPERIMENTAL

1. Adsorption Isotherm Experiments

Adsorption isotherm experiments were conducted with volumetric using the system described in Fig. 1. The pressures were measured with digital pressure gauges (Sensys, PMHB0010KAAA) and the loading and adsorption cells made of stainless steel were placed in a water bath operated with constant temperature. Approximately 12 g of sample was placed in the adsorption cell for each adsorbent. Achievement of adsorption equilibrium was determined when there was no significant pressure change in terms of time.

The employed adsorbents were Zeolite 5A (Sigma: Z5A), Zeolite 13X (Sigma: ZX), Sodium Aluminosilicate 10 Å (Sigma: Z10A), coconut-shell based activated carbon (Daelim Carbon Co., 8-12 mesh: AC-1), two coal based activated carbons (Northwestern, LB-1240: AC-2, Dongyang Carbon Co., 8-30 mesh: AC-3) which were readily available. The purchased adsorbents were pre-treated at 180 °C for at least 12 hours under vacuum to remove adsorbed water and any volatile impurities. The characteristics of the adsorbents including BET surface areas and pore volumes were listed in Table 1. The employed adsorbates were SF$_6$ (Matheson, 99.999%) and N$_2$ (Dukyang Gas Co., 99.999%). Detailed description of the system and oper-
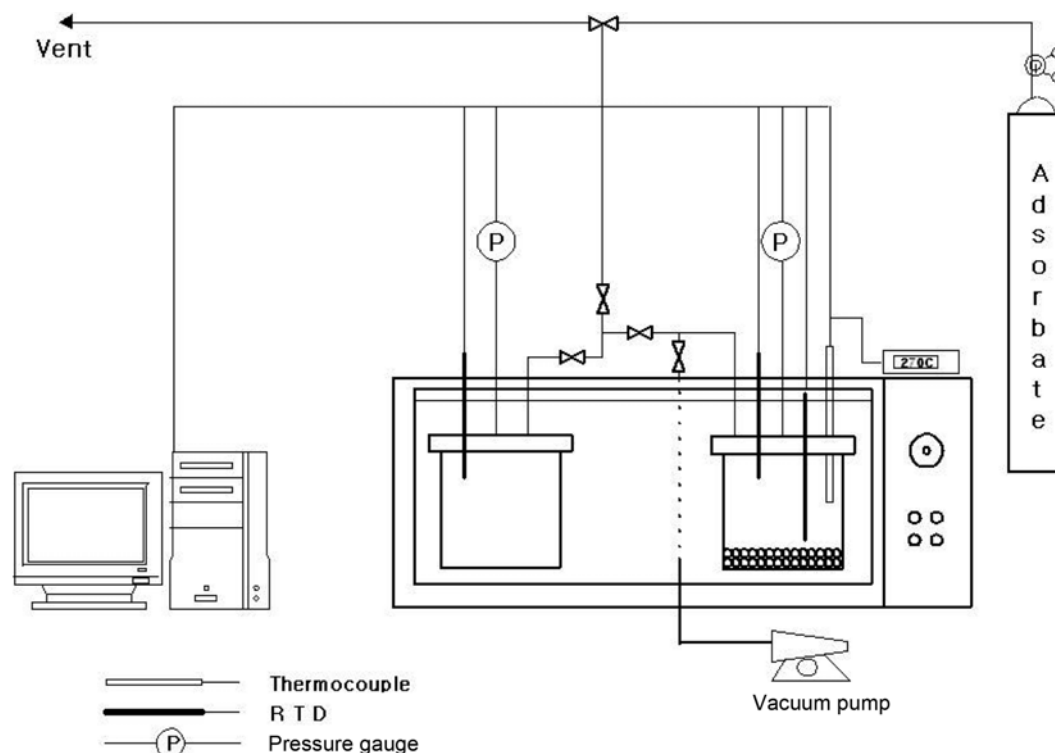
Fig. 1. Schematic diagram of the adsorption experimental system.

Table 1. Characteristics of the adsorbents employed

Adsorbents		BET surface area (m^2/g)	Pore volume (cc/g)
Activated carbon (8-12 mesh)	AC-1	1101	0.61
Activated carbon (8-12 mesh)	AC-2	893	0.49
Activated carbon (8-12 mesh)	AC-3	563	0.43
Zeolite 13X	ZX	398	0.30
Zeolite 10A	Z10A	304	0.17
Zeolite 5A	Z5A	-	-

ating methods can be found elsewhere [17].

2. Pressure-temperature Swing Adsorption

The PTSA system to recover SF$_6$ from the synthetic gas mixture of 1.3% SF$_6$ with N$_2$ balance was prepared as shown in Fig. 2. The adsorption tower of 25.4 mm i.d. and 1,000 mm in height packed with the adsorbent, AC-1, of approximately 300 g. Since AC-1 sample revealed the highest adsorption capacity and the best selectivity for SF$_6$, it was selected to recover SF$_6$.

Composition and flow rate of input gases were maintained with mass flow controllers (MFC: Tylan, FC-280SAV) and flow rate of the effluent gas mixture was recorded with a wet gas meter (Ritter, J.421.856).

For adsorption, 1.1-2.5 atm pressure was applied at 25±2 °C. For SF$_6$ desorption, temperatures of 100-200 °C and pressure up to 0.03 atm were applied with a vacuum pump (ULVAC, DAH-60). The composition of the output gas mixture was analyzed with a gas chromatograph equipped with the electron capture detector (Hewlett Packard, 6890). To monitor SF$_6$ concentration change during break-

through experiment, an on-line non-dispersive infrared spectrophotometer (CLEANSENS, CIP0948I D) was attached. The column pressures were maintained with a back pressure regulator (Tescom, 44-1767-24). Details of the PTSA system can be found elsewhere [18].

The cycle for operating the PTSA system to recover SF$_6$ from the synthetic gas mixture consisted of the following steps: pressurizing, adsorption, desorption and recovery with heating and evacuation. The AC-1 in the adsorption column was pre-treated at 200 °C for 3 hours under vacuum, which turned out to be sufficient in our preliminary research. After cooling to 25±2 °C, the adsorption column was pressurized with the gas mixture of 1.3% SF$_6$ in N$_2$ to the selected pressure, either 1.1, 1.5, 2.0, or 2.5 atm. Then, the exit valve was opened and the adsorption step began. When the concentration of SF$_6$ of the effluent reached 200 ppm, the valves at the feed end and exit were closed. At the desorption and recovery step, the adsorption column was heated at 200 °C with evacuation. The concentration of SF$_6$ and recovered amount of gas mixture were analyzed with the GC and the wet gas meter. The sequence was repeated and the purity and recovery was obtained. The adsorption pressure, flow rate of the mixed gas, desorption temperature and time were varied to investigate their effect on the performance of the PTSA system.

RESULTS AND DISCUSSION

1. Adsorption Experiment

Adsorption characteristics of SF$_6$ and N$_2$ gases on the selected adsorbents were studied by varying equilibrium pressure. In this experiment, it took 10 to 15 minutes for 12 g of activated carbon
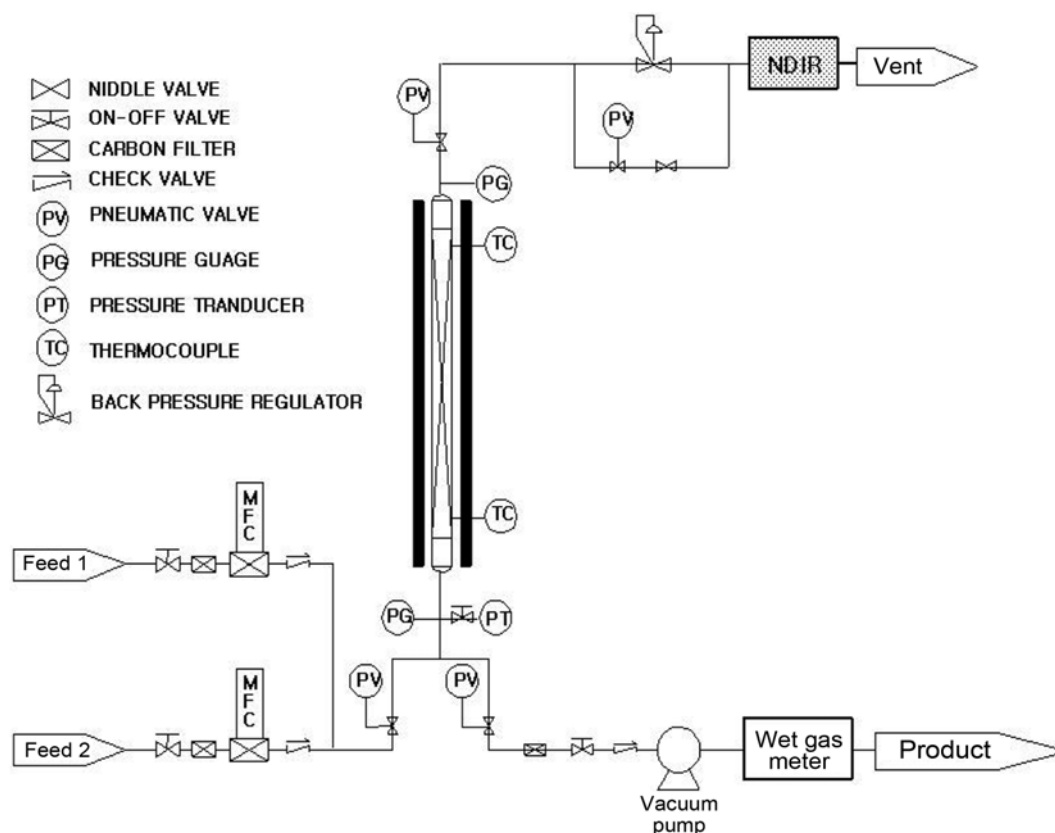
Fig. 2. Schematic diagram of pressure-temperature swing adsorption system.

and zeolite samples to reach adsorption equilibrium. The adsorption equilibrium data was calculated using the following mass balance equation; before adsorption equilibrium (1), after adsorption equilibrium (2).

$$\left.\frac{yPV_1}{Z_lRT_l}\right|_1 = \left.\frac{yP_1V_1}{Z_lRT_l}\right|_2 + \frac{yP_aV_a}{Z_aRT_a} + Mn$$

Z : compressibility factor
y : mole fraction of bulk phase
x : mole fraction on adsorbent
l : loading cylinder
a : adsorption cell
M : adsorbent mass
n : adsobed mole number per g adsorbent

Adsorption experimental result is presented in Fig. 3. It turns out that adsorption capability for SF_6 was in the following order: AC-1>AC-2>ZX>AC-3>Z10A>Z5A. The activated carbon samples usually exhibited better adsorption performance compared to zeolite samples. The adsorption behavior on both activated carbon and zeolite samples was similar, showing that the adsorption amount increased with increasing equilibrium pressure, and above a certain equilibrium pressure the amount adsorbed reached asymptotic values. It turned out that the adsorption isotherm fitted to Langmuir-Freundlich model better than Langmuir model; the related parameters are summarized in Table 2. Since the Langmuir model was developed under the assumptions that the solid surface is uniform regardless of its coverage and there is no interaction between adsorbed
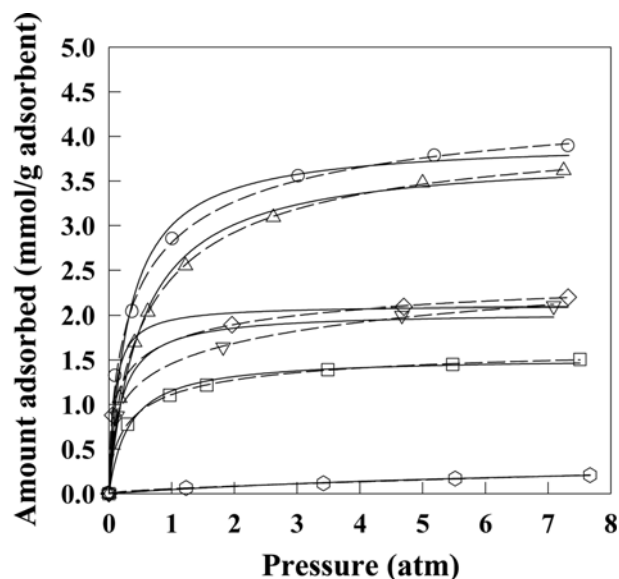

Fig. 3. Adsorption isotherms of SF_6 for each adsorbent at 303.65 K. ○: AC-1 △: AC-2 □: AC-3 ◇: ZX ▽: Z10A ⬡: Z5A. —: Langmuir model - - -: Langmuir-Freundlich model.

molecules, it seems reasonable that the empirical Langmuir-Freundlich model better predicts adsorption of SF_6 on both activated carbon and zeolite samples. The better adsorption behavior of SF_6 gas on activated carbon than zeolite can be interpreted as the less steric hindrance effect due to the large surface area and large pore size.

Table 2. Related parameter values of Langmuir-Freundlich isotherm for SF$_6$ on AC-1 at three different temperatures
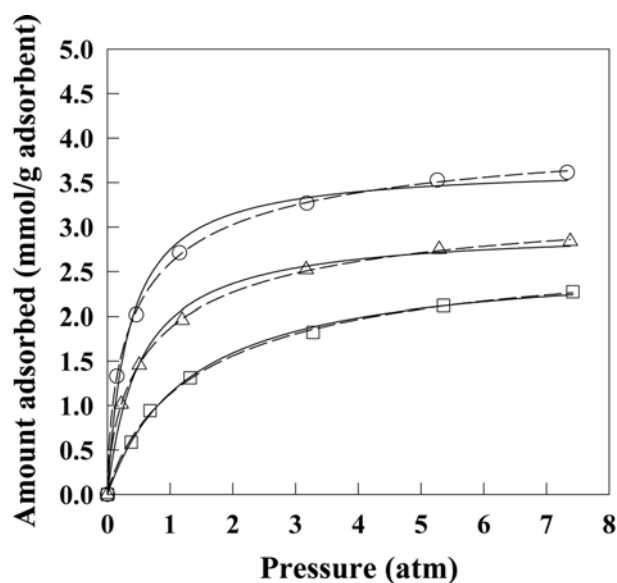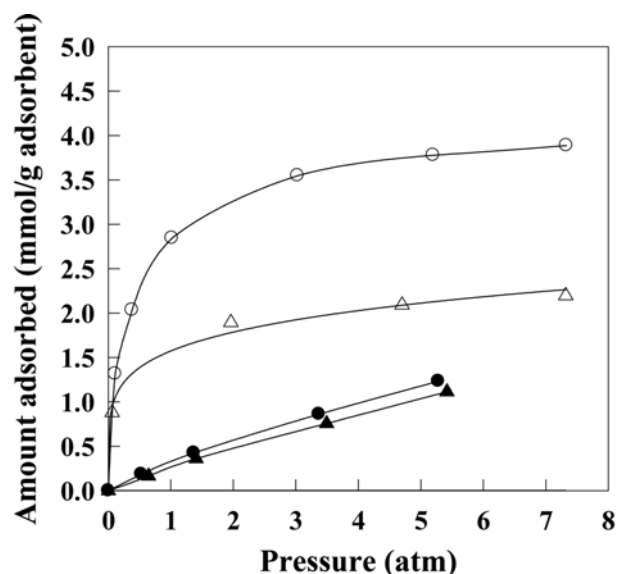
Adsorbate	Temperature (K)	q_m (mmol/g)	B (1/atm)	n
SF$_6$	303.65	4.6450	1.5276	1.5807
	323.65	3.9287	1.0438	1.2339
	353.65	4.0304	0.6288	1.3762

Besides, the superior affinity between the activated carbon and SF$_6$ gas might induce better adsorption results. The total adsorption amount of the activated carbon (AC-1) was almost ten-times larger than that of the zeolite Z5A.

In Fig. 4, the isothermal adsorption behavior of SF$_6$ on AC-1 is shown at different temperatures of 303.65, 323.65, 353.65 K, and the total adsorption amount decreased with increasing temperature. Again, the Langmuir-Freundlich model explained adsorption behavior better than Langmuir model.

Usually, the separation process using adsorption and desorption is dominated by not only the equilibrium adsorption amount, but also the adsorption selectivity between two gas mixtures. As shown in Fig. 5, the adsorption isotherms of SF$_6$ and N$_2$ gases on the AC-1 and ZX, the best ones among the activated carbon and zeolite samples tested, were compared. The adsorption amount of SF$_6$ on AC-1 was almost ten times larger than that of N$_2$ at atmosphere pressure and three times larger than N$_2$ at 5 atm. Regarding these results, separation/concentration of SF$_6$ by adsorption in N$_2$ balance using AC-1 seems to be very feasible. Considering that the adsorption amount of SF$_6$ on AC-1 flattened while that of N$_2$ increased more sharply as adsorption pressure was increased (approximately 8% increased for SF$_6$ while 30% increased for N$_2$ when comparing adsorption amount), separation/concentration of SF$_6$ in N$_2$ should be operated under low pressure: less than 3 atm.
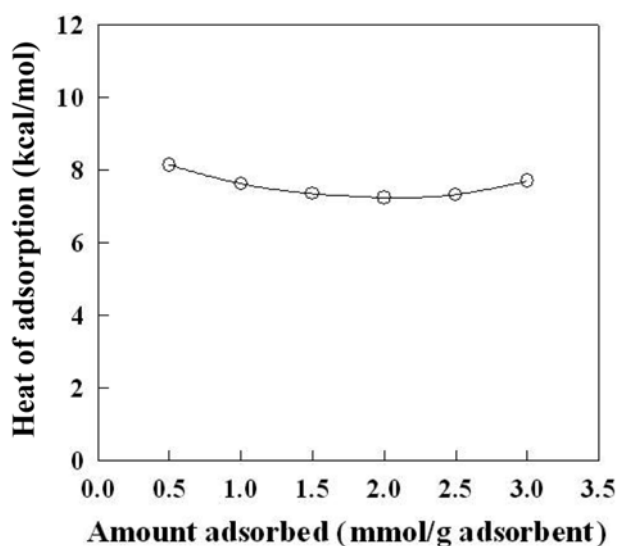
The isosteric heat of adsorption was calculated using equilibrium

Fig. 5. Adsorption isotherms of SF$_6$ and N$_2$ on AC-1 and ZX at 303.65 K. ◯: SF$_6$ (AC-1) △: SF$_6$ (ZX) ●: N$_2$ (AC-1) ▲: N$_2$ (ZX).

adsorption experimental results at three different temperatures and shown in Fig. 6. Depending upon the adsorption amount, 7.7-8.2 kcal/mol of the isosteric heat of adsorption resulted for SF$_6$. This value is somewhat consistent with the result reported by Barrer et al. [18], in which 5-10 kcal/mol for SF$_6$ adsorption was obtained when zeolite NaX was used for an adsorbent.

2. Pressure-temperature Swing Adsorption

To concentrate SF$_6$ in N$_2$, a lab-scale TPSA system was operated. Based on the results presented in the previous section, AC-1 was chosen for the TPSA process among the six adsorbents tested. The purity and recovery of SF$_6$ were obtained to evaluate the process efficiency of the TPSA system. The purity and recovery were calculated averaging the PTSA cycle more than three times after reaching cycle steady state. The recovery was calculated with the

Fig. 4. Adsorption isotherms of SF$_6$ at three different temperatures on AC-1. ◯: 303.65 K △: 323.65 K □: 353.65 K. —: Langmuir model - - -: Langmuir-Freundlich model.

Fig. 6. Isosteric heat of adsorption for SF$_6$ over AC-1.

formula below:

Recovery (%)=(Amount of SF_6 in the product)
/(Supplied SF_6 during pressurizing and adsorption stage)

2-1. Effect of Adsorption Pressure

To evaluate the effect of adsorption pressure on concentration of SF_6 the overall flow rate of the feed was set at 5 LSTP (liter per minute at standard temperature and pressure), and the breakthrough curves of SF_6 were shown in Fig. 7. The adsorption amount of SF_6 and breakthrough time increased with increasing pressure. The purity and recovery data obtained from the product before the effluent concentration of SF_6 reached 200 ppm are presented in Fig. 8. Desorption was carried out at 200 °C and for 1 hour under vacuum. With increasing pressure, the recovery as well as the purity of SF_6 in the gas mixture increased. The maximum purity of 19.5% and recov-

ery of 50.1% was obtained at 2.5 atm. Regarding the fact that the recovery and purity increase at 2 atm were almost identical to those obtained at 2.5 atm, operating the TPSA process under 2 atm seemed to be more efficient.

2-2. Effect of Feed Flow Rate

The effect of feed flow rate was studied at a fixed adsorption pressure of 2 atm and shown in Fig. 9. The breakthrough point shifted from 82 min to 18 min with increasing feed flow rate from 3.0 to 15.1 LSPT/min. Fig. 10 shows the purity and recovery at adsorption pressure of 2 atm, desorption temperature and time of 200 °C and 1 hour. With increasing flow rate up to 15 LSTP/min, both purity and recovery decreased. It is obvious that slow feed flow rate induced longer contact time with the adsorbent, which resulted in higher purity and recovery of SF_6. The maximum purity and recovery of 19.4% and 50.4% were obtained, respectively, with the feed flow
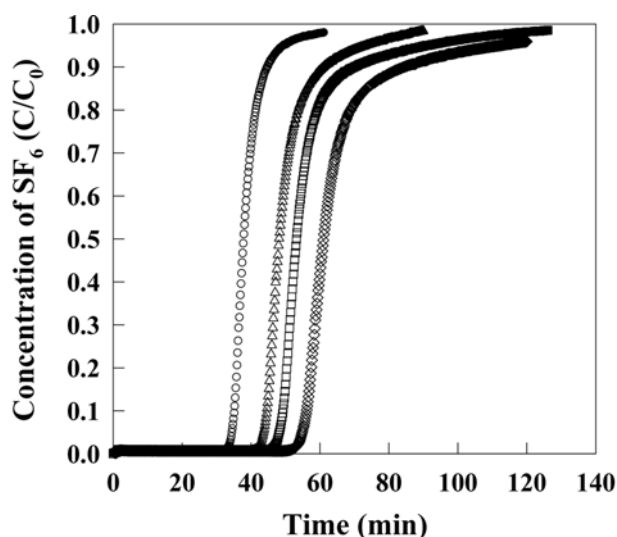

Fig. 7. Breakthrough curves of SF_6 under several pressures of 1.1-2.5 atm with feeding rate of 5 LSTP/min at 298 K. ○: 1.1 atm △: 1.5 atm □: 2.0 atm ◇: 2.5 atm.
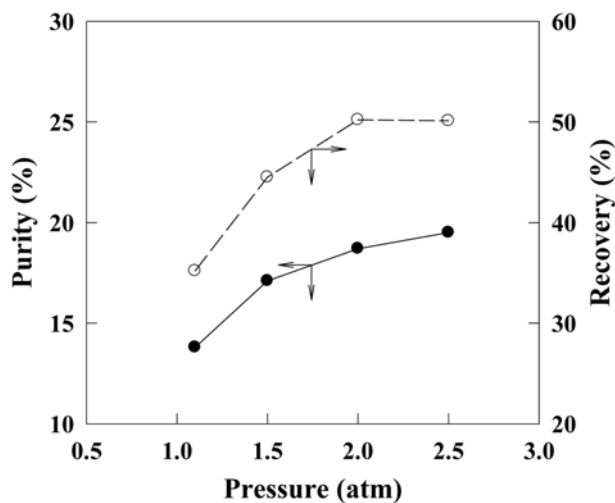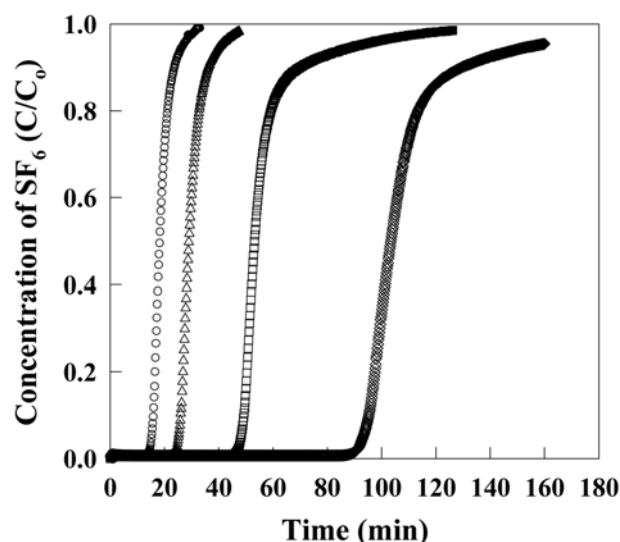

Fig. 9. Breakthrough curves of SF_6 for several feeding rates with adsorption pressure of 2 atm at 298 K. ○: 15.1 LSTP/min △: 10.1 LSTP/min □: 5.0 LSTP/min ◇: 3.0 LSTP/min.

Fig. 8. Effect of adsorption pressure on purity and recovery of SF_6 with feeding rate of 5 LSTP/min, desorption temperature of 200 °C, and evacuation time of 1 h.
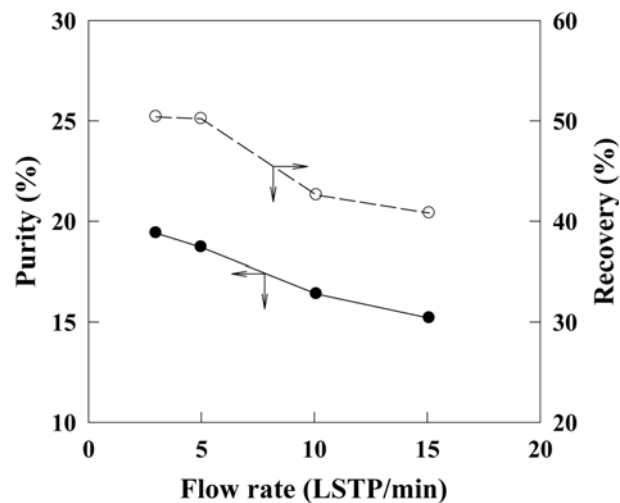

Fig. 10. Effect of feeding rate on purity and recovery with adsorption pressure of 2 atm, desorption temperature at 200 °C, and evacuation time of 1 h.
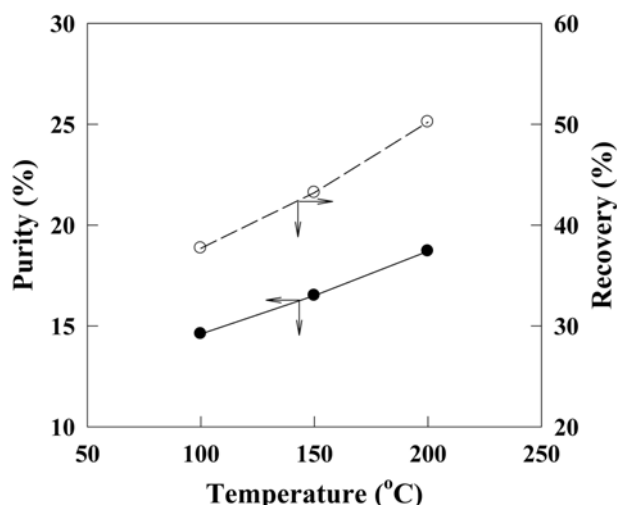
Fig. 11. Effect of desorption temperature on purity and recovery with adsorption pressure of 2 atm, feeding rate of 5 LSTP/ min, and evacuation time of 1 h.
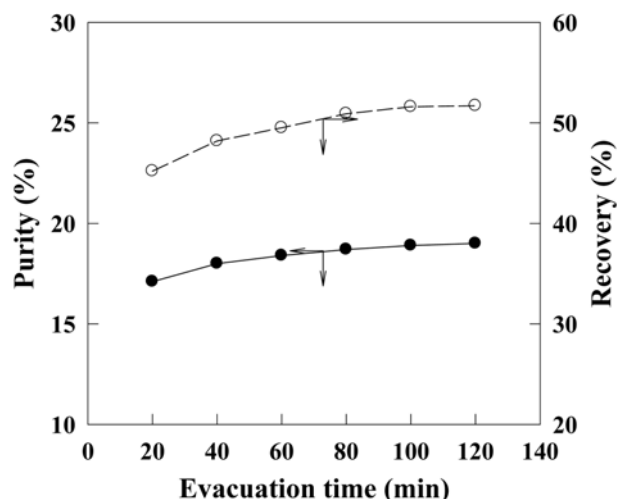

Fig. 12. Effect of evacuation time on purity and recovery with adsorption pressure of 2 atm, feeding rate of 5 LSTP/min, and desorption temperature of 200 °C.

rate of 3 LSTP/min. To reduce total operating time, the rest of the experiments were carried out with the feed flow rate of 5 LSTP/min.
2-3. Effect of Desorption Temperature and Time

The effect of desorption temperature on the purity and recovery is shown in Fig. 11. Increasing desorption temperature resulted in higher purity and recovery. When desorption temperature of 150 °C was applied, the initial concentration of SF$_6$ was above 200 ppm. Thus, it was necessary to set the desorption temperature of above 150 °C in order to satisfy the allowable emission concentration. With increasing desorption time, the purity and recovery of SF$_6$ increased and at least 80 min desorption time was required for 19.0% purity and 51.7% recovery (Fig. 12).

CONCLUSION

The separation/concentration of SF$_6$, one of the global warming PFC gases, was studied using PTSA process. Regarding adsorption isotherm results, the activated carbon samples exhibited usually better adsorption performance compared to zeolite samples. Its adsorption isotherm data well fit into the Langmuir-Freundlich model. The heat of adsorption of SF$_6$ on AC-1 was 7.7-8.2 kcal/mol. In 3-step PTSA cycle to concentrate SF$_6$, maximum purity of 19.5% and recovery of 50.1% were obtained with adsorption pressure of 2.5 atm, desorption temperature of 200 °C and evacuation of 1 hour. The purity and recovery of SF$_6$ increased with higher adsorption pressure, desorption temperature and evacuation time.

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