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Application of pressure swing adsorption technology combined with 13X molecular sieves for the regenerative air cleaning systems with a dimethyl sulfide as a contaminant

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The use of pressure swing adsorption (PSA) system in the air cleaning technology for the application of regenerative air cleaning systems, which have wide applications in the defence sector has been reported. For this, a test procedure has been established and is elucidated for air purification using dimethyl sulfide (DMS) as a contaminant with 13X molecular sieves as the adsorbent at 4 kg/cm^2. The dynamic adsorption capacities of 13X molecular sieves for DMS decreases from 14 to 0.3 wt% by increasing the flow rate from 3 to 15 lpm at 25°C, and at 4 kg/cm^2. The flow rate and contact time are optimized as 6.5 lpm and 5.8 s, respectively for a selected PSA system. No DMS break through has been observed in 80 hr of continuous operation at an average feed concentration of 130 ppm. The 13X molecular sieves are further characterized by BET-SA, FT-IR, XRD and TPD. The TPD data reveal that the regeneration of 13X molecular sieves can be effectively achieved at ~180°C. The PSA system combined with 13X molecular sieves appears to be the promising technology for regenerative air purification applications and specific to the reduced sulfur compounds.

Keywords: Pressure Swing Adsorption, 13X molecular sieves, DMS, Adsorption, Air purification

Air is a unique source of oxygen needed by a human being for respiration and it should be free from pollutants and in the breathable form to support the life. The contamination of air makes the life difficult and it can occur either intentionally or accidentally. Hence, the removal of contamination from the air vastly required. In recent years, many pollution treatment technologies such as absorption, neutralization, adsorption, incineration, catalytic incineration, advanced oxidation and combined technologies developed for the removal of contamination mostly volatile organic compounds (VOCs)[1-6]. But in the defence sector, the absorption process is using in the filtration systems since many years due to its simple and versatile applications and in most of the filtration systems (canisters and filters) contain activated carbon as an adsorbent material. Hence, the service life of these filtration systems mostly limited by the amount of activated carbon. Often these filtration systems affected by the moisture. Nevertheless, this problem can be address by replacement with the re-generable adsorption systems. Regenerative adsorption systems can provide the user with the required level of contaminated air protection continuously, for an indefinite period, without filter change-out and service; life of these systems is more. These regenerative filtration systems make use of cyclic adsorption processes. Pressure swing adsorption (PSA) is one such cyclic adsorption process, for providing extended service life against air contamination. PSA systems use multiple beds, and adsorbent material undergoes successive pressurization and depressurization steps in order to produce a continuous stream of purified product gas[7].

The applications of PSA are reported in the removal of carbon dioxide (CO_2) for the commercial synthesis of hydrogen (H_2) in oil refineries, separation of CO_2 from bio gas, and in the production of ammonia[8-10]. In addition to refineries PSA is used in the removal of hydrogen sulfide from hydrogen feed and recycle streams of hydro treating and hydro cracking units. Nitrogen generators andmedical industries also employed the PSA to produce high-purity nitrogen and oxygen gases (99.5% or greater), respectively from the compressed air[11-]13. However, there is no significant work has been reported in the application of PSA technology in the pollution treatment technologies.

In contrast, zeolites are widely used in PSA for gas separation and purification processes and are particularly suitable for oxygen enrichment, CO_2 capture, H_2 recovery from refinery fuels, coke oven gases, etc. Zeolites were also employed for removal of DMS and t-butyl mercaptan from city gas[11, 14-18]. For purification and up gradation of bio gas also various synthetic (5A and 13X) and natural (Clinoptilolite) molecular sieves have been employed as an adsorbents[9]. The higher self-life, excellent adsorption properties and re-generable nature of zeolites provides them as the preferred choice compared to that of conventional adsorbents (activated carbon).

In the present study, we have worked for the development of air filtration systems based on the adsorption process by using PSA technology and also focused on the development of PSA process, test procedures and its evaluation using 13X molecular sieves as an adsorbent with di methyl sulfide (DMS) as probe molecule. DMS has a low olfactory threshold (0.02-0.1 ppm) with an unpleasant smell and it is used as a simulant for sulfur mustered and many volatile sulfur organic compounds. Hence, the removal of DMS at trace level is still debatable for environmental clean-up applications.

Experimental Section

Characterization of 13X molecular sieves

The 13X molecular sieves, 1.9 to 4.1 mm spherical beads were purchased from Sorbead India Pvt Ltd, India and employed as an adsorbent material. Further, the 13X molecular sieves were characterized for its physical properties like BET-SA, BJH pore size distribution, X-ray diffraction, and FTIR techniques. The temperature programmed desorption of ammonia and DMS were performed to ascertain the acid sites distribution and regeneration temperature at atmospheric pressure, respectively.

The N_2-BET surface area is 746 m^2/g and the N_2 adsorption and desorption isotherm profile (Fig. 1a) represents the micro porous nature of 13X. The pore size (Fig. 1b) observed to be 8.15Å which is well acceptable for the removal of the majority of organo-sulfur and phosphorus compounds (critical diameter range from 2 to 8 Å)[19,36]. The XRD pattern (Fig. 2a) shown the diffraction signals at 2θ = 10, 11.6, 15.4, 20, 23.3, 26.7, 29.3 and 31 which correspond to the typical pattern of crystalline 13X molecular sieves

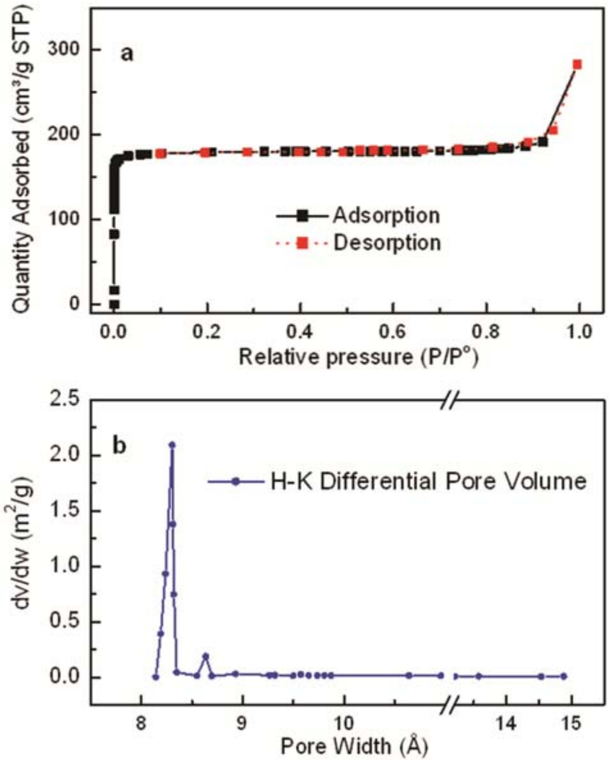


Fig. 1 — (a) BET adsorption and desorption isotherm (b) Pore size distribution of 13X molecular sieves

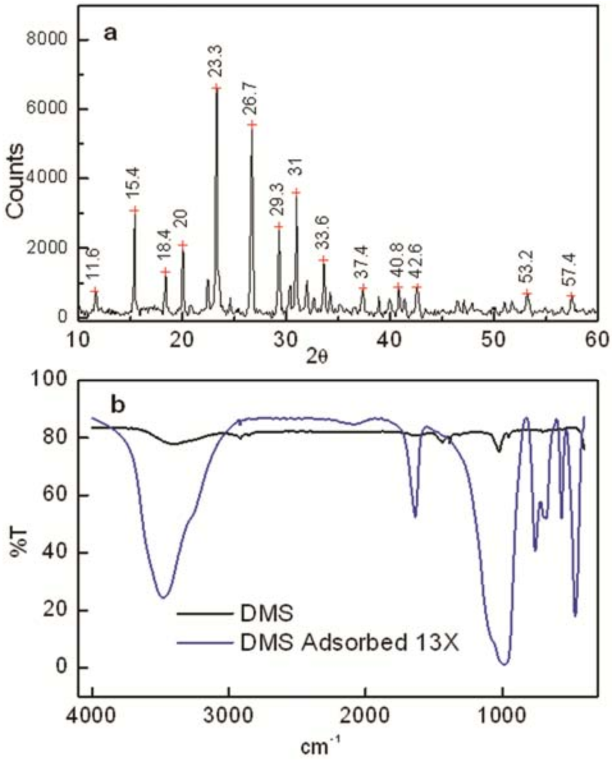


Fig. 2 — (a) X-ray diffraction pattern of 13X Mol. Sieves (b) FTIR spectra of pure DMS and DMS adsorbed 13X molecular sieves.

matching with FAU structure[20,35]. The FTIR data (Fig. 2b) reveal that, the bands that present in the spectrum are characteristic for the molecular sieves with Zeolite X type FAU structure[21,37]. The spectral bands around 3479, 1000, 672 and 464 cm^{-1} were ascribed to the vibrations of Si-O-H, internal tetrahedral unit and the bands around 1100, 758, 565 cm^{-1} are ascribed to pore opening and external linkage vibrations[22,38]. The band at 1626 cm^{-1} corresponds to bending frequency of surface adsorbed H_2O.

Temperature programmed desorption (TPD) was performed on 13X molecular sieves to determine the total acidity using ammonia as probe molecule. The TPD was performed on TPD / Pulse Chemisorptions Unit (Newchrome technologies, New Delhi) equipped with a TCD detector and helium as a carrier gas. The 13X (100mg) was preheated to remove the adsorbed moisture at 400°C under the flow for 2 hr further, 13X was saturated with 1.6%ammonia in Helium at 80°C. Desorption profile of ammonia was monitored by raising the temperature form 80 to 450°C at a rate of heating 8°C /min. The TPD of ammonia (Fig. 3) reveals that, the 13X molecular sieves possesses wide range of acid sites with varying the strength. Based on the ammonia TPD the total acid site distribution is 2780µmole/g. This is in good agreement for the zeolites[23,39].

The TPD of DMS was performed to identify desorption temperature of DMS over 13X molecular sieves at atmospheric pressure. The DMS was adsorbed on 13X (100mg) at 50°C by injecting the liquid DMS intopreheated injector using Helium (50 mL/min) as a carrier. Desorption profile was monitored by increasing the temperature from 50 to 250°C at a rate of heating 8°C/min.The DMS desorption pattern (Fig. 3) reveals that multi step desorption with an onset temperature of 50°C with a T_{max} 80°C (as shoulder peak) followed by an intense desorption peak centred at 170°C approximate amounts desorbed on 13X was 1790 µmole/g when the amount adsorbed was 2120 µmole/g almost 80% 0f DMS desorbed. The TPD of DMS experiments clearly demonstrates that the 13X can be easily regenerated at ~ 200°C.

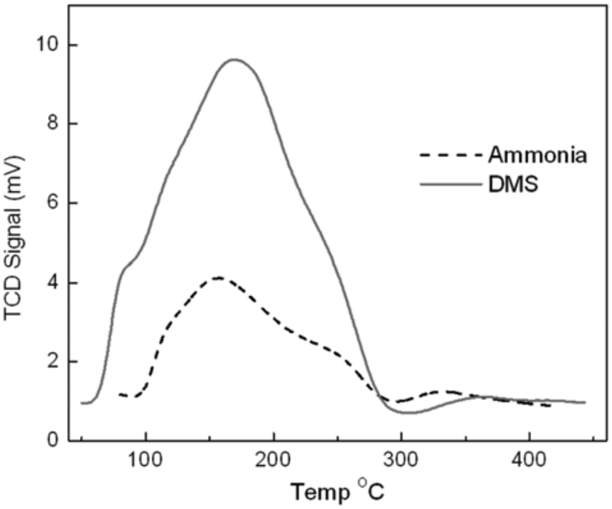


Fig. 3 — Temperatured programmed desorption profile of ammonia (dotted line) and DMS (thick line)

Gas generation and PSA description

The DMS(Sigma Aldrich 99.99%) gas was generated by the diffusion method in a thermo-stated vessel (Fig. 4).The generated gas mixture was expanded into the 0.04 m^3 SS lined chamber, which was used as the source for compressor succession point. The chamber also fitted with homogenizer and a rota meter (50 lpm), which takes additional air (dilution) from the environment through a dust filter. The PSA was equipped with a displacement compressor (Frank technologies, India, 50 lpm) 20 lit receiver tank with pressure switch for precise pressure regulation and operates between 5-7 kg/cm^2 pressures. The PSA test system was also equipped with the appropriate pressure gauges at various points. The PSA operated with a standard time combination controller (EAPL Pvt. Ltd. India) with eight relays, and two are connected to the 5/2 way control valves. The twin tower PSA (Trident Pneumatics Pvt. Ltd, India) equipped with standard cylindrical pipes (40 cm height, 6 cm diameter) which can accommodate 750g of 13X molecular sieves for each tower. In order to avoid the dust entering into the valves the PSA towers were fitted with built in diffuser dust filters made-up of perforated Teflon.

The PSA utilizes an air compressor with the variable pressure regulators and also fitted with a mass flow controller (MFC) (Sierra instruments, USA) to control the PSA outlet flow. Whereas, the purge flow was controlled by a high pressure needle valve and was measured by digital flow meter (TSI instruments, UK). The system was equipped with stream selection valve (VICI instruments, Switzerland) which was interfaced with compressor inlet (chamber), PSA inlet, Dry air, and purge flow streams. The selection valve also interfaced with calibration system and online GC.

Calibration of the DMS

In order as certain the generated DMS concentrations in the feed gas phase the PID/FID

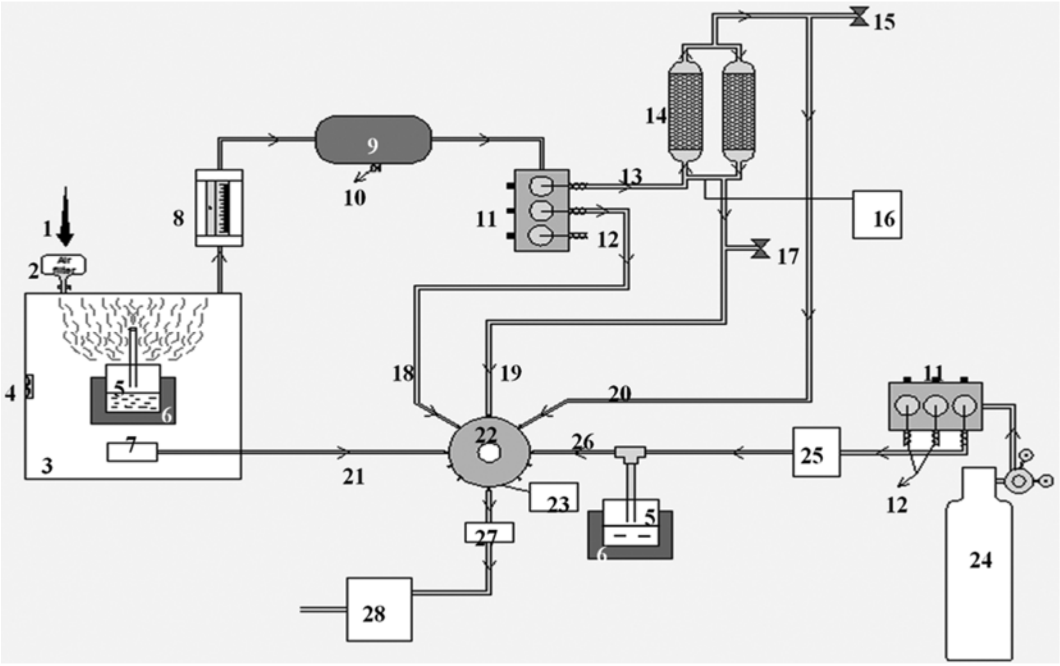


Fig. 4 — PSA test rig

1. Air flow direction 2. Dust filter 3. Gas generation chamber 4. Homogenizer 5. Diffusion vessel 6. Thermo stat 7. KNF pump 8. Rota meter 9. Compressor 10. Drain valve 11. Gas distribution panel 12. Optional port 13. PSA inlet stream 14. PSA system 15. Dry air outlet 16. PSA control unit 17. Purge outlet 18. PSA inlet stream for analysis 19. Purge stream for analysis 20. Dry air stream for analysis 21. Chamber stream for analysis 22. Selection valve 23. Position controller 24. Nitrogen gas cylinder 25. MFC 26. Calibration stream for analysis, 27. RH and temperature sensor 28. Online GC.

detectors in the GC are calibrated with the known concentrations of feed gas. Diffusion methods offer one of the least complex methods of generating low parts per million analytical standard vapours. Gases have the property of diffusing through tubes at a uniform rate, if the concentration gradient, temperature, and tube geometry remain constant. DMS (15ml) was placed in a steel diffusion vessel with diffusion tube length 16cm and cross-sectional area of 0.125 cm^2 and was thermo-stated (Poly science 9102, USA) at 5^{o}C. The diffusion concentrations were varied by changing the carrier gas flow rate (nitrogen) from 50 to 150 cc/min and were analysed by GC with PID/FID tandem detector (5765, Nucon Engineers Pvt. Ltd, India) containing the capillary column (Rtx-1, Restek Corporation, US). The five sample analysis was taken at each flow rate and the average value was reported for the calibration. The DMS peak area was plotted as a function of concentration to obtain the calibration.

The calibration was standardized by using the diffusion method and the concentrations were calculated using following equation[24,40]. The calculated concentrations were 81.6, 97.9, 122.4, 163.2, 244.8 ppm for 100, 75, 50, 30 cc/min of carrier gas respectively.

$$C_{ppm} = \frac{10^6 q_d}{V} \qquad \dots (1)$$

q_d = diffusion rate (ml/min)

V= flow rate (ml/min)

$$q_d = \frac{DAln(\frac{P}{P-P_v})}{L} \qquad \dots (2)$$

D = 0.092 cm^2/sec (diffusion coefficient of DMS at 5 ^{o}C calculated from Antoine equation)

A = 0.125 cm^2 (diffusion tube cross-sectional area)

P = 760 mm Hg (atmospheric pressure)

P_v = 209.3 mm Hg (vapor pressure of DMS)

L = 16 cm (length of diffusion tube)

Results and Discussions

Contaminated air streams profile of PSA inlet and chamber concentrations

When the high-volume, low concentration (HVLC) streams are treated by the PSA process, initially the HVLC streams get converted to lower-volume high concentration (LVHC) streams; there is a possibility of condensation of water / DMS by compression of the contaminated air, which intern effect the adsorbent challenging concentrations. Therefore, it is essential to know the actual concentrations in evaluating the molecular sieves performance. Hence a set of experiments was conducted to conclude the gas chamber concentration (compressor inlet) as well as PSA inlet concentrations (compressor outlet).

Initially, the compressor outlet flow was maintained constant for half an hour at 3 lpm to attain the equilibrium concentrations. The chamber (with the help of KNF pump, Fig. 4) and PSA inlet concentrations were measured by using the stream selection valve with an interval of 10 min and the average concentrations were ascertained for a given flow rate. Similarly, the experiments were repeated with the 5, 10 and 15 lpm. Prior to the each experiment, the compressor was drained to remove the moisture and residual contaminant and all the test lines were flushed with fresh air to avoid any contamination transfer during the experiments.

The chamber and PSA inlet concentrations were plotted as a function of flow rate was depicted in Fig. 5. The results reveal that at 3 and 5 lpm, the chamber concentrations almost same and further increase in flow, the chamber concentration is steeply decreased to 50 ppm, which is attributed to the dilution of chamber concentrations with increasing flow rate. In contrast, the PSA inlet concentrations are increased with flow rate marginally to 50 ppm at 15 lpm. However, it is interesting to observe that the chamber concentrations and the PSA inlet concentrations are equal at 15 lpm, indicating the compressor succession rate and discharge of contaminated air to the PSA is in equal.

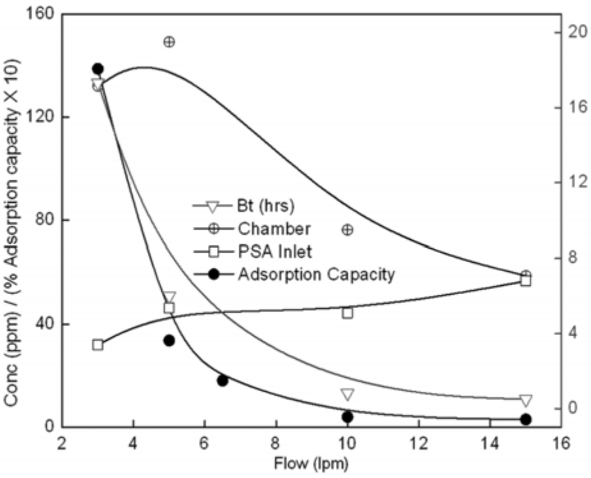


Fig. 5 — Effect of flow rate on chamber, PSA inlet concentrations, DMS dynamic adsorption, and Single tower Bt profile (blue line) at 3, 5, 10 and 15 lpm; Pressure = 4 Kg/cm^2

Dynamic adsorption studies with a single tower

The aim of these experiments is to 1) Determine the dynamic adsorption capacity of 13X molecular sieves at working pressure . 2) Draw a base line for optimum contact time (Ct =Volume of the Sorbent (0.63 liters) / Volume of flow (lpm). 3) Identify the maximum adsorption capacity in terms of saturation time in the tower. This contact time can be extrapolated for the sizing of the PSA systems within the tolerances.

The single tower breakthrough studies were performed at the flow of 3, 5, 10 and 15 lpm at 4kg/cm^2 to optimize the flow rate for PSA system. The oven-dried molecular sieves was charged into the PSA tower by agitating manually and mounted on the PSA blocks. The purge air valve was closed and the control measurements were performed for quality checks, which include leak test. The PSA control panel was programmed to run the PSA in single tower mode followed by interfacing the contaminant chamber to the compressor. The chamber, PSA inlet and dry air concentrations were measured at regular time intervals by stream selection valve, which was directly interfaced with online GC.

The concentration profile at various flow rates were depicted in Table 1 and the PSA inlet concentrations at 30 min were 30, 38, 60 and 75 ppm at 3, 5, 10 and 15 lpm respectively. The point at which adsorption has ceased in one of the bed is known as the breakthrough time.The breakthrough time (Bt) was plotted against flow rateand depicted in fig. 5and itis following the second order exponential decay. The results reveal that higher Bt (~1000 min) is noticed at 3 lpm and with increasing the flow rate, the breakthrough of DMS is observed after 30 min at 15 lpm. The earlier breakthrough times at higher flow rates is ascribed to a) decrease in contact time. b) Variation in the PSA inlet concentrations. However, the influence of flow rate on the PSA inlet concentrations (Fig. 6) is marginal whereas, the effect

Table 1— Summary of DMS breakthrough studies

S. No	Flow (Lpm)	PSA Inlet conc.* (PPM)	Contact time (Sec)	Break through time (min)	Adsorption capacity (wt%)
1	3	30	12.6	1040	13.9
2	5	38	7.6	360	3.4
3	6.5	44	5.8	170	1.8
4	10	60	3.8	50	0.4
5	15	75	2.5	30	0.3

* Average inlet concentrations at 30 min

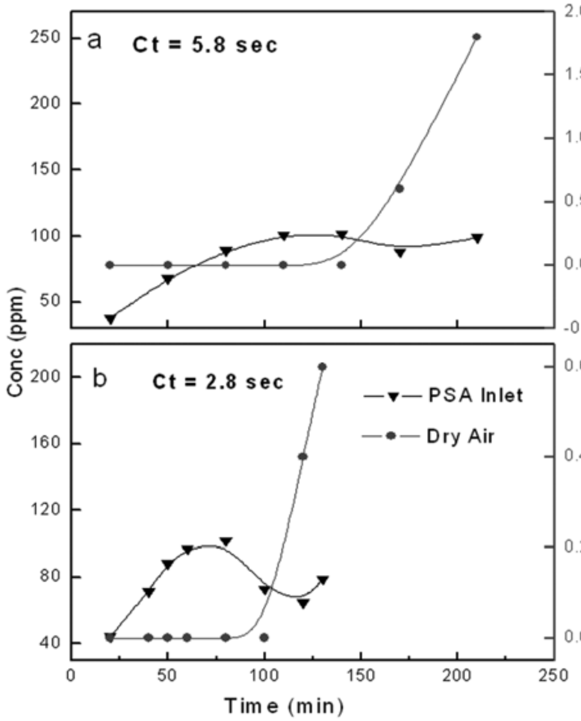


Fig. 6 — PSA inlet and dry air concentration profile at 6.5 lpm for single tower experiments (a) at 5.8 s (b) at 2.8 s

of contact time is more significant with respect to Bt values. It is observed that the breakthrough time is directly proportional to the contact time, however, it is non-linear. Hence, the factor of Bt/Ct is taken as the normalized factor for optimization studies. The Bt and the flow rate are plotted as a function of Bt/Ct (Fig. 7).

The results reveal that the Bt/Ct value is almost linear with the Bt. In contrast, flow rate appears to be the exponential decay with Bt/Ct. The flow rate corresponds to the intersection of both lines, i.e. at 6.5 lpm (contact time) chosen as an optimum value for given PSA, which will give better performance. The contact time corresponds to 6.5 lpm ~5.8 sec is found to be optimum for the PSA

Validation of breakthrough of DMS at optimized contact time 5.8 sec

In order to validate the optimum contact time a set of experiments were conducted at the 6.5 lpm. The results reveal (Fig. 6) that the experimental breakthrough time was identified as ~170 min. The PSA inlet concentration at 30 min was 44 ppm and it was marginally increased with time and the average concentration observed as 80 ppm. Based on the optimization plot (Fig. 7) the theoretical Bt value is approximately ~230 min, which is in good agreement with experimental. However, the little deviation in the value is attributed to the nonlinear relation between flow rate and the Bt values and also the variations in the concentrations in the PSA inlet during the experiments.

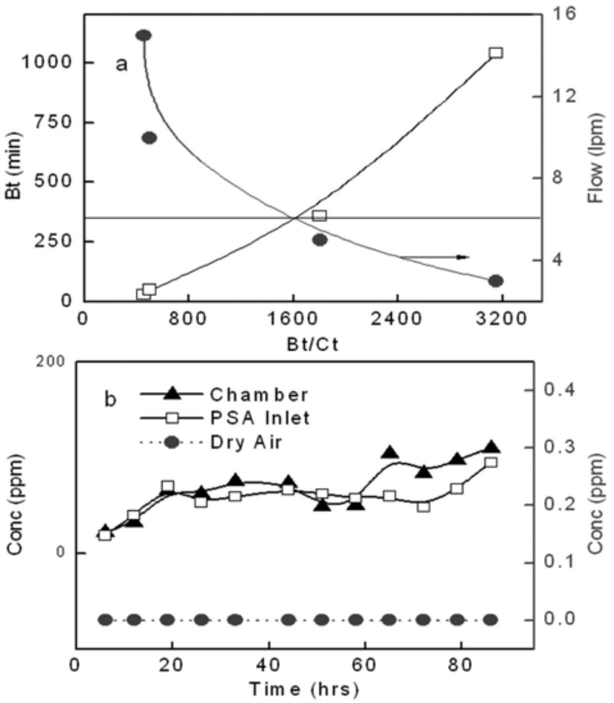


Fig. 7 — (a) Bt/Ct as function of Bt and Flow rate using single tower (b) DMS concentration profile as function of time
Pressure = 4Kg/cm^2, V_{total}= 6.5 lpm, Dry Air flow rate= 4 lpm , Purge Air flow rate = 2.5lpm, Cycle Time: 2 hr, Adsorbent =750 g. (each tower)

Sizing of PSA tower at reduced contact time of 2.8 sec

Sincerapid cycle times would cause the adsorbent beads to float or fluidize in the vessel, causing the abrasion of the beads leads to the significant lowering the performance. To achieve the optimum performance the conventional PSA systems must utilize large PSA towers to compensate for the slow cycle times, leading to higher costs and large vessels are typically erected in the field. Hence, it is essential to optimize the tower size and cycle time to achieve better performance.

In order to optimize the tower size the PSA towers are replaced with the 20 cm length towers (half of the earlier tower size, molecular sieves wt= 375 g) with a factor of 50% to get the contact time of 2.8 sec. The breakthrough was observed at ~85 min at 6.5 lpm, 4 kg/cm^2 and 50 ppm of DMS inlet concentration (Fig. 6). It is noteworthy in mentioning that the single tower breakthrough studies clearly demonstrate the value is ~50% of the full tower breakthrough time i.e. 170 min. The results reveal that Bt is proportional to tower size. Based on this breakthrough study the maximum cycle time can be given for the designed PSA is ~80 min with a factor of 50% additional safety parameter at a concentration of 80 ppm of DMS.

Dynamic adsorption capacity of 13X molecular sieves

One of the important parameters to size the PSA is the adsorption capacity of the adsorbent with respect to the probe molecule. The dynamic adsorption capacities were determined by the adsorbed amount under working conditions as described below. The dynamic adsorption capacities are calculated at 3, 5, 6.5, 10 and 15 lpm at 4 kg/cm^2 and 25 ^{o}C using the following equation.

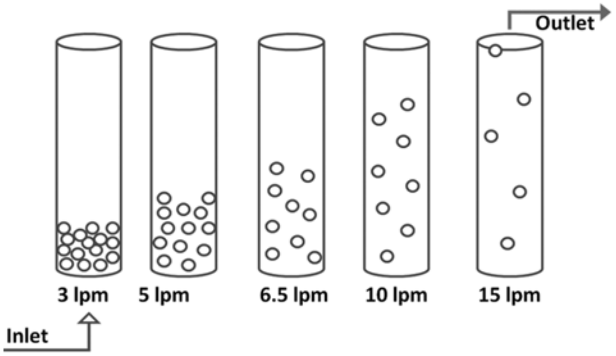
$$\% Adsorption capacity = \frac{Bt * Conc(g/l)}{amount of adsorbent(g)} \times 100 \quad \ldots (3)$$

The dynamic adsorption capacities (Fig. 5) of DMS are decreased sharply with increasing flow from 3 to 5 lpm. The dynamic adsorption data clearly demonstrates that the adsorption capacities are following the first order exponential decay with respect to the flow rate.

$$\%\ \text{dynamic adsorption of DMS} = 114 \times \exp^{(\text{-flow rate}/1.4)} + 0.4$$

The dynamic adsorption capacity of DMS is identified as 1.7 wt% on 13X mol. sieves at 25°C and 4 kg/cm^2 at a contact time 2.8 sec. Whereas the dynamic adsorption capacity at contact time 5.8 sec was 1.8wt%.

A typical cycle time for given PSA process, the adsorbent is used to adsorb and desorbs a certain amount of gas. Within each column of the PSA, the amount adsorbed will be distributed in an initial zone at low flow rate where equilibrium has been achieved and where the adsorbent is not completely saturated. The effect of radial distribution is normalized as a Teflon diffuser is placed at the beginning of the tower to maximize the dispersion of the flow across the PSA tower. The mass transfer zone is related to kinetic limitations to diffuse into the adsorbent and axial dispersion. By increasing the flow rates, the dynamic adsorption capacity is decreased due to the reduction in the contact time and the contaminant will distribute in the axial direction towards the end of the PSA tower (PSA outlet as shown in the Scheme 1) which is reflected in the breakthrough behaviour.



Scheme 1 — Schematic representation of concentration gradient in PSA tower at various flow rates

Evaluation of the PSA under Optimized conditions

Further the PSA studies were performed at optimum values based on dynamic adsorption capacity and the contact time results obtain as mentioned above. The PSA studies were performed at the total flow of 6.5 lpm, with a purge flow of 2 lpm (30 % of V_{total}), cycle time of 60 min at 4 kg/cm^2. The results (Fig. 7) reveal that there is no breakthrough of DMS for80 hours of continuous operation. The results reveal that the PSA combined with 13X molecular sieves appears to be the promising technology for the removal of reduced sulfur compounds specific to the DMS like low boiling molecules.

Conclusion

The dynamic adsorption capacities of 13X molecular sieves are at various flow rates and the PSA system is systematically elucidated. Single tower Breakthrough studies of DMS reveal that the adsorption capacity of 13X molecular sieves is varied from 13.8 to 0.3 % at 3 to 15 lpm, respectively. Under employed conditions there was no breakthrough was observed for 100 hrs at a cycle time of 60 min. Based on these studies the PSA combined with 13X molecular sieves can efficiently work for air purification can be scaled up for desired concentrations and flow rates by tuning the cycle time.

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