# On the Mechanism of Separation of Mixtures by Adsorption

*S.V. Sivakumar and D.P. Rao*
*Department of Chemical Engineering, Indian Institute of Technology Kanpur,*
*Kanpur – 208 016, INDIA*
*sivaku@iitk.ac.in , dprao@iitk.ac.in*

Countercurrent flow of the phases is the most efficient mode of contact for achieving sharp separation of mixtures and it is used for distillation, absorption and liquid extraction. However, in adsorption, the recirculation of solids through the adsorber requires very elaborate equipment and leads to attrition and loss of adsorbent. Therefore, alternate modes of contact are used and more so when gas phase is involved. Further, the regeneration of adsorbent adds another dimension.

The combination of

nature of adsorption equilibria:
- absorption-like and vapor-liquid-like phase equilibria,

modes of contact of phases:
- moving-bed, simulated moving-bed, fixed beds and circular beds,

methods of regeneration:
- thermal swing, pressure swing and elution,

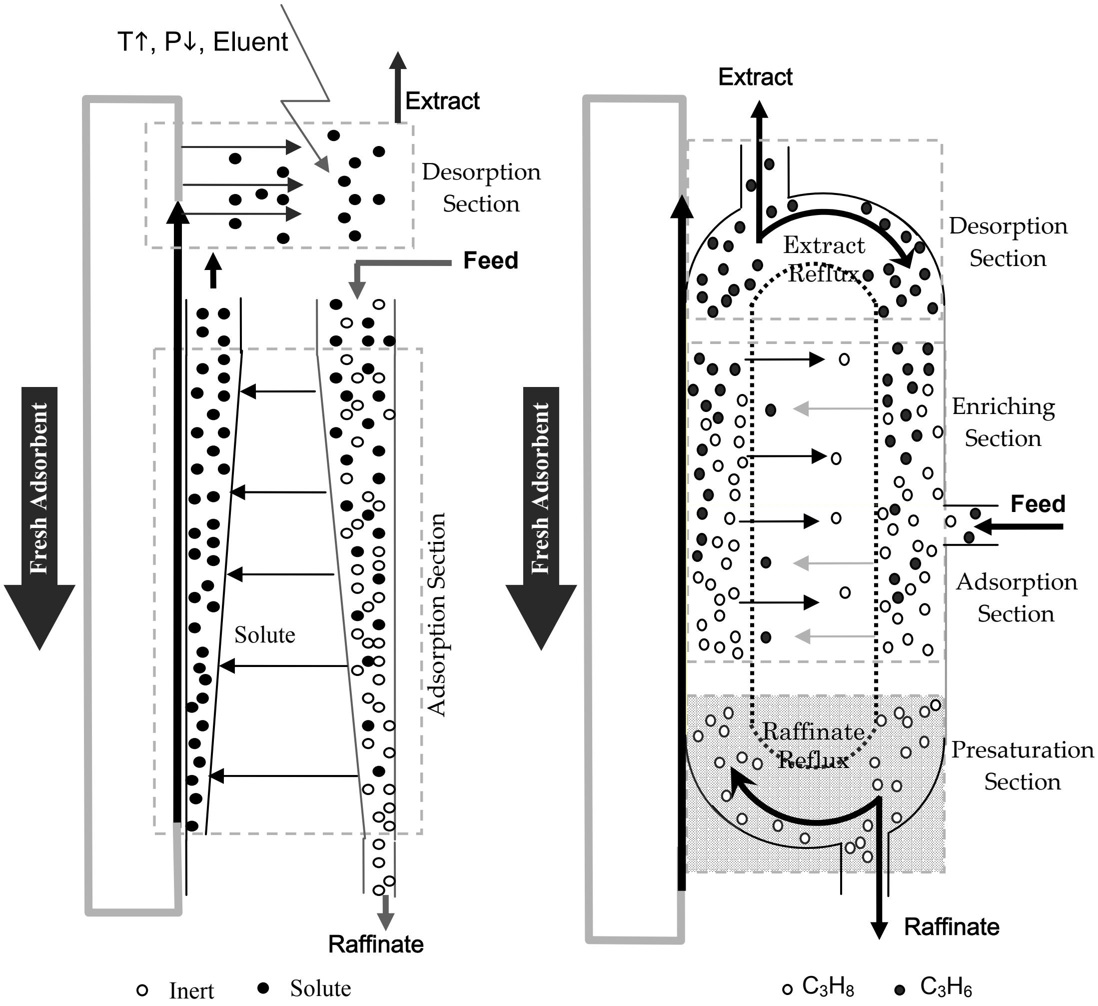
types of operation:
- steady-state and cyclic operation.

and, states of feed mixture:
- gas and liquid

leads to a rich variety of processes unlike for distillation, absorption and extraction. Some of these are: moving-Bed or simulated moving beds (SMB) with regeneration by thermal swing, pressure swing or elution; rotary circular bed with cross flow with thermal swing, pressure swing or elution; the conventional PSA (pressure swing adsorption) based on the Skarstrom cycle and its variants; Duplex PSA, Molecular-gate or Piston PSA with pressure or thermal swing; and rapid pressure swing adsorption. A few of these are relatively new and appeared first in patent literature.

The mechanism of separation and interrelation of these processes among themselves and with other separation processes like distillation, absorption and liquid extraction are not obvious. Understanding of these aspects would enable one to improve the performance of the existing ones and to devise new processes.

We have classified the processes based on the phase equilibria as absorption-like processes and distillation-like processes. In the former, the exchange of mass occurs by the Stefan diffusion, whereas in the latter it is by counter diffusion. If these processes are carried out in countercurrent mode of contact, the mechanism of exchange takes place as depicted in Figure 1. It is seen that the absorption-like processes require no reflux, whereas the distillation-like processes require both raffinate and extract refluxes. The mass transfer zones formed in conventional PSA is a kin to that of countercurrent contact processes. It is shown that in an idealized condition for both absorption- and distillation-like processes, it is possible to accomplish sharp separation in the moving-bed, SMB and conventional PSA by complete regeneration of adsorbent. For the partial regeneration, the use of purge with raffinate and extract can lead to sharp separation.



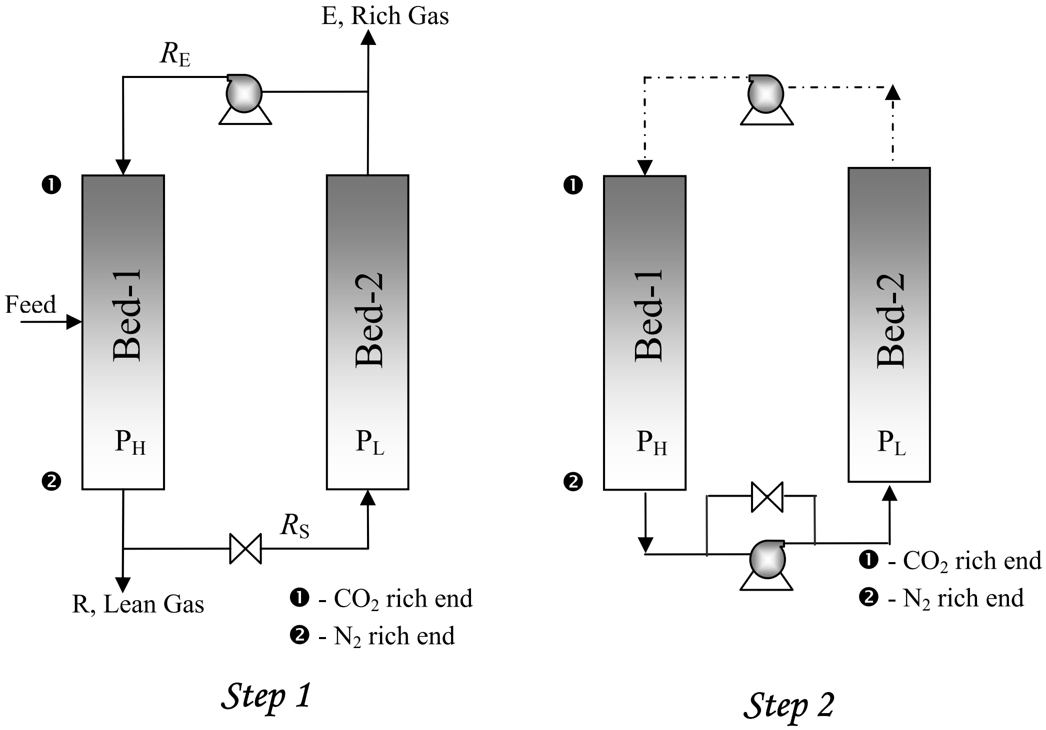
(a) Absorption-like processes

(b) Distillation-like processes

Figure 1: Mechanistic view of separation

The Duplex PSA proposed by Leavitt (1992), Dual-reflux PSA by Hirose and his coworkers (1995), Molecular-gate PSA by Keller and Kuo (1982), or the Piston PSA (2002) do not employ the complete regeneration of the adsorbent. We show that the separation mechanism of these processes is a kin to that heat transfer mechanism in a two-bed regenerator and there is no parallel for it in the other separation processes.

A schematic diagram of the duplex PSA is shown in Fig. 2. It employs two beds and operates in a cycle. Bed-1 is at high pressure and Bed-2 at low pressure. The feed is introduced in Bed-1 somewhere in-between the ends as in distillation. In Step-1, a part of the raffinate drawn from Bed-1 is recycled to Bed-2 and a part of the extract drawn from Bed-2 is recycled to Bed-1. In the next step, the pressure is equalized by connecting either of the ends of the beds. The pressure in Bed-1 is reduced to $P_L$ by transferring the gas from the raffinate



*Step 1*

*Step 2*

Figure 2: A schematic diagram of the Duplex PSA

end into Bed-2 so that Bed-2 reaches pressure, $P_H$. This constitutes Step-2. In Step-3, the feed is switched to Bed-2 and the end streams are recycled in the reverse direction to that in Step-1. Step-4 is similar to Step-2 but carried out in the reverse direction. The above four steps completes one cycle. Separations can be carried for both absorption-like and distillation-like processes.

Figure 3 shows the separation mechanism of absorption-like duplex process for an ideal case. The unidirectional transfer prevails. In the beginning of Step-1, the amount of heavy component in the adsorbent in Bed-1 corresponds to the profile represented by $Q_{1.}$ It can be seen that the adsorbate amount is nearly zero at the bottom of the bed and hence the raffinate rich in the light component is obtained. The incoming extract is rich in the heavy component and hence the bed is nearly saturated with the heavy component at the top. At the end of the step, the profile shifts to the profile shown as $Q_2$, as the heavy component coming with the extract and the feed is adsorbed. In Step-2, the initial profile is the same as $Q_2$. It shifts to $Q_3$ at the end of Step-2. At the end of Step-3, the profile shifts to $Q_4$ as the heavy component is desorbed all along the bed. On resetting the pressure in Bed-1 to $P_H$ and Bed-2 to $P_L$ in Step-4, the profile moves to $Q_1$. We see that the mass transfer zone is spread over the entire length of the bed, and it is possible to obtain extract rich in heavy component and the raffinate rich in the light component, if the profile is maintained as shown in Figure 3.

The Step-2 and Step-4 of the duplex PSA can be eliminated from the above cycle by varying the pressure $P_H$ to $P_L$ in the half of the cycle and reversing the flow. If we carry it out with a single bed, it becomes the molecular gate processes proposed By Keller and Kuo

(1982). The separation mechanism is same as of the duplex. The profile shifts from $Q_2$ to $Q_4$ in the first half of the cycle and retraces in the other half of the cycle.

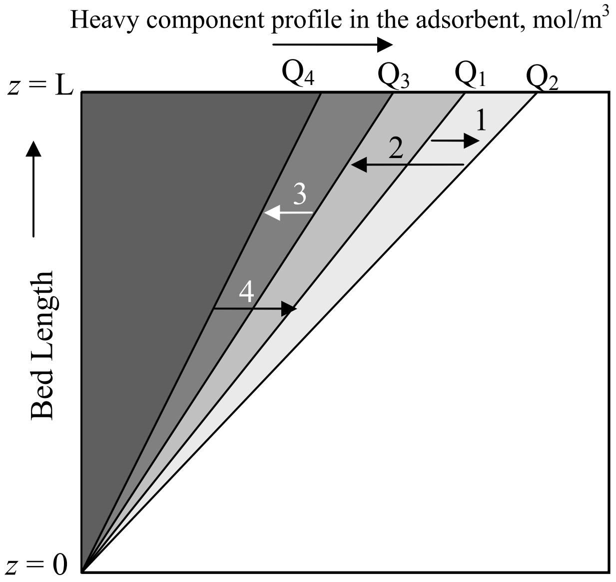


Figure 3: Duplex PSA – q-profiles for the heavy component with linear isotherm for absorption-like process

We have presented computer simulated profiles to validate the proposed mechanism of these processes. We have proposed new processes with thermal swing. These hold promise for large separation of gas mixtures, like upgrading of natural gas and $CO_2$ recovery from flue gases.

References:

1. F.W. Leavitt, US Patent 5,085,674 (1992)
2. D. Diagne, M. Goto and T. Hirose, Ind. Eng. Chem. Res., 34 (1995), 3083.
3. G.E. Keller II and C.H.A. Kuo, US Patent 4,354,859 (1982)
4. R. Arvind, S. Farooq and D.M. Ruthven, Chem. Engg. Sci., 57 (2002), 419.