Importance of Density in the Design of New Adsorbents for Technological Applications

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ABSTRACT: There are new and interesting adsorbents that show very high levels of adsorption on a mass basis. As one looks for viable new materials that can be moved from the bench to a pilot and then to full-scale units, a gap in adsorption results of these adsorbents immediately emerges. There has been a lack of consideration given to adsorbent density. When the transition is made from science to technology, density is critical because this variable will control the volume of the adsorbent bed and the size of the unit, both of which determine capital outlay.

There are new and interesting adsorbents that show very high levels of adsorption on a mass basis (moles of adsorbate per gram of adsorbent) with molecules such as carbon dioxide.[1,2] It is also the case that new adsorbents are considered for the storage of hydrogen and methane.[3−7] Because laboratory studies typically are focused on the science of the adsorbate−adsorbent interaction, in most of these papers adsorption results are reported on this basis. In some studies, the total adsorption may be given on a mole per unit area basis. This basis amounts to the same thing as a per gram basis since it is just the product of the latter and the reciprocal surface area per gram (or kilogram).

However, as one looks for viable new materials that can be moved from the bench to a pilot and then to full-scale units, a gap immediately emerges. There has been a lack of consideration given to adsorbent density. When the transition is made from science to technology, density is critical because this variable will control the volume of the adsorbent bed and the size of the unit, both of which determine capital outlay. This issue of densification has recently been examined nicely in the case of hydrogen storage over MOF-177.[8]

We can see how important this is with a simple analysis. Consider a bed of adsorbent of volume V_b. The adsorbent will be particulate, and so the bed will have a void fraction of ε_b. Hence, the volume of adsorbent is $V_{ads} = \varepsilon_b V_b$. For the sake of the analysis, we can divide this bed into n slices having a thickness of δ and a cross-sectional area of A_b. Let us also assume for the sake of the analysis that there are no radial gradients in concentration and that the mass of adsorbent is equal in every direction. While mass and heat transfer undoubtedly play a role in some real systems, for the sake of the analysis, we will assume that adsorption between the adsorbate and adsorbent comes to equilibrium instantaneously. Instantaneous means that the time constants for adsorption are fast compared to the residence time of the gas in any given slice of the bed. So in essence we are assuming that each slice is well mixed, and the governing equations become a series of n coupled ordinary differential equations for the adsorption of component a:

$$\frac{d(C_{a1}\varepsilon_b A_b \delta)}{dt} = (C_{af} - C_{a1})q - (r_{a-} + r_{a+})(1-\varepsilon_b)A_b\delta$$

$$\frac{d(C_{a2}\varepsilon_b A_b \delta)}{dt} = (C_{a1} - C_{a2})q - (r_{a-} + r_{a+})(1-\varepsilon_b)A_b\delta$$

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$$\frac{d(C_{an}\varepsilon_b A_b \delta)}{dt} = (C_{a(n-1)} - C_{an})q - (r_{a-} + r_{a+})(1-\varepsilon_b)A_b\delta$$

where C_{af} is the concentration of A in the gas phase at the top of the bed (mol/L), C_{an} is the concentration of A in the gas phase of the nth slice of the bed (mol/L), r_{a-} is the rate of adsorption of A or of its disappearance from the gas phase (mol/L/sec), r_{a+} is the rate of desorption of A or of its reappearance in the gas phase, (mol/L/sec), q is the volumetric flow rate (L/sec) in each slice. The adsorption process is assumed to come to equilibrium "instantaneously" meaning that the net rate of adsorption is zero and that in any slice just as in the nth slice, we have

$$\frac{d(C_{an}^s \varepsilon_b A_b \delta)}{dt} = -(r_{a-} + r_{a+})(1-\varepsilon_b)A_b\delta$$

$$0 = -(r_{a-} + r_{a+})$$

$$r_{a-} = -r_{a+}$$

If the rate of adsorption is expressed as the product of gas phase concentration of component a and the net concentration of adsorbent sites unoccupied by a and the rate of desorption is expressed as being first order in the number of adsorbent sites occupied by a, then this results in the Langmuir adsorption isotherm. The Langmuir isotherm reduces to a Henry's Law isotherm in the limit of weak adsorption energy or at low occupancy.

For our purposes, when the rates are equal, and the adsorbate and adsorbent come to equilibrium instantaneously, the series of equations reduces as such to these:

$$\frac{d(C_{a1}\varepsilon_b A_b \delta)}{dt} = (C_{af} - C_{a1})q$$

$$\frac{d(C_{a2}\varepsilon_b A_b \delta)}{dt} = (C_{a1} - C_{a2})q$$

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$$\frac{d(C_{an}\varepsilon_b A_b \delta)}{dt} = (C_{a(n-1)} - C_{an})q$$

For the nth slice of the bed as for each of the others, we see that the concentration leaving the slice is the same as the concentration within that slice. This result rests on the assumption that the slice is thin enough to be gradientless or well-mixed. The concentration in the nth slice and exiting the unit at any time t then is given as

$$C_{an} = C_{a(n-1)}\left(1 - \exp\left[-\frac{qt}{\varepsilon_b A_b \delta}\right]\right) - C_{a0}\exp\left[-\frac{qt}{\varepsilon_b A_b \delta}\right]$$

where C_{a0} is the concentration of component a in the gas phase at time $t = 0$; we can take this as zero for the sake of the analysis. Now, we can see that $[-qt/\varepsilon_b A_b \delta]$ can be rewritten as $[-t/\tau]$ Here τ is the holding time in the any slice of thickness δ.

$$C_{an} = C_{a(n-1)}\left(1 - \exp\left[-\frac{t}{\tau}\right]\right)$$

We want the concentration in the nth slice and that leaving the unit in terms of the known inlet concentration. Because the system is a series of slices, this leads to the well-known result that

$$C_{an} = C_{af}\left(1 - \exp\left[-\frac{t}{\tau}\right]\right)^n$$

This solution tells us early on after the flow is established that the concentration of component a exiting the bed is close to zero. Breakthrough begins, and the concentration rises to the concentration of the feed, wherein $C_{an} = C_{af}$.

Next we can ask the question of how much of component a will be adsorbed by a bed of a given volume at breakthrough. Let us assume that we want to know this when C_{an} is very close to C_{af} but not quite equal to it, to avoid the limit problem when $C_{af}/C_{an} = 1$. The time t that we are seeking is given as follows:

$$t = \left(\frac{\tau}{n}\right)\ln\left[1 - \frac{C_{an}}{C_{af}}\right]$$

The total moles adsorbed by the bed will then be just the product of the concentration of a in the feed, the flow rate, and the time on stream to breakthrough.

$$\text{total moles of A adsorbed} = C_{af}qt$$

$$= C_{af}q\left(\frac{\tau}{n}\right)\ln\left[1 - \frac{C_{an}}{C_{af}}\right]$$

But the total number of moles adsorbed on the bed can also be expressed in terms of the volume of adsorbent. The number of moles adsorbed on the adsorbent per gram at equilibrium and the density of the adsorbent are

$$\text{total moles of A adsorbed} = \varepsilon_b V_b M^* \rho$$

where M^* is the moles of component A adsorbed per gram of adsorbent at equilibrium and ρ is the density of the adsorbent. Therefore

$$C_{af}q\left(\frac{\tau}{n}\right)\ln\left[1 - \frac{C_{an}}{C_{af}}\right] = \varepsilon_b V_b M^* \rho$$

From this, we can see that the volume of the bed needed to adsorb a given amount of component a is given by this equation:

$$V_b = \frac{C_{af}q\left(\frac{\tau}{n}\right)\ln\left[1 - \frac{C_{an}}{C_{af}}\right]}{\varepsilon_b M^* \rho}$$

We can see that the density of the adsorbent figures into the volume of the bed needed as an inverse dependence. We also know that the cost of the unit scales with the volume to some power such as $^2/_3$. So immediately we can see how density is crucial to the design of the unit even under the ideal conditions shown here (in the absence of mass and heat transfer). Clearly as the density of the adsorbent drops, the volume of the bed must increase for the adsorption of a fixed amount of component a. But this is not the whole story, because we also know that for most real adsorbents the density is coupled to the pore volume and to the surface area of the adsorbent, meaning that for real adsorbents as the density rises, the volume of bed must once again increase to accommodate an adsorbent that has lessening surface area and internal porosity. Hence, the skeletal density of the adsorbent or its internal void fraction now become key adsorbent design parameters. These must be considered when we make the jump from a scientific result to a technological application of that result, but how to show this explicitly?

For the sake of the analysis and to learn even more about the dependence of bed volume, and since cost depends on density of the adsorbent, we need to introduce as an ansatz two ideas that can be reduced to simple constitutive relationships. First, we can think of the adsorbent as a porous solid that is derived from a nonporous solid of the same material. So, for example, we can think of activated carbon as being a highly porous version of graphite, wherein graphite is the nonporous "parent" solid. Similarly, activated aluminas such as alpha and gamma can be thought of as derived from the nonporous parent corundum because these are all higher energy states of Al_2O_3. In the same way, silica and silica gels are derivative of nonporous SiO_2. This idea of a high surface area material being derived from a nonporous parent compound is a new one, but it is consistent with thermodynamics. When these high surface area materials are heated to high temperatures, they lose surface area and porosity and tend to restructure themselves under this stress in a way that leads to the nonporous parent. This approach will allow us to get at the importance of skeletal density of the adsorbent.

Second, while this is a conceptually appealing idea we need to reduce it to constitutive relationships. We can make no further progress without an ansatz. Therefore, we will state that

the density of a porous material depends on the internal void fraction ε_s and the intrinsic density of the parent compound, ρ_o as follows:

$$\rho = \rho_0(1 - \varepsilon_s)$$

This expression is consistent with our observation that when the internal void fraction is zero, the density is a maximum and the same as that of the parent material. At the other end of the spectrum of internal void fractions, when it goes to unity the material has no materiality and hence no density.

We can introduce this, and we now see that the volume of adsorbent is inversely proportional to the void fraction of the adsorbent:

$$V_b = \frac{C_{af}q\left(\frac{\tau}{n}\right)\ln\left[1 - \frac{C_{an}}{C_{af}}\right]}{\varepsilon_b M^* \rho_0(1 - \varepsilon_s)}$$

We can now introduce a second concept and ansatz, and that is that the surface area of the material is also dependent on void fraction. Again let us think of the parent compound as nonporous having only a geometric external surface area, with no internal surface area, which we can take as effectively zero surface area. Hence, when there is no internal void fraction the internal surface area is effectively zero. What about at the other end of the spectrum, when the void fraction goes to unity? Here there is no solid and hence once again there is no surface area. Therefore, the second ansatz is to introduce the following constitutive relationship for the surface area per gram:

$$SA = SA_0\varepsilon_s(1 - \varepsilon_s)$$

where SA_0 is a proportionality constant or intrinsic geometric factor. It relates the shape and topology of the pores to the extent of void fraction, and it carries the dimensions of area per mass or the units of meters^2/g.

We recall that M^* is the extent of adsorption at equilibrium given in moles of adsorbate per gram of adsorbent. If we know the area occupied by each molecule, A_m, on the surface of the adsorbent, then we can express M^* as follows:

$$M^* = SA/A_m L$$

$$= SA_0\varepsilon_s(1 - \varepsilon_s)/(A_m L)$$

where M^* is moles of adsorbate per g of adsorbent, SA = meters^2/g; A_m = meters^2/molecule; L is Avogadro's number in molecules/mol.

We can no see the fullness of the relationship between the skeletal density of the adsorbent and the volume of the bed:

$$V_b = \frac{C_{af}q\left(\frac{\tau}{n}\right)\ln\left[1 - \frac{C_{an}}{C_{af}}\right]}{\frac{\varepsilon_b SA_0\rho_0(1 - \varepsilon_s)\varepsilon_s(1 - \varepsilon_s)}{A_m L}}$$

$$V_b = \frac{C_{af}q\left(\frac{\tau}{n}\right)\ln\left[1 - \frac{C_{an}}{C_{af}}\right]}{\left(\frac{\varepsilon_b SA_0\rho_0}{A_m L}\right)\varepsilon_s(1 - \varepsilon_s)^2}$$

$$\frac{V_b}{\varphi} = \frac{C_{af}q\left(\frac{\tau}{n}\right)\ln\left[1 - \frac{C_{an}}{C_{af}}\right]}{\left(\frac{\varepsilon_b SA_0\rho_0}{A_m L}\right)\varepsilon_s(1 - \varepsilon_s)^2}$$

$$\varphi = \frac{\left(\frac{\varepsilon_b SA_0\rho_0}{A_m L}\right)}{C_{af}q\left(\frac{\tau}{n}\right)\ln\left[1 - \frac{C_{an}}{C_{af}}\right]}$$

Once all the parameters are fixed, then we can see how V_b depends on the skeletal density of the adsorbent. At low or high skeletal density, the size and cost of the bed are steeply dependent upon this critical variable (Figure 1).
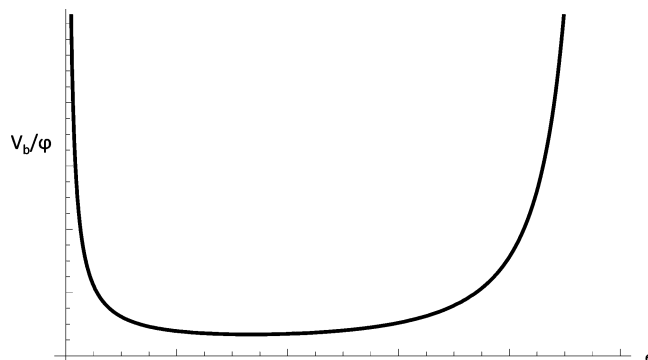

Figure 1. Dimensionless bed volume (V_b/ϕ) versus ε_s.

There is a wide region of optimality within which the bed size and cost are not critically dependent upon the skeletal density. However, at either end of the spectrum of adsorbent's skeletal void fraction, the bed volume rises exponentially. The general nature of this result leads to the conclusion that the void fraction within the adsorbent is a critical factor to control in the design of an adsorbent. Thus, density must be considered when the material is being transitioned from the laboratory toward working units. Hence as we look at new adsorbent materials, these sorts of practical considerations must be kept in mind if the science is to be the basis for new technology.

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Notes
The authors declare no competing financial interest.

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