

Adsorption Basics: Part 1

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Adsorption can be used to treat waste streams or purify valuable components of a feed. This article describes both equilibrium and mass-transfer considerations, and reviews the fundamentals of adsorption system design.

Adsorption takes advantage of the tendency of one or more components of a liquid or gas to collect on the surface of a solid. This tendency can be leveraged to remove solutes from a liquid or gas or to separate components that have different affinities for the solid. The process objective may be either waste treatment or the purification of valuable components of a feed stream. In an adsorption process, the solid is called the adsorbent and the solute is known as the adsorbate.

Commercial adsorbents are highly porous, with pore surface areas ranging from about 100 to 1,200 m²/g. The large surface area allows a large amount of adsorption relative to the weight of the adsorbent, well in excess of its own weight in some cases. Moreover, solute levels in the treated fluid can be reduced to a fraction of a ppm.

The affinity of a fluid component for a particular adsorbent depends on molecular characteristics such as size, shape, and polarity, the partial pressure or concentration in the fluid, and the system temperature. The attraction is caused by van der Waals forces and hydrophobic interactions (not covalent bonding). Bonding energies in adsorption range from about 10 to 70 kJ/mol, much lower than typical covalent bond energies of 200 to 500 kJ/mol. The adsorption bonding energy is high enough for adsorption to occur, yet low enough to allow the adsorbent to be regenerated by removing the adsorbed molecules.

Equilibrium considerations

The adsorption process can be considered a partitioning of the adsorbate between the fluid phase and the adsorbent. If the solid and fluid are placed in contact for a long time, an equilibrium distribution is reached, and this equilibrium can be described quantitatively.

Equilibrium behavior is characterized by expressing the amount of adsorbate adsorbed as a function of partial pressure (gases) or concentration (liquids) at a fixed temperature. Such an equilibrium model is called an isotherm, and many have been proposed. The simplest, yet one that works surprisingly well for many systems (notably gases that are weakly adsorbed), is the Langmuir isotherm (1). This model assumes that the surface of the adsorbent is homogeneous and flat, that the adsorbate forms a single layer on the surface, and that there are no interactions between adsorbed molecules.

For a gas containing a single adsorbate, the Langmuir isotherm is:

$$\theta = \frac{Kp}{Kp + 1} \quad (1)$$

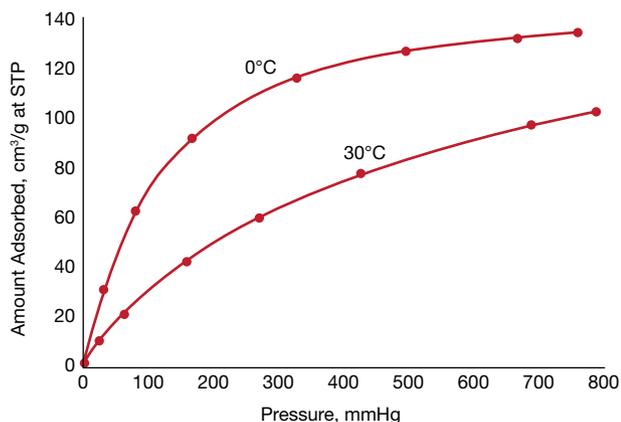
where θ is the fraction of the total available adsorption sites that are occupied, K is the adsorption equilibrium constant, and p is the adsorbate partial pressure. Equation 1 is easily derived, as detailed in Ref. 2 and other sources.

At low partial pressures, the denominator approaches 1, and the fraction adsorbed varies linearly with partial pressure in what is known as the first-order region or the Henry's law region. In this region, consistent with our intuition, a higher partial pressure increases the tendency toward adsorption.

However, as the pressure increases, the number of available adsorption sites decreases, and further adsorption becomes increasingly difficult. At high pressures, the denominator of Eq. 1 approaches Kp , and the fraction of occupied sites increases asymptotically to 1. Because there is little change in the amount of adsorbate adsorbed with pressure, this is called the zero-order region. Equation 1 also applies to liquids, with partial pressure replaced by concentration. The equations for multicomponent systems are given in Ref. 2.

In practice, isotherms are usually expressed in terms of the amount of adsorbate adsorbed per unit weight of adsorbent, rather than the fraction of sites occupied. Such data are shown in Figure 1 (3) for the adsorption of ammonia onto charcoal at two temperatures. These data follow the Langmuir model reasonably closely, and the first-order regions lie on the far left of the curves. The start of the zero-order region of the 0°C curve can also be seen, while the zero-order portion of the 30°C curve occurs at pressures higher than those shown.

Because the adsorption process is exothermic, the temperature significantly affects the amount of adsorbate adsorbed. In accordance with Le Chatelier's principle, operation of exothermic processes at higher temperature favors conditions that evolve less heat. Consequently, at a given pressure, the amount of adsorbate adsorbed at equilibrium decreases with increasing temperature. For this reason, adsorption processes are usually operated at room temperature. The exception is viscous feeds such as sugar



▲ **Figure 1.** These data for the adsorption of ammonia onto charcoal follow the Langmuir isotherm reasonably closely. Data are from (3).

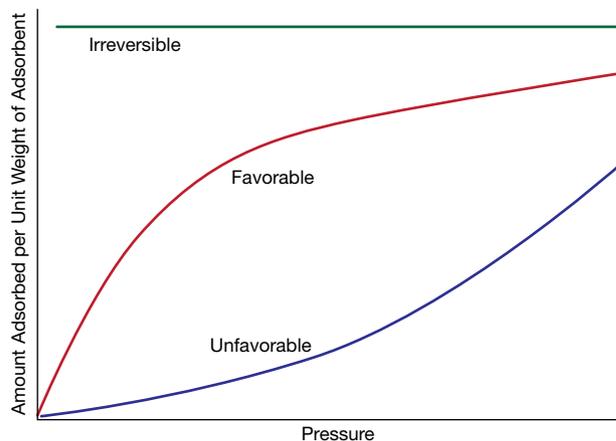
solutions, which are decolorized at elevated temperatures using activated carbon.

For situations where the Langmuir assumptions do not hold, numerous other models have been proposed. Most, like the Langmuir isotherm, contain first- and zero-order regions over certain ranges of partial pressure or concentration. One common model is the Freundlich isotherm:

$$n = kp^{1/m} \quad (2)$$

where n is the weight adsorbed per unit weight of adsorbent, and k and m are temperature-dependent constants, with m usually between 1 and 5 (4). In general, k decreases and m increases with increasing temperature, which equates to less equilibrium adsorption. Note that this model does not contain a Henry's law region at low pressures, except when $m = 1$ and the isotherm is linear. As with Eq. 1, pressure is replaced with concentration for liquids. The Freundlich isotherm works well for applications involving heterogeneous adsorbents — for example, adsorption of hydrocarbons by activated carbon.

Favorable and unfavorable isotherms are shown in Figure 2 (5). A favorable isotherm is one that has a convex shape, representing a large amount of adsorption at a low partial pressure (or for liquids, concentration). Conversely, an unfavorable isotherm has a concave shape, and a relatively high partial pressure is needed to achieve economic adsorption. The ultimate in favorable isotherms is irreversible adsorption, where maximum adsorption is reached at very low partial pressures. Note that an isotherm that is favorable for adsorption is unfavorable for desorption. In particular, the most favorable isotherm is the most difficult to desorb — hence the name irreversible.



▲ **Figure 2.** A favorable adsorption isotherm has a convex shape, which represents a large amount of adsorption at low partial pressures. An unfavorable adsorption isotherm has a concave shape, meaning a high partial pressure will be needed to achieve economic adsorption. Source: Adapted from (5).

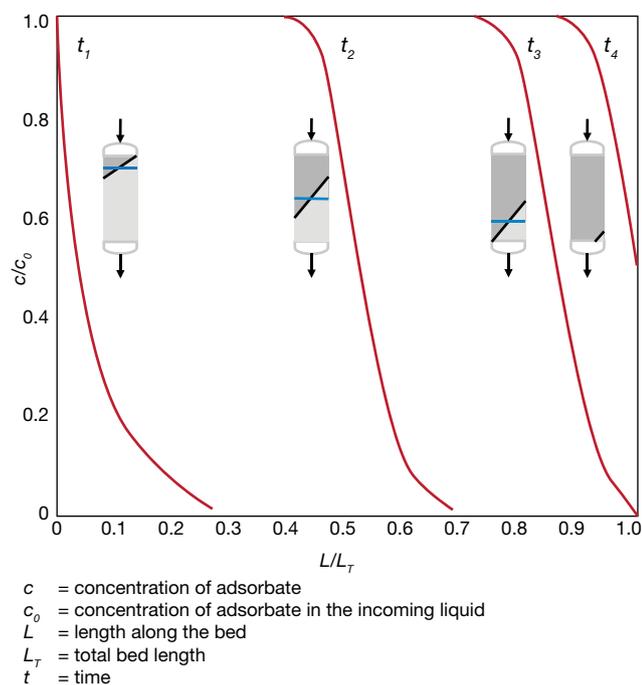
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Mass-transfer considerations

To be adsorbed, an adsorbate molecule must find its way to the adsorbent particle by convection, diffuse through the fluid film surrounding the particle, travel by diffusion along the length of a pore until it finds a vacant adsorption site, and then adsorb onto the solid surface. As in any transport process, these mass-transfer steps are driven by a departure from equilibrium, with the equilibrium described by an isotherm such as Eq. 1 or Eq. 2.

Common industrial practice is to pass the fluid to be treated through a column packed with the adsorbent, allowing this transport from the fluid to the adsorbent to take place. Such an operation is illustrated in Figure 3 (5, 6), which shows concentration profiles along the length of a fixed adsorbent bed at four different times. We assume the operation begins with a clean bed, *i.e.*, the adsorbent has been fully regenerated and contains no adsorbate. Mass transfer starts immediately upon introduction of the feed (a liquid in this case), causing the adsorbate concentration to decrease along the length of the bed until it reaches nearly zero.

Meanwhile, fresh feed continues to enter the column, so that the portion of the bed the feed contacts initially is continually exposed to fluid at the feed concentration. Eventually that part of the bed reaches equilibrium with the feed, and no additional net mass transfer occurs. When the feed reaches a section of the bed that has not yet achieved equilibrium, mass transfer resumes, and the fluid concen-



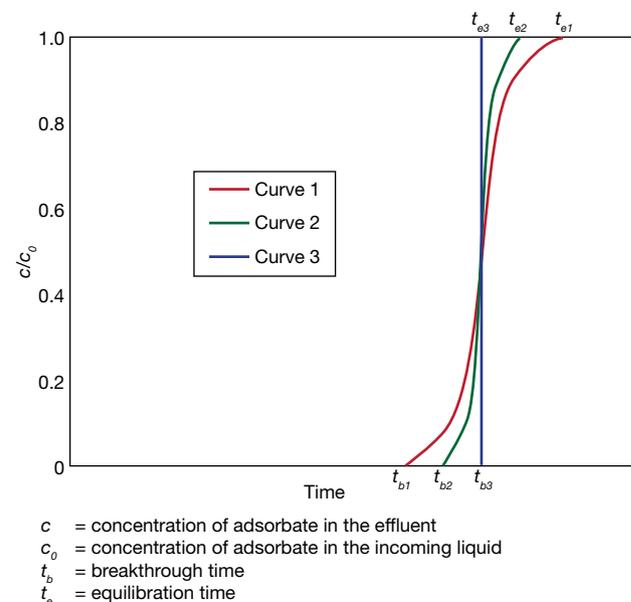
▲ **Figure 3.** The mass-transfer zone, indicated by the black diagonal line on each column, moves along the length of a fixed bed of adsorbent. Source: Adapted from (5, 6).

tration again decreases with increasing bed length, until it reaches nearly zero. The length over which the concentration changes is called the mass-transfer zone.

As the process continues, more and more of the adsorbent reaches equilibrium with the feed, as indicated by the advancing dark color in the depictions of the column in Figure 3. The feed must travel farther and farther before encountering the portion of the bed that has not yet reached equilibrium. In this manner, the mass-transfer zone progresses along the length of the bed and an increasing portion of the bed becomes used or inactive.

The mass-transfer zone, represented by the black diagonal line on each column in Figure 3, reaches the end of the bed at time t_3 . Subsequently, some adsorbate leaves with the column effluent, which usually is not desirable. This is called breakthrough, and time t_3 is referred to as the breakthrough time. The concept is illustrated by the breakthrough curves in Figure 4, which plot the adsorbate concentration in the column effluent as a function of time.

Prior to breakthrough, the concentration of adsorbate in the effluent is nearly zero, then it increases as the mass-transfer zone exits the end of the column. Ultimately, the trailing edge of the mass-transfer front reaches the end of the bed, and the effluent concentration increases to the feed value (*i.e.*, $c/c_0 = 1$). This occurs at the equilibration time (t_e), the time at which the entire bed is in equilibrium with the feed.



▲ **Figure 4.** Breakthrough occurs when adsorbate reaches the end of the column and leaves with the column effluent. Breakthrough curves are plots of the adsorbate concentration in the column effluent as a function of time. In the breakthrough curves shown here, mass transfer is slower for Curve 1 than Curve 2. Curve 3 is the ideal breakthrough curve, where mass transfer is instantaneous.

The length of the mass-transfer zone or, equivalently, the difference between breakthrough and equilibration times, depends on the mass-transfer rate. For example, in Figure 4, the mass-transfer rate for Curve 2 is higher than the rate for Curve 1, and the increase in adsorbate concentration in the effluent after initial breakthrough is steeper, indicating that the bed is being utilized more efficiently. As shown in the column depiction in Figure 3 for time t_3 , a portion of the bed below the mass-transfer front is still active at breakthrough. A higher mass-transfer rate creates a shorter mass-transfer zone. For the ideal case of no mass-transfer resistance, mass transfer is instantaneous, and the length of the mass-transfer zone approaches zero. The zone advances as a flat front, the bed is fully equilibrated at breakthrough, and the breakthrough curve is a vertical line (Curve 3 of Figure 4).

The amount of adsorbate adsorbed at any given time is directly related to the area above the breakthrough curve at that time, bounded by $c/c_0 = 1$. The portion of the bed that has equilibrated with the feed is the ratio of this area to the corresponding area at full equilibration. Consider Curve 1 of Figure 4 as an example. The amount adsorbed at breakthrough is indicated by the area of the rectangle with corners $(0, 0)$, $(t_{b1}, 0)$, $(t_{b1}, 1)$, and $(0, 1)$. The fraction equilibrated is this area divided by the area above the curve passing through $(0, 0)$, $(t_{b1}, 0)$ and $(t_{e1}, 1)$, bounded by $c/c_0 = 1$. Equivalently, if breakthrough follows theory and has a symmetrical S-shape (which is not always the case in real columns, of course), the area of full equilibration is equal to that of the rectangle with corners $(0, 0)$, $(t_{b3}, 0)$, $(t_{b3}, 1)$, and $(0, 1)$.

Put another way, if the breakthrough curve has a symmetrical S-shape, the operation can be described as an ideal adsorption process with a flat mass-transfer front, as depicted by the blue advancing horizontal line in the column drawings of Figure 3. The breakthrough time for this ideal process, which occurs at the midpoint of the real S-shaped breakthrough curve, is known as the stoichiometric time, or t^* . The portion of the bed that is equilibrated is the real breakthrough time divided by the stoichiometric time. Conversely, the portion still active is:

$$\frac{LUB}{L_T} = 1 - \frac{t_b}{t^*} \quad (3)$$

where L_T is the total bed length and LUB is the length of the unused bed at breakthrough.

If we assume that the mass-transfer zone moves through the bed unchanged, then for a given adsorption process, the LUB does not change with bed length. Consequently, bed utilization efficiency improves with length, because the unused portion becomes a smaller fraction of the overall bed. However, in a real column, the mass-transfer zone does

change at least slightly as it moves through the bed due to backmixing and axial dispersion.

Example 1. A 10-cm-dia. column is packed with adsorbent to a bed height of 1 m. A liquid with a density of $1,000 \text{ kg/m}^3$ containing 0.5% adsorbate is delivered at a flowrate of five bed volumes per hour. The breakthrough vs. time curve is approximately S-shaped, like Curve 1 and Curve 2 of Figure 4. Adsorbate is first detected in the effluent after 10 hr, and the concentration reaches that of the feed after 11 hr. What are (a) the capacity of the adsorbent at breakthrough, (b) the full equilibration capacity, and (c) the length of the unused bed?

a. The bed volume is:

$$\frac{\pi(0.1 \text{ m})^2}{4} \times 1 \text{ m} = 0.0079 \text{ m}^3$$

and the flowrate is $5/\text{hr} \times 0.0079 \text{ m}^3 = 0.0395 \text{ m}^3/\text{hr}$. The adsorbate feed rate is $0.0395 \text{ m}^3/\text{hr} \times 1,000 \text{ kg/m}^3 \times 0.005 = 0.1975 \text{ kg/hr}$. The adsorbent capacity at breakthrough is:

$$\frac{0.1975 \text{ kg/hr} \times 10 \text{ hr}}{0.0079 \text{ m}^3} = 250 \text{ kg/m}^3$$

b. The capacity at full equilibration is determined using the stoichiometric time, which is the midpoint of the breakthrough curve, or 10.5 hr. Repeating Step (a) using this time, the capacity at full utilization is 262.5 kg/m^3 .

c. From Eq. 3:

$$LUB = 1 \text{ m} \left(1 - \frac{10 \text{ hr}}{10.5 \text{ hr}} \right) = 0.048 \text{ m}$$

Nomenclature

A	= cross-sectional area
c	= concentration of adsorbate
c_0	= concentration of adsorbate in the incoming liquid
D	= column diameter
K	= adsorption equilibrium constant
k	= temperature-dependent constant
L	= length along the bed
L_T	= total bed length
LUB	= length of the unused bed at breakthrough
m	= temperature-dependent constant
n	= weight adsorbed per unit weight of adsorbent
p	= adsorbate partial pressure
t	= time
t^*	= stoichiometric time
t_b	= breakthrough time
t_e	= equilibration time

Greek Letters

θ	= the fraction of the total available adsorption sites that are occupied
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Regeneration

Once breakthrough occurs, the adsorbent must be regenerated — that is, adsorbed molecules are removed (*i.e.*, desorbed) so that the column is ready for the next adsorption cycle. Adsorbents are regenerated by shifting the equilibrium distribution using one of several methods, including:

- contacting the adsorbent with gas or liquid that contains little or no adsorbate. For example, when treating an air or wastewater stream, regeneration may be done using clean air or water.
- contacting the adsorbent with a solvent that has a higher affinity for the adsorbate. For example, a hydrophobic polymer treating an aqueous stream is typically regenerated with ethanol or other polar solvent.
- increasing the temperature, a technique called temperature swing adsorption. This method leverages the exothermic nature of the adsorption process, as explained earlier. Options include regeneration in place using steam or hot gas, or for more complete regeneration, removal and heating in a kiln.
- in gas service, reducing the pressure, a method known as pressure swing adsorption.

Pilot testing and design

For applications that are routine, equipment manufacturers can often recommend a suitable adsorbent and system design without the need for pilot testing. Off-the-shelf units are available in some cases. On the other hand, if there is little experience with the application, pilot testing is required. Objectives of pilot work include determining the adsorbent capacity, ease of regeneration, required residence time, and particle size effects.

One challenge of pilot testing is to minimize the impact of backmixing and axial dispersion, which increase upon scale-up. Wall effects, which refer to the effects of fluid contact with the column wall rather than the adsorbent itself, must also be considered. Wall effects are larger in smaller columns; because the surface-to-volume ratio is higher, a larger percentage of the fluid contacts the wall. To minimize scale-up risk, pilot columns should be at least 3 in. in diameter, or larger for scale-up to very large production columns.

Adsorption system design consists of three steps:

Step 1. Choose the adsorbent and particle size. The choice of adsorbent is governed by many considerations, including:

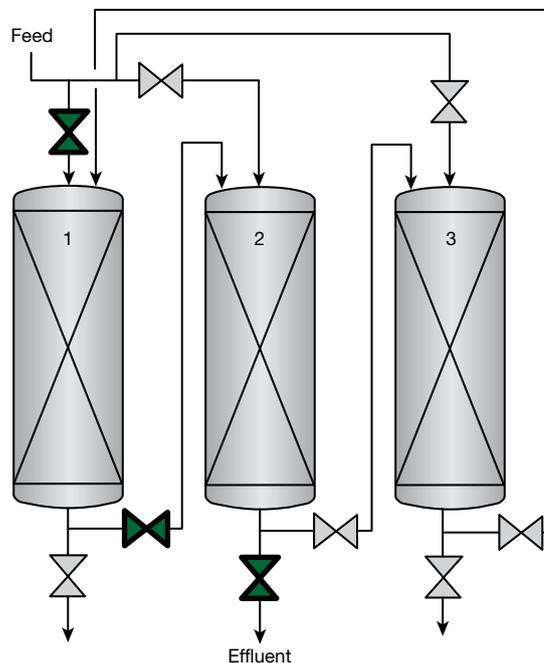
- the nature of the stream to be treated (*e.g.*, aqueous liquid, stack gas)
- characteristics of the adsorbates to be removed, their level in the feed, and the degree of removal required
- required throughput
- required extent of regeneration
- process objective (purification or waste treatment).

A smaller particle size enables a higher mass-transfer rate (*i.e.*, a shorter mass-transfer zone), because the intra-particle diffusion path is shorter. Note that the improved mass transfer is not attributable to additional surface area — surface area varies little with particle size, because nearly all of the active area is in the internal pores, with an insignificant amount on the exterior surface.

The preferred particle size is the smallest one that still has a tolerable pressure drop. In general, gas adsorption employs larger particles than liquid adsorption, because gas diffusion rates are higher. For example, a carbon adsorber in gas service may use a 4×6 or 4×10 mesh particle, while an 8×30, 12×40 or 20×50 mesh size may be chosen for a liquid.

Step 2. Choose the superficial velocity and calculate the required diameter. The length of the mass-transfer zone increases with increasing velocity, with a corresponding decrease in bed utilization efficiency. The economic velocity is the highest velocity that provides sufficient residence time (a function of both velocity and column length) for the required adsorption, adequate bed utilization, and acceptable pressure drop. Higher velocities can be used for gases than for liquids (again because diffusion rates are higher for gases), which translates to a shorter residence time. Typical velocities are 0.15–0.6 m/sec for gases and 0.001–0.004 m/sec for liquids.

The column diameter is calculated from the required throughput and the chosen velocity. When selecting the



▲ **Figure 5.** In this three-column arrangement, Column 1 and Column 2 serve as the lead and guard, respectively, while Column 3 is on regeneration or standby. Valves in bold are open, the others are closed.

diameter, the exothermic nature of the adsorption process must be considered. Heat loss from small columns is usually sufficient to avoid a significant increase in temperature. On the other hand, a lower surface-to-volume ratio causes large columns to operate nearly adiabatically. Temperature rise can be as high as 50°C with only 1% adsorbate in the feed (5). For this reason, multiple small columns in parallel rather than one large column may be needed for high-throughput applications.

Step 3. Select the bed length. A longer bed contains more adsorbent, which allows longer online time before regeneration is needed. Moreover, bed utilization efficiency increases with bed length, because the unused part becomes a smaller portion of the overall bed, as explained previously. On the downside, a taller column is more expensive, and the pressure drop is higher. Choose a bed length that is the longest one that provides reasonable breakthrough time, pressure drop, and cost.

Most large-volume operations employ three columns (or parallel banks of columns) in series (Figure 5). Column 1, the lead column, can be operated to full equilibration without loss of adsorbate, because the breakthrough is captured in Column 2, the guard column. When Column 1 is fully equilibrated with the feed, it is taken offline for regeneration, Column 2 becomes the lead column, and freshly regenerated Column 3 becomes the guard column. In this manner, each column cycles through lead, guard, and standby, without the interruption for regeneration that would be needed for a process with a single column. If an installed spare is desired for maintenance outage, four columns (or parallel banks of columns) may be used.

Example 2. 100,000 L/day of liquid containing 0.1% adsorbate is to be treated. During pilot plant testing of the selected adsorbent, performance was acceptable at a super-

ficial velocity of 0.003 m/sec, with tolerable pressure drop and an adsorption capacity of 0.3 kg adsorbate/kg adsorbent. The feed density is 1,000 kg/m³, the adsorbent bulk density is 640 kg/m³, and the desired online time (prior to regeneration) is 48 hr. What column diameter and packed height are needed?

Solution: The volumetric flowrate in m³/sec is:

$$100,000 \frac{\text{L}}{\text{day}} \times \frac{1 \text{ day}}{86,400 \text{ s}} \times \frac{1 \text{ m}^3}{1,000 \text{ L}} = 0.00116 \frac{\text{m}^3}{\text{s}}$$

The required cross-sectional area is:

$$A = \frac{0.00116 \text{ m}^3/\text{s}}{0.003 \text{ m/s}} = 0.386 \text{ m}^2$$

The diameter is:

$$D = \sqrt{\frac{4A}{\pi}} = \sqrt{\frac{4 \times 0.386 \text{ m}^2}{\pi}} = 0.7 \text{ m}$$

The amount of adsorbate delivered to the column per cycle is:

$$48 \text{ hr} \times \frac{100,000 \text{ L}}{24 \text{ hr}} \times \frac{1 \text{ m}^3}{1,000 \text{ L}} \times \frac{1,000 \text{ kg}}{\text{m}^3} \times 0.001 = 200 \text{ kg}$$

The adsorbent needed is:

$$\frac{200 \text{ kg}}{0.3 \text{ kg adsorbate/kg adsorbent}} \times \frac{1 \text{ m}^3}{640 \text{ kg}} = 1.04 \text{ m}^3$$

The packed height is:

$$\frac{1.04 \text{ m}^3}{0.386 \text{ m}^2} = 2.7 \text{ m}$$

Concluding remarks

The next article in this two-part series covers specific types of adsorbents, including the physical characteristics, suitable applications, and regeneration requirements of each type. Ion exchange, a topic that comprises types of polymers used, ion exchange chemistry, equilibrium considerations, and process operations, is also reviewed.

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