Carbon Adsorption for VOCs

Course Number: EN-02-110

PDH: 4

Approved for: AK, AL, AR, DE, FL, GA, IA, IL, IN, KS, KY, LA, MD, ME, MI, MN, MO, MS, MT, NC, ND, NE, NH, NJ, NM, NV, NY, OH, OK, OR, PA, SC, SD, TN, TX, UT, VA, VT, WI, WV, and WY

State Board Approvals

Florida Provider # 0009553 License #868
Indiana Continuing Education Provider #CE21800088
Maryland Approved Provider of Continuing Professional Competency
New Jersey Professional Competency Approval #24GP00025600
North Carolina Approved Sponsor #S-0695
NYSED Sponsor #274

Instructor: Mathew Holstrom

How Our Written Courses Work

This document is the course text. You may review this material at your leisure before or after you purchase the course.
After the course has been purchased, review the technical material and then complete the quiz at your convenience.
A Certificate of Completion is available once you pass the exam (70% or greater).
If a passing grade is not obtained, you may take the quiz as many times as necessary until a passing grade is obtained).
If you have any questions or technical difficulties, please call (508) 298-4787 or email us at admin@PDH Pro.com.

1.0 Introduction

In air pollution control, adsorption is employed to remove volatile organic compounds (VOCs) from low to medium concentration gas streams, when a stringent outlet concentration must be met and/or recovery of the VOC is desired. Adsorption itself is a phenomenon where gas molecules passing through a bed of solid particles are selectively held there by attractive forces which are weaker and less specific than those of chemical bonds. During adsorption, a gas molecule migrates from the gas stream to the surface of the solid where it is held by physical attraction releasing energy—the "heat of adsorption", which typically equals or exceeds the heat of condensation. Adsorptive capacity of the solid for the gas tends to increase with the gas phase concentration, molecular weight, diffusivity, polarity, and boiling point. Gases form actual chemical bonds with the adsorbent surface groups. This phenomenon is termed "chemisorption".

Most gases ("adsorbates") can be removed ("desorbed") from the adsorbent by heating to a sufficiently high temperature, usually via steam or (increasingly) hot combustion gases, or by reducing the pressure to a sufficiently low value (vacuum desorption). The physically adsorbed species in the smallest pores of the solid and the chemisorbed species may require rather high temperatures to be removed, and for all practical purposes cannot be desorbed during regeneration. For example, approximately 3 to 5 percent of organics adsorbed on virgin activated carbon is either chemisorbed or very strongly physically adsorbed and is difficult to desorb during regeneration.[1]

Adsorbents in large scale use include activated carbon, silica gel, activated alumina, synthetic zeolites, fuller's earth, and other clays. This section is oriented toward the use of activated carbon, a commonly used adsorbent for VOCs.

1.1 Types of Adsorbers

Five types of adsorption equipment are used in collecting gases: (1) fixed regenerable beds; (2) disposable/rechargeable cannisters; (3) traveling bed adsorbers; (4) fluid bed adsorbers; and (5) chromatographic baghouses.[2] Of these, the most commonly used in air pollution control are fixed-bed systems and cannister types. This section addresses only fixed-bed and cannister units.

1.1.1 Fixed-bed Units

Fixed-bed units can be sized for controlling continuous, VOC-containing streams over a wide range of flow rates, ranging from several hundred to several hundred thousand cubic feet per minute (cfm). The VOC concentration of streams that can be treated by fixed-bed adsorbers can be as low as several parts per billion by volume (ppbv) in the case of some toxic chemicals or as high as 25% of the VOCs' lower explosive limit (LEL). (For most VOCs, the LEL ranges from 2500 to 10,000 ppmv.[3])

Fixed-bed adsorbers may be operated in either intermittent or continuous modes. In intermittent operation, the adsorber removes VOC for a specified time (the "adsorption time"), which corresponds to the time during which the controlled source is emitting VOC. After the adsorber and the source are shut down (e.g., overnight), the unit begins the desorption cycle during which the captured VOC is removed from the carbon. This cycle, in turn, consists of three steps: (1) regeneration of the carbon by heating, generally by blowing steam through the bed in the direction opposite to the gas flow;[1](2) drying of the bed, with compressed air or a fan; and (3) cooling the bed to its operating temperature via a fan. (In most designs, the same fan can be used both for bed drying and cooling.) At the end of the desorption cycle (which usually lasts 1 to 1½ hours), the unit sits idle until the source starts up again.

In continuous operation a regenerated carbon bed is always available for adsorption, so that the controlled source can operate continuously without shut down. For example, two carbon beds can be provided: while one is adsorbing, the second is desorbing/idled. As each bed must be large enough to handle the entire gas flow while adsorbing, twice as much carbon must be provided than an intermittent system handling the same flow. If the desorption cycle is significantly shorter than the adsorption cycle, it may be more economical to have three, four, or even more beds operating in the system. This can reduce the amount of extra carbon capacity needed or provide some additional benefits, relative to maintaining a low VOC content in the effluent. (See Section 1.2 for a more thorough discussion of this.)

A typical two-bed, continuously operated adsorber system is shown in Figure 3.1. One of the two beds is adsorbing at all times, while the other is desorbing/idled. As shown here, the VOC-laden gas enters vessel #1 through valve A, passes through the carbon bed (shown by the shading) and exits through valve B, from whence it passes to the stack. Meanwhile, vessel #2 is in the desorption cycle. Steam enters through valve C, flows through the bed and exits through D. The steam-VOC vapor mixture passes to a condenser, where cooling water condenses the entire mixture. If part of the VOC is immiscible in water, the condensate next passes to a decanter, where the VOC and water layers are separated. The VOC layer is conveyed to storage. If impure, it may receive additional purification by distillation. Depending on its quality (i.e., quantity of dissolved organics), the water layer is usually discharged to a wastewater treatment facility.

---

[1] Although steam is the most commonly used regenerant, there are situations where it should not be used an example would be a degreasing operation that emits halogenated VOCs. Steaming might cause the VOCs to decompose.

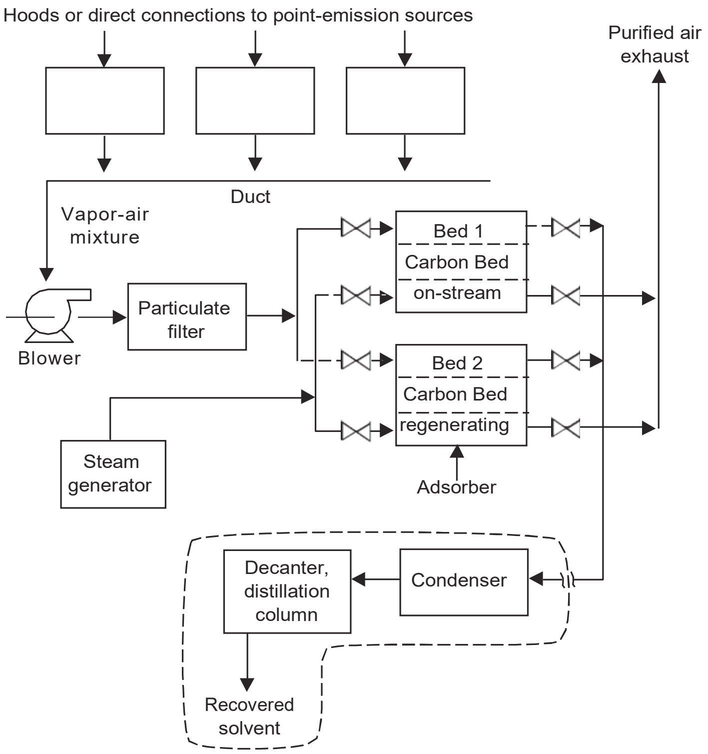

Figure 1.1: Typical-Two-Bed, Continuously Operated Fixed Bed Carbon Adsorber System

1.1.2 Cannister Units

Cannister-type adsorbers originally referred to relatively small returnable containers, such as 55-gallon drums. Cannisters differ from fixed-bed units, in that they are normally limited to controlling lower-volume and intermittent gas streams, such as those emitted by storage tank vents, where process economics dictate that off-site -regeneration is appropriate. The carbon cannisters are not intended for desorption on-site. However, the carbon may be regenerated at a central facility. The term cannister is becoming something of a misnomer as much of the growth in the industry is in larger vessels without regeneration capabilities. Calgon provided information on standard systems as large as 8,000 cfm and carbon capacitates of 2,000 pounds; TIGG Corporation reported systems as large as 30,000 cfm. [4][5]

Once the carbon reaches a certain VOC content, the unit is shut down and either the carbon or the cannister is replaced. The carbon or cannister is then returned to a reclamation facility or regenerated at the central facility. Each cannister unit consists of a vessel, activated carbon, inlet connection and distributer leading to the carbon bed, and an outlet connection for the purified gas stream. In one design (Calgon's Ventsorb®), 180 lbs of carbon are installed on an 8-inch gravel bed, in a 55-gallon drum with an internal collector. The type of carbon used depends on the nature of the VOC to be treated [6]. Non-regenerable vessels can be placed in a series, this protects against breakthrough because in the event that the first cannister or vessel becomes saturated with VOC, the second then becomes the primary carbon adsorber. One option would be to periodically remove the most saturated cannister or carbon bed and add a fresh cannister or carbon bed to the clean end. Periodic sampling for breakthrough between the carbon beds would assure that replacement occurred frequently enough to avoid breakthrough to the atmosphere. This approach also improves cost effectiveness of carbon replacement because the carbon is at or near its saturation point when it is replaced.

In theory, a cannister unit would remain in service longer than a regenerable unit would stay in its adsorption cycle due to a higher theoretical capacity for fresh carbon compared to carbon regenerated on-site. The service life is based on a service factor determined by the ratio of the theoretical capacity to the working capacity. Determining service factors help to ensure the allowable outlet concentration from being exceeded. In reality, however, poor operating practice may result in the cannister remaining connected until the carbon is near or at saturation. This is because: (1) the carbon (and often the vessel) will probably be disposed of, so there is the temptation to operate it until the carbon is saturated; and (2) unlike fixed-bed units, whose outlet VOC concentrations are usually not monitored continuously (via flame ionization detectors, typically), canisters are usually not monitored. Adequate recordkeeping and periodic monitoring for breakthrough can be supported by bed life modeling provided by vendors to ensure that cannister replacement occurs with sufficient frequency and that breakthrough does not occur.

1.1.3 Adsorption Theory

At equilibrium, the quantity of gas that is adsorbed on activated carbon is a function of the adsorption temperature and pressure, the chemical species being adsorbed, and the carbon characteristics, such as carbon particle size and pore structure. For a given adsorbent-VOC combination at a given temperature, an adsorption isotherm can be constructed which relates the mass of adsorbate per unit weight of adsorbent ("equilibrium adsorptivity") to the partial pressure of the VOC in the gas stream. The adsorptivity increases with increasing VOC partial pressure and decreases with increasing temperature.

A family of adsorption isotherms having the shape typical of adsorption on activated carbon is plotted in Figure 3.2. This and other isotherms whose shapes are convex upward throughout, are designated “Type I” isotherms. The Freundlich isotherm, which can be fit to a portion of a Type I curve, is commonly used in industrial design. [2]

$$W_e = k\,P_m \tag{1.1}$$

where

w_e = equilibrium adsorptivity (lb adsorbate/lb adsorbent)
P = partial pressure of VOC in gas stream (psia)
k, m = empirical parameters

The treatment of adsorption from gas mixtures is complex and beyond the scope of this chapter. Except where the VOC in these mixtures have nearly identical adsorption isotherms, one VOC in a mixture will tend to displace another on the carbon surface. Generally, VOCs with lower vapor pressures will displace those with higher vapor pressure, resulting in the former displacing the latter previously adsorbed. Thus, during the course of the adsorption cycle the carbon’s capacity for a higher vapor pressure constituent decrease. This phenomenon should be considered when sizing the adsorber. To be conservative, one would normally base the adsorption cycle requirements on the least adsorbable component in a mixture and the desorption cycle on the most adsorbable component.[1]

The equilibrium adsorptivity is the maximum amount of adsorbate the carbon can hold at a given temperature and VOC partial pressure. In actual control systems where there are not two beds operating in series, however, the entire carbon bed is never allowed to reach equilibrium. Instead, once the outlet concentration reaches a preset limit (the “breakthrough concentration”), the adsorber is shut down for desorption or (in the case of cannister units) replacement and disposal. At the point where the vessel is shut down, the average bed VOC concentration may only be 50% or less of the equilibrium concentration. That is, the carbon bed may be at equilibrium (“saturated”) at the gas inlet, but contain only a small quantity of VOC near the outlet.

As Equation 3.1 indicates, the Freundlich isotherm is a power function that plots as a straight line on log-log paper. Conveniently, for the concentrations/partial pressures normally encountered in carbon adsorber operation, most VOC-activated carbon adsorption conforms to Equation 3.1. At very low concentrations, typical of breakthrough concentrations, a linear approximation (on arithmetic coordinates) to the Freundlich isotherm is adequate. However, the Freundlich isotherm does not accurately represent the isotherm at high gas concentrations and thus should be used with care as such concentrations are approached.

Adsorptivity data for selected VOCs were obtained from Calgon Corporation, a vendor of activated carbon.[6] The vendor presents adsorptivity data in two forms: a set of graphs displaying equilibrium isotherms [6] and as a modification of the Dubinin-Radushkevich (D-R) equation, a semi-empirical equation that predicts the adsorptivity of a compound based on its adsorption