Adsorption with Granular Activated Carbon (GAC)

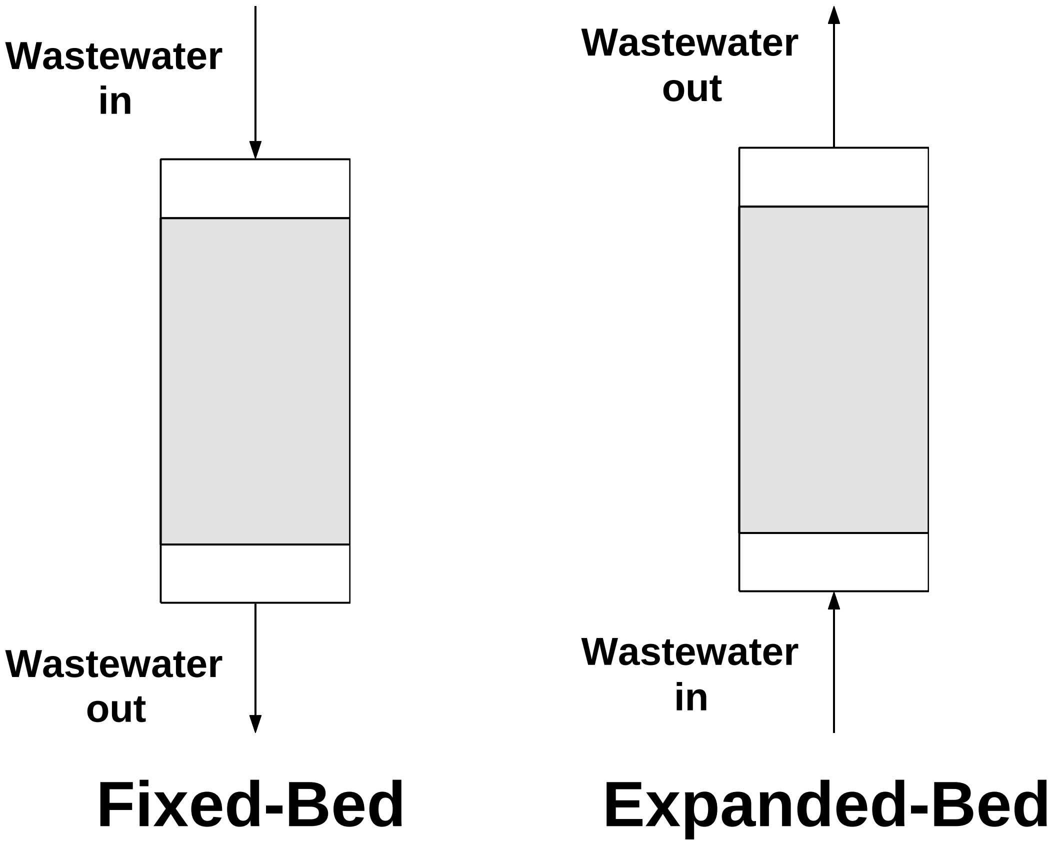
PIERO M. ARMENANTE
NJIT

Adsorption Processes Utilizing Granular Activated Carbon (GAC) for Wastewater Treatment

In all these processes the wastewater is contacted with granular activated carbon (GAC) typically in a semi-batch or continuous operation. Processes that utilize this type of carbon include:

- **Fixed-bed or expanded-bed adsorption**
- **Moving-bed adsorption**
- **Fluidized-bed adsorption**

Fixed-Bed and Expanded-Bed Adsorption Systems



Modes of Operation of Fixed-Bed and Expanded-Bed Systems

- **Downflow ® Fixed-bed**
- **Upflow**
  - **Expanded-bed (if the wastewater velocity expands the bed by about 10% or higher)**
  - **Fixed-bed**

Downflow Fixed-Bed Adsorbers

- **This is the most common type of adsorption column for wastewater treatment**
- **These columns must be provided with a system for the removal of spent carbon and the addition of fresh or regenerated carbon**
- **Because or their construction and operation downflow fixed-bed adsorbers also acts as depth filters for particles that can be contained in the wastewater**
- **Therefore this adsorption column must also be provided with facilities for backwashing (including air scouring, if necessary)**

Typical GAC Contactor

After Metcalf and Eddy, *Wastewater Engineering*, 1991, p. 316

Characteristics of Commercial Adsorbers

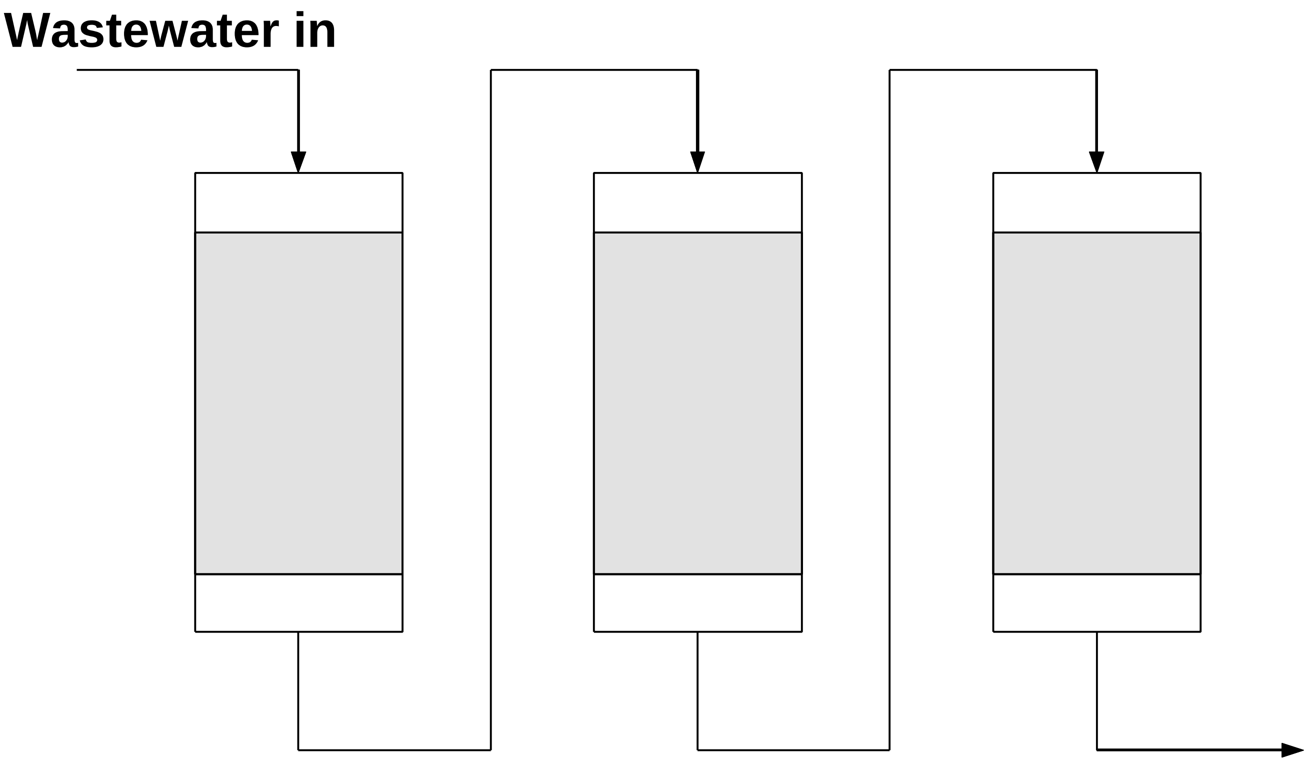
Height of packing	3 - 9 m (10 - 30 ft)
Particle size	8 - 40 mesh
Hydraulic loading	1.4 - 6.8 L/m^2 s (2 -10 gpm/ft^2)
Residence time	10 - 60 min (typically 20 -30 min)
Typical carbon requirements - pretreatment - tertiary treatment	(in g carbon/m^3 wastewater) 60 - 200 25 - 50
Operating pressure	< 20 KPa/m of bed

After Sundstrom and Klei, *Wastewater Treatment*, 1979, p. 270 and
Metcalf and Eddy, *Wastewater Engineering*, 1991, p. 753

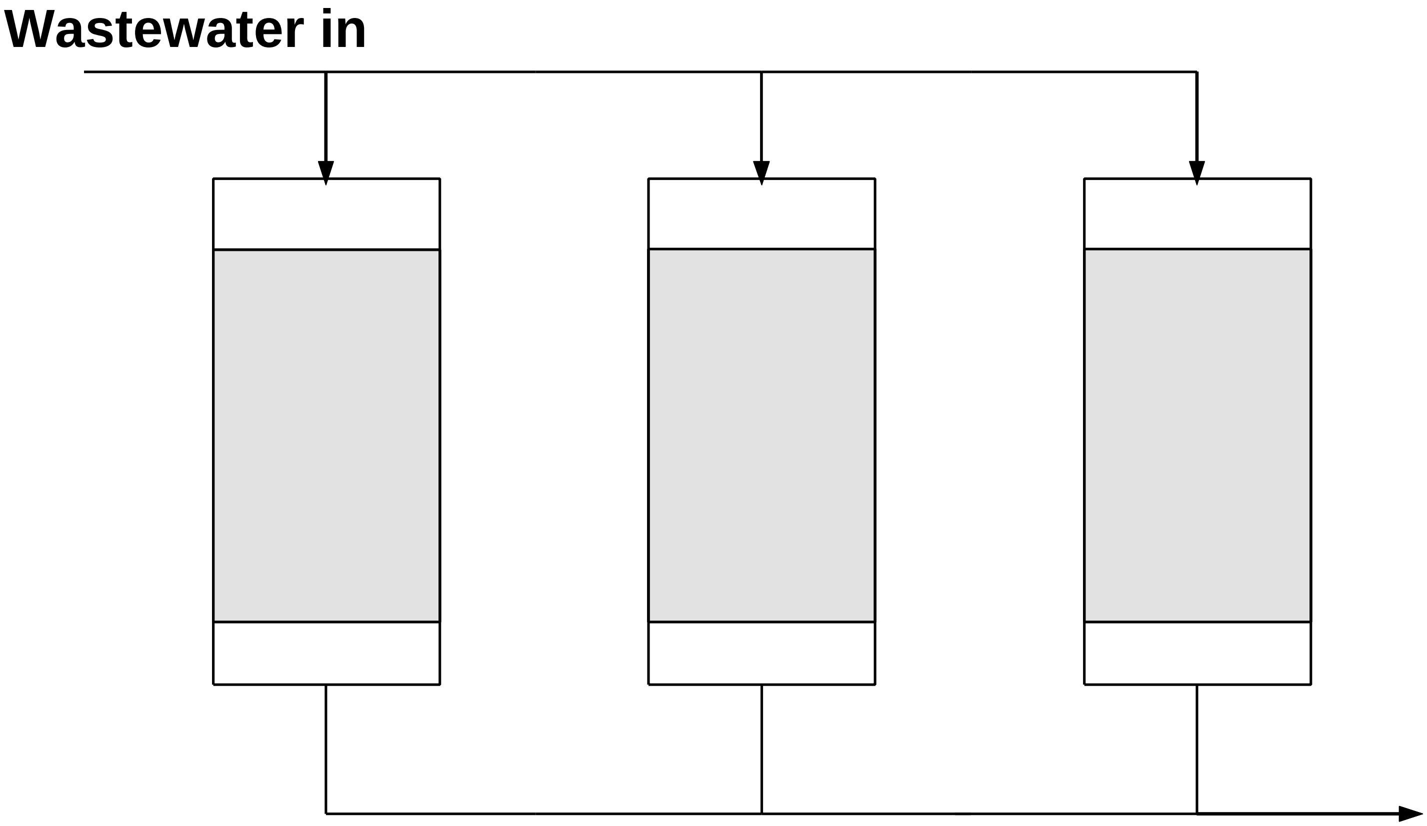
Properties of Commercially Available Carbons

After Eckenfelder, *Industrial Water Pollution Control*, 1989, p. 268

Downflow Fixed-Bed Adsorbers in Series



Downflow Fixed-Bed Adsorbers in Parallel



Granular Activated Carbon Process Flow Diagram

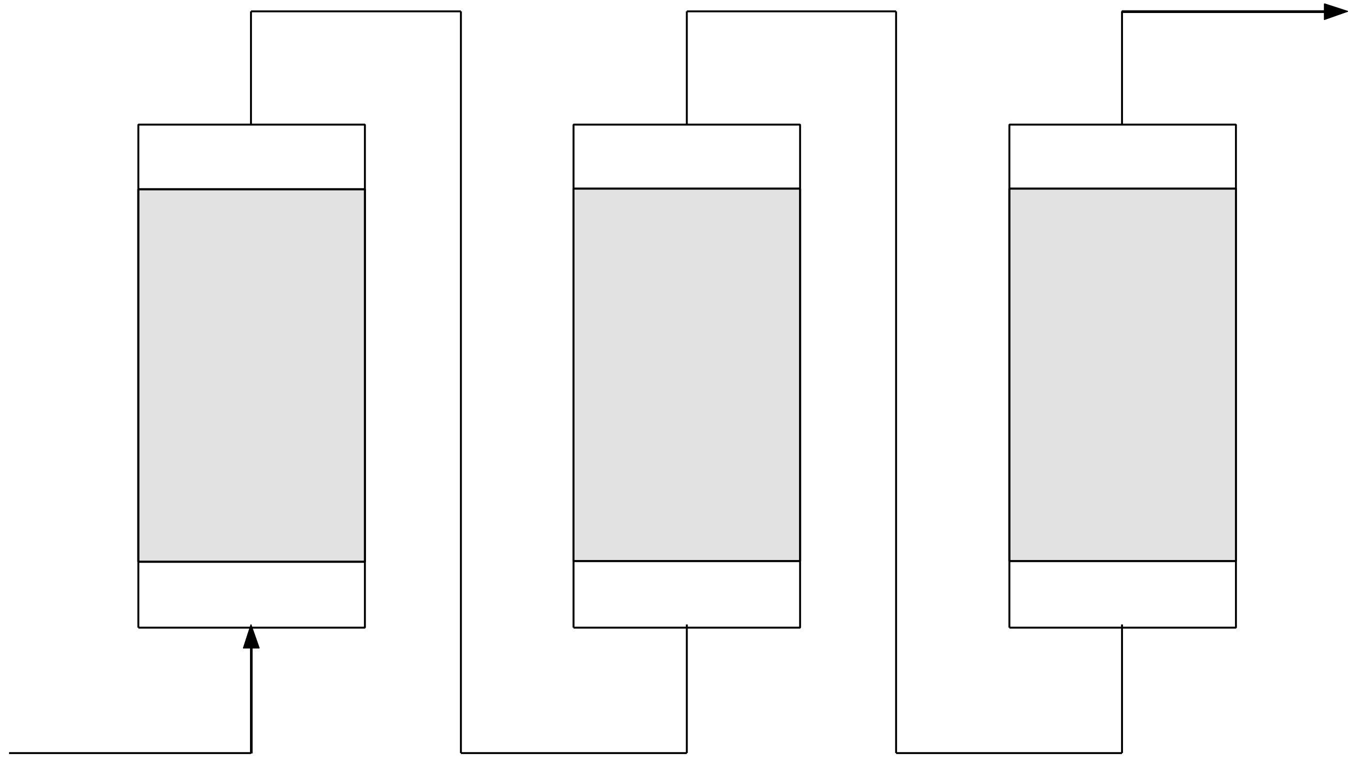
After Corbitt, R. A. 1990, *The Standard Handbook of Environmental Engineering*, p. 6.199

Results of Adsorption Tests on Typical Industrial Wastewaters

Upflow Expanded-Bed Adsorbers

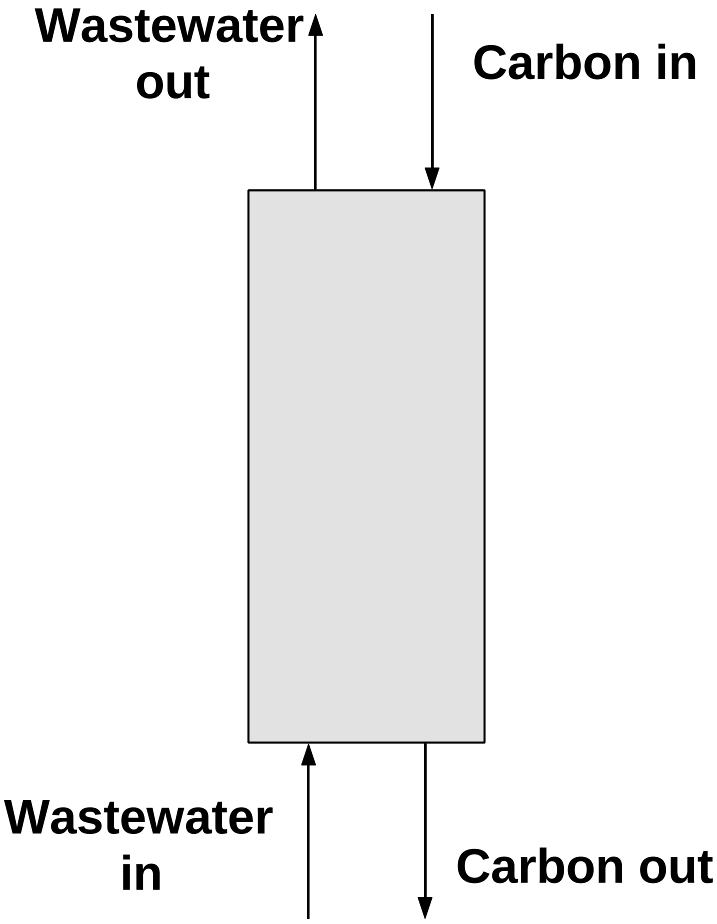
- In general, most upflow adsorbing columns operate in the expanded-bed mode
- Expanded-bed adsorbers are used when the wastewater fed to the column contains a significant fraction of suspended particles
- Since the bed is always expanded the column does not act as a filter for the suspended particles

Upflow Fixed-Bed Adsorbers in Series



Wastewater in

Moving-Bed Adsorption



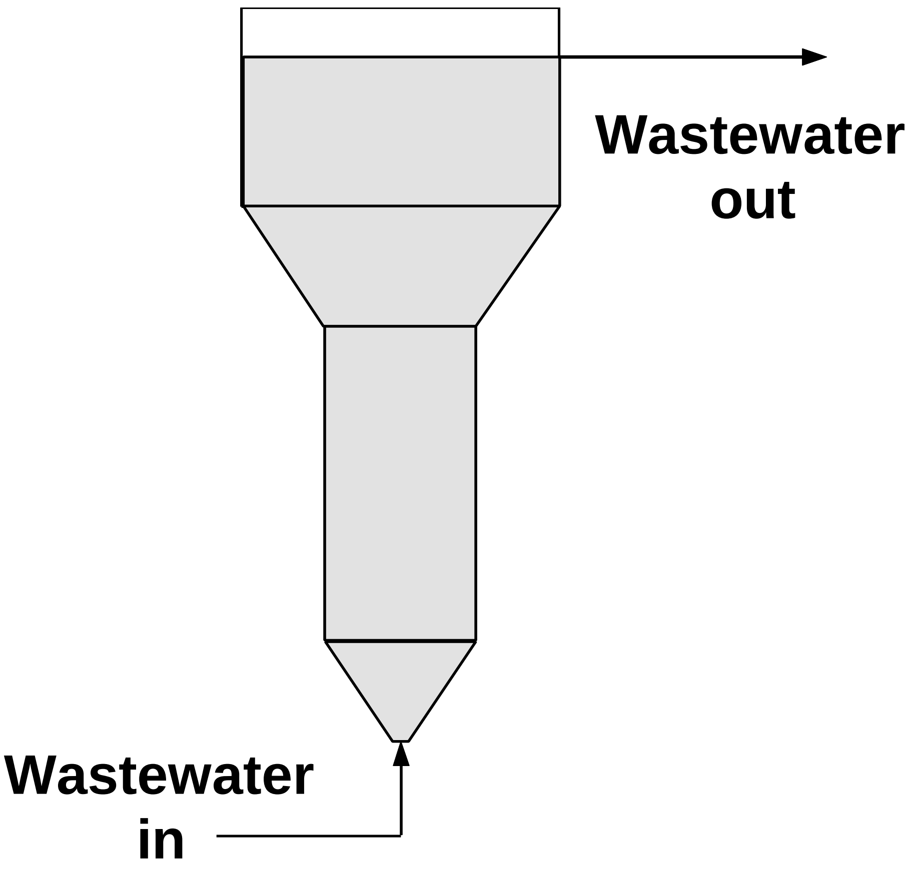
Wastewater out

Carbon in

Wastewater in

Carbon out

Fluidized-Bed Adsorption



Adsorption Beds as Filter Beds and Heavy Metal Adsorbers

- **GAC beds are sometimes used as deep-bed filters (as well as adsorbers)**
- **the capital cost associated with dual purpose adsorber-filter beds is typically lower than separate beds**
- **the regeneration of the adsorptive capacity of the bed should be followed by the removal of solids via bed fluidization**
- **most heavy metals are also adsorbed on activated carbon beds**

Biological Reactions in Adsorption Beds

The presence of organic material in a typical activated carbon bed coupled with the presence of microorganisms in the wastewater makes the bed an ideal breeding ground. This can have both negative and positive effects:

- **the microorganisms may contribute to the breakdown of pollutants adsorbed on the bed, thus improving its performance**
- **the presence of excessive organic material and the typical lack of oxygen may result in anaerobic growth (associate with the potential for odor generation) and the plugging of the bed due to excessive growth**

Most Important Design Factors in Fixed-Bed Adsorption Systems

- Particle size
- Diameter of column
- Flow rate of incoming wastewater (or residence time)
- Height of adsorption bed
- Pressure drop
- Time required to achieve breakthrough
- (Time of exhaustion)

Analysis of Fixed-Bed Adsorption Systems

Steps Involved in Adsorption

As the wastewater moves through a fixed bed of carbon the pollutant to be adsorbed will move from the wastewater to the carbon bed. Several steps are involved in the overall adsorption process of a single molecule of pollutant:

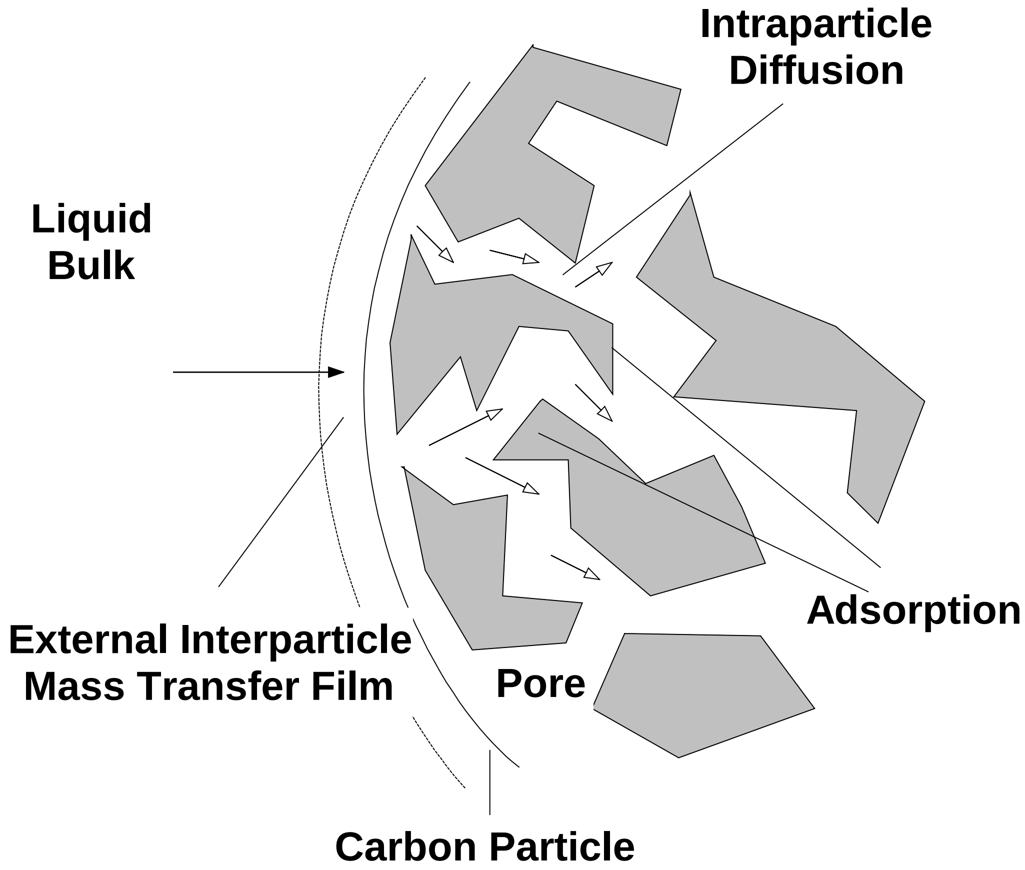
- ***Mass transfer step*. Mass transfer from the bulk of the wastewater to the surface of the carbon particle through the boundary layer around the particle**
- ***Diffusion step*. Internal diffusion through a pore**
- ***Adsorption step*. Adsorption on to the surface of the particle**

Relative Magnitude of the Rates Involved in Adsorption Process

In most wastewater treatment applications the overall adsorption process is dominated by mass transfer, especially *intraparticle* mass transfer. A qualitative ranking of the magnitude of the resistances is:

- *External interparticle mass transfer step* ® slow to not-so-slow, depending on the operation
- *Intraparticle diffusion step* ® typically slow
- *Adsorption step* ® typically fast

Transport Processes During Adsorption



Effect of Carbon Particle Size on Pressure Drop and Intraparticle Mass Transfer

The size of the activated carbon particle has an opposite impact on the pressure drop across the bed and the intraparticle diffusion resistance (and hence on the overall adsorption process)

Effect of Carbon Particle Size on Pressure Drop

The effect of particle size, D_p, on pressure drop, DP, can be determined recalling equations such as the Ergun Equation for pressure drop in granular media:

$$\Delta P = \left[\frac{150}{\mathrm{Re}_p}\left(1 - e\right) + 175\right]\left(\frac{1 - e}{e^3}\right)\frac{L}{D_p}\, r_L\, u_s^2$$

or the Fair-Hatch equation (laminar flow):

$$\Delta P = 36\, k\, m \frac{\left(1 - e\right)^2}{e^3}\frac{L}{D_p^2} u_s$$

Effect of Carbon Particle Size on Pressure Drop

The pressure drop in a carbon bed is inversely proportional to the particle size. In particular it is:

$$\Delta P \propto \frac{1}{D_p}$$

for *turbulent* flow through granular media, and:

$$\Delta P \propto \frac{1}{D_p^2}$$

for *laminar* flow in granular media.

Effect of Carbon Particle Size on Intraparticle Mass Transfer

As a first approximation the effect of particle size on the intraparticle mass transfer of pollutant can be estimated as follows:

$$\frac{\text{pollutant transferred inside the particle}}{\text{bed volume}} \approx -D\,\frac{dC}{dr}\,\frac{A_p}{V_p} \approx$$

$$\approx -D\,\frac{\Delta C}{\Delta r}\,\frac{6}{D_p} \approx D\,\frac{C-0}{D_p-0}\,\frac{12}{D_p}$$

$$\frac{\text{pollutant transferred inside the particle}}{\text{bed volume}} \propto \frac{1}{D_p^2}$$

Effect of Carbon Particle Size on Pressure Drop and Diffusion Resistance

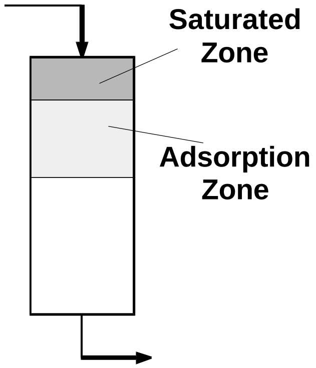
Larger carbon particle size	Smaller carbon particle size
–	–
Smaller pressure drop	Larger pressure drop
–	–
Smaller mass of pollutant diffusing inside the particle	Larger mass of pollutant diffusing inside the particle

Size of Activated Carbon Particles Used in Fixed-Bed Adsorption

- Typically carbon particle sizes between 0.4 and 2.5 mm are used in fixed bed adsorption applications
- This size range results from a practical compromise between limiting the pressure drops on one hand and providing adequate surface area and promote mass transfer for pollutant adsorption on the other
- Larger sizes also minimize losses during carbon handling and packed bed operation

Adsorption Zone and Adsorption Wave

- **In fixed bed adsorption, at any given time the bed can be divided into three approximate zones, i.e., the saturated zone (containing carbon nearly saturated with the pollutants), followed by the *adsorption zone* (were adsorption actually takes place), followed by a zone in which the carbon contains little or no adsorbed pollutant**



- **The size and location of the three zones within the bed change with time**

Adsorption Zone and Adsorption Wave (continued)

- As the wastewater enters the bed it first encounters the saturated zone in which the carbon is already nearly saturated with the pollutant (this is not true for fresh completely "clean" beds just being put on line, of course). Practically no adsorption occurs in the saturated zone
- As more wastewater travels through the bed the saturated zone expands progressively through the bed, eventually including it completely

<u>Adsorption Zone and Adsorption Wave (continued)</u>

- **Pollutant adsorption occurs nearly exclusively over a portion of the bed called the *<u>adsorption zone</u>*, downstream of the saturated zone**
- **The concentration of pollutant *in the carbon* varies from near saturation (at the beginning of the adsorption zone) to near zero (toward the end of the adsorption zone). Conversely, the pollutant concentration *in the wastewater* in contact (at *that* time) with the carbon changes from nearly full load (at the beginning of the adsorption zone) to nearly zero (at the end)**

Adsorption Zone and Adsorption Wave (continued)

- **At any given time the portion of the bed downstream of the adsorption zone contains very little adsorbed pollutant since the wastewater it is in contact with has already been nearly completely depleted of the pollutant(s)**
- **As time goes by a greater portion of the bed becomes saturated with the pollutant and the adsorption zone moves downstream forming an *adsorption wave***

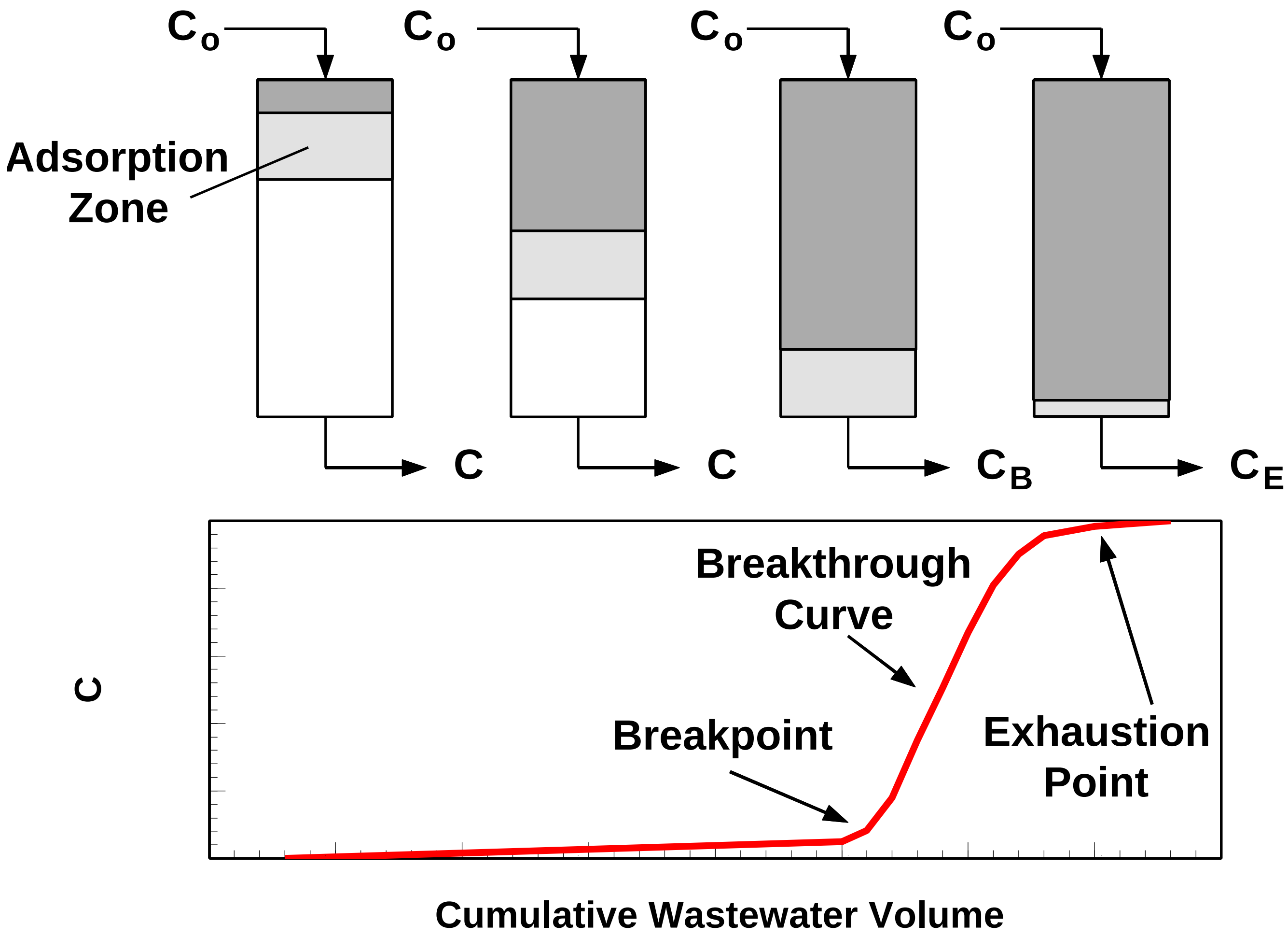
Breakpoint and Breakthrough Curve

- Eventually the forward part of the adsorption wave reaches the end of the bed. When this happens the bed begins to release wastewater having a concentration of pollutant higher than the desired value (typically 5-10% of the influent concentration). This point is called the ***breakpoint***
- The corresponding curve of pollutant concentration in the effluent vs. time is called the ***breakthrough curve***

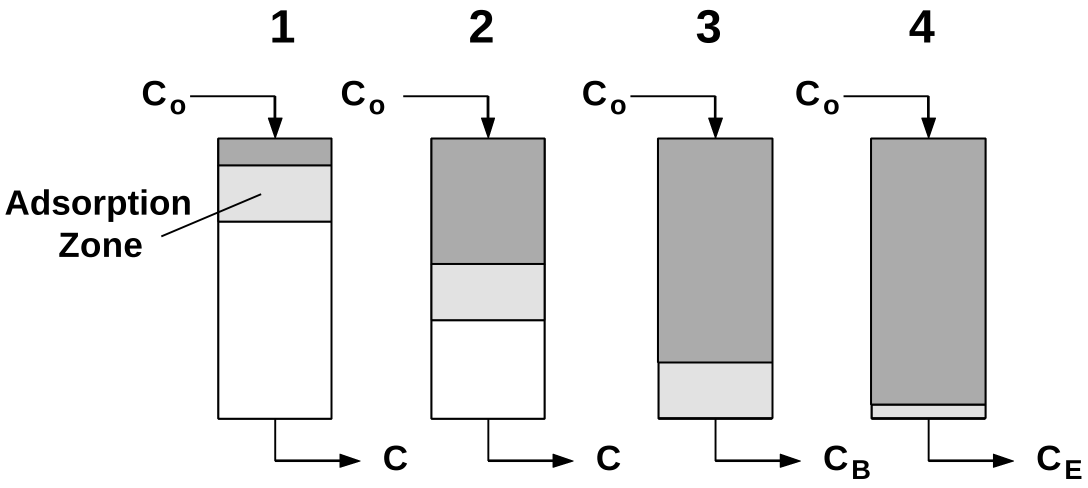
Exhaustion Point and Bed Saturation

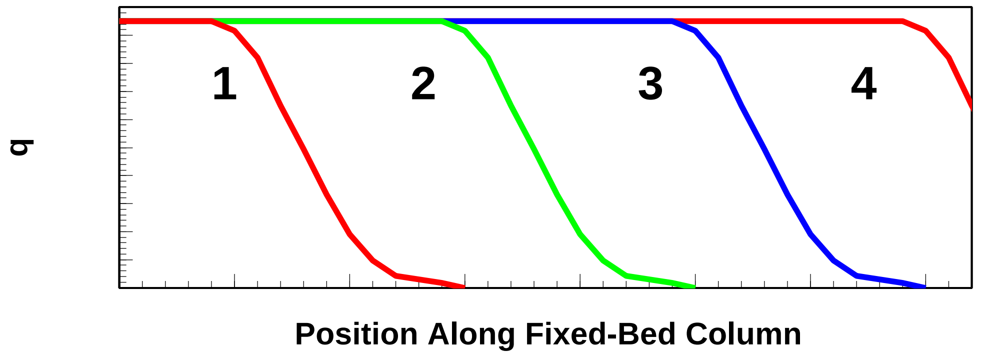
- **Past the breakpoint the pollutant concentration in the effluent rises rapidly (i.e., the breakthrough curve is typically steep), until it reaches an arbitrarily defined *exhaustion point* where the column approaches saturation**
- **If more wastewater is passed through the bed the entire carbon content of the bed becomes saturated. Then, the wastewater leaving the bed has, for all practical purposes, the same concentration of pollutant as the incoming wastewater**

Breakpoint and Breakthrough Curve

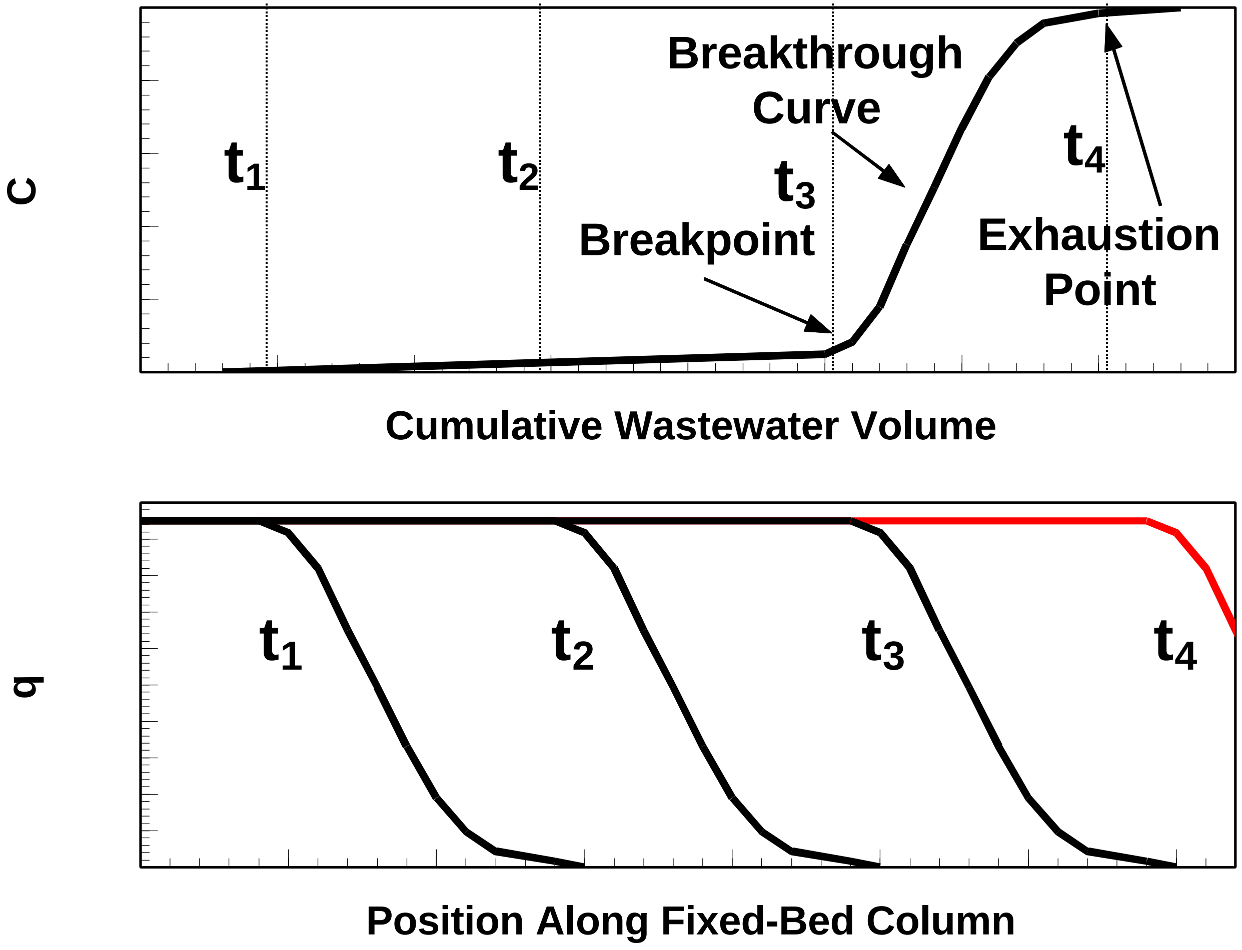


Concentration of Adsorbate in the Carbon Along a Fixed-Bed Column

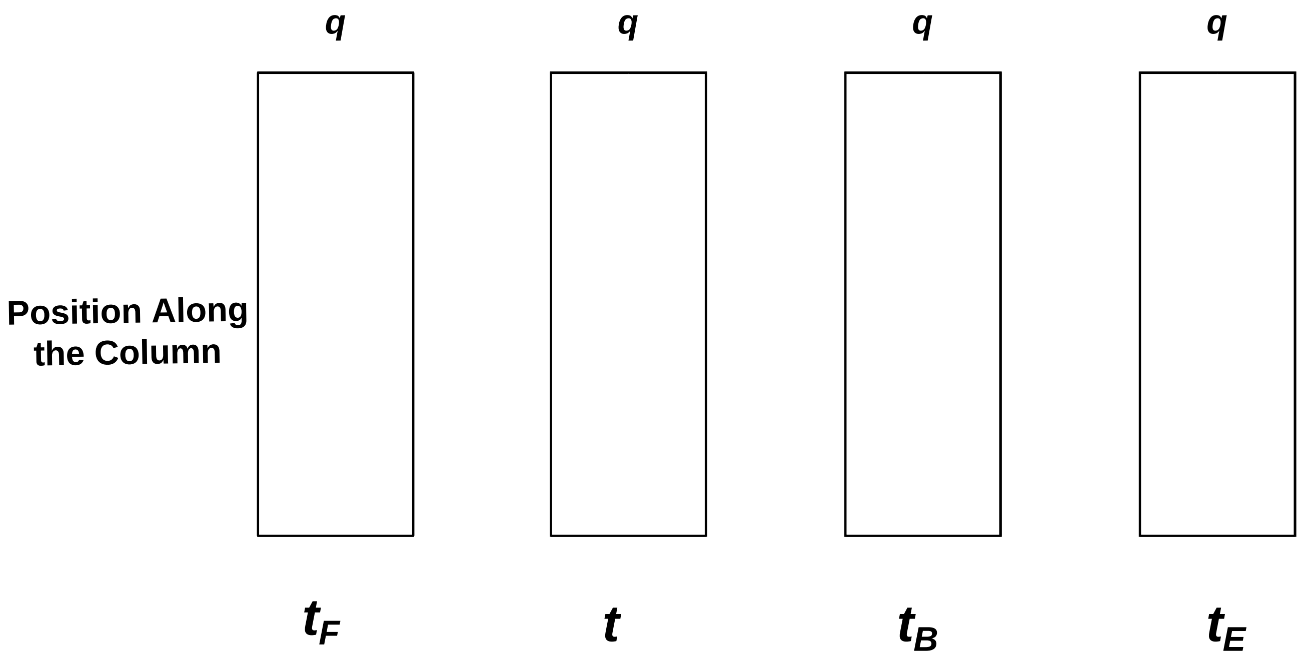




Evolution of Concentration Profiles in in the Wastewater Leaving the Column and in the Carbon Bed as a Function of Time



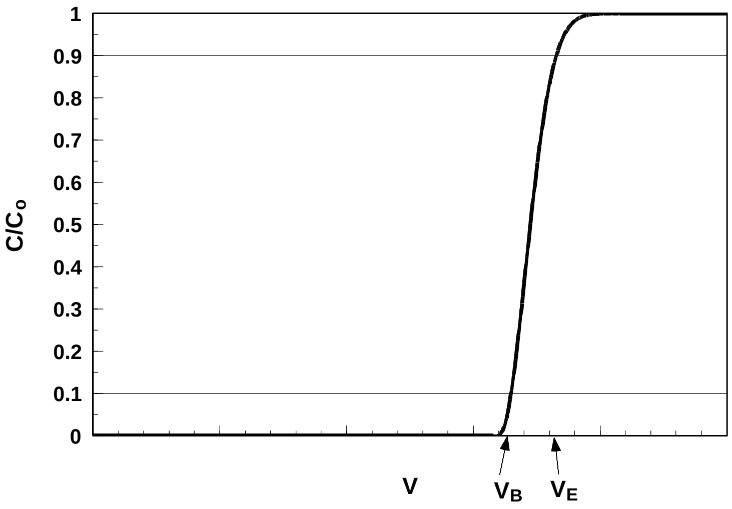
Progressive Saturation of Adsorber in Column as a Function of Time



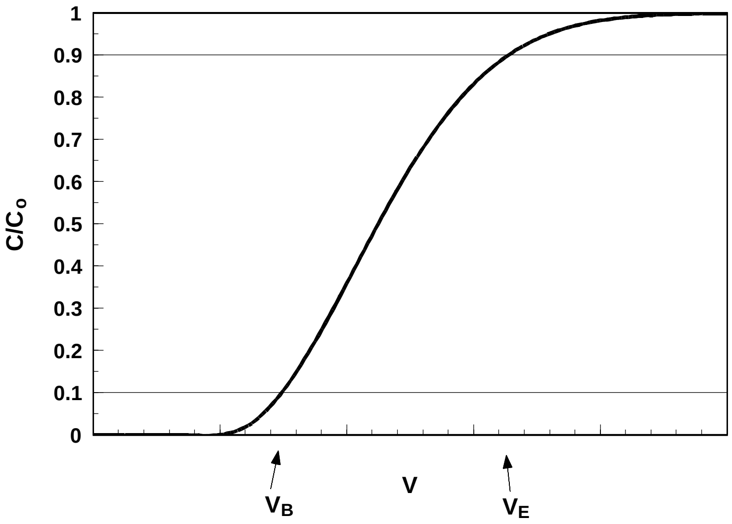
Typical Breakthrough Curves

After Eckenfelder, *Industrial Water Pollution Control*, 1989, p. 272

Shapes of Breakthrough Curves



Short Depth of Adsorption Zone



Large Depth of Adsorption Zone

Analysis of Fixed-Bed Adsorption Columns

The primary objectives of such an analysis are:

- determination of the total (maximum) column adsorption capacity;
- determination of the depth of the adsorption zone and the shape of the breakthrough curve;
- determination of the breakpoint, including the volume of wastewater that can be treated before the breakpoint is reached, the time at which this happens, and the degree of column saturation at breakpoint.

Total Column Adsorption Capacity

If the adsorption equilibrium curve is known then by knowing the volume of the column and its void fraction, one can calculate the total cumulative volume of wastewater, V_{max}, that *could* be treated if the column became completely saturated:

$$V_{\max} = S\,L\left(1-e\right)\,r_s\,\frac{q_{So}}{C_o} = S\,L\,r_{s\,app}\,\frac{q_{So}}{C_o}$$

where: S = column cross sectional area

L = height of packing

e = void fraction

q_{So} = $g(C_o)$ = value of q in equilibrium with C_o

r_s and $r_{s\,app}$ = real and apparent density of solid

Approaches to the Design of Adsorption Columns

Many different approaches are available. In general, partial differential equations can be written, incorporating the different mass transfer and adsorption mechanisms. Typically these models are complex and require numerical solutions.

Other models rely on experimental data and the use of simpler models to interpret them so as to produce satisfactory designs. These models can be used to size the column by determining the depth of the adsorption zone, the shape of the breakthrough curve, the time at breakpoint and the pollutant removed at breakpoint.

Models Examined Here

Three models will be examined here in some detail:

- **Simplified Method for Estimation of Fixed-Bed Adsorption Performance**
- **Design of Adsorption Columns Based on Capacity of Adsorption Zone (Mass Transfer Model)**
- **Design of Adsorption Columns Based on Bed Depth Service Time (BDST) Method (Surface Reaction Model)**

Simplified Method for the Estimation of Fixed-Bed Adsorption Performance

Simplifying assumptions:

- **the pollutant concentration in the effluent wastewater from the column increases linearly with time until it reaches the breakpoint value, C_B**
- **at breakpoint the average concentration of pollutant in the bed is only a fraction, z, of the saturation value (typically 50%)**
- **the wastewater flow rate to the column is constant and equal to Q**

Simplified Method for the Estimation of Fixed-Bed Adsorption Performance

From a mass balance for the pollutant at breakpoint it is:

$$M = q_B B = z\ q_{so} B = Q t_B \left(C_o - \frac{C_B}{2} \right) \cong Q t_B C_o$$

where:

M **= cumulative mass of pollutant adsorbed at breakpoint**

B **= mass of carbon in bed =** $r_{s\,app}$ ***S L*****, and:**

$$q_{so} = K_F C_o^{1/n}$$

Simplified Method for the Estimation of Fixed-Bed Adsorption Performance

Hence, the time required to reach breakthrough is:

$$\boxed{t_B = \frac{q_B\,B}{Q\left(C_o - \dfrac{C_B}{2}\right)} = \frac{z\;K_F\,C_o^{1/n}\,B}{Q\left(C_o - \dfrac{C_B}{2}\right)}}$$

The cumulative volume of wastewater, V_B, treated at breakpoint is given by:

$$\boxed{V_B = Q\,t_B}$$

Design of Adsorption Columns Based on Capacity of Adsorption Zone (Mass Transfer Model)

This model assumes that the adsorption zone has a constant shape that moves down the column with time and that the process is controlled by the mass transfer around the carbon pellets.

Definitions

L = height of packed bed

t_F = time required for the adsorption zone to form

t_L = time required for the fully formed adsorption zone to move down the length of the column, L, until the effluent concentration is equal to C_E

t_E = time required for the effluent concentration to reach the exhaustion point, C_E

t_A = time, required for the adsorption zone to move its own height down the column

Time Required to Exhaust the Bed

The time, t_E, required for the effluent concentration to reach the exhaustion point, C_E, is equal to the sum of:

- **the time, t_F, required for the adsorption zone to form**
- **the time, t_L, required for the fully formed adsorption zone to move down the length of the column, L, until the effluent concentration is equal to C_E**

Then, it is:

$$t_E = t_F + t_L$$

i.e.:

$$t_L = t_E - t_F$$

Time Required to Exhaust the Bed

The time, t_E, required for the effluent concentration to reach the exhaustion point, C_E, is also equal to:

$$t_E = \frac{V_E}{Q} = \frac{V_E / S}{Q / S}$$

where:

V_E = cumulative wastewater volume passed through the column during the time interval 0 - t_E

Q = wastewater flow rate

Time Required for Adsorption Zone to Move Its Own Height

The time, t_A, required for the adsorption zone to move its own height down the column is:

$$t_A \cong \frac{V_E - V_B}{Q}$$

where:

V_B = cumulative wastewater volume passed through the column during the time interval 0 - t_B

t_B = time required for the effluent concentration to reach the breakpoint, C_B

Adsorption Wave Velocity

The velocity, u_A, of the adsorption zone (equal to the wave velocity, u_w) is given by:

$$u_W = \frac{L}{t_L} = \frac{L}{t_E - t_F} = u_A = \frac{L_A}{t_A}$$

which can be rearranged to give:

$$\frac{L_A}{L} = \frac{t_A}{t_L} = \frac{t_A}{t_E - t_F}$$

where:

L = height of column

L_A = height of adsorption zone

Fractional Pollutant Removed in the Adsorption Zone

If additional wastewater is passed through the column after the effluent concentration has reached the breakpoint, C_B, more pollutant will be removed until the effluent concentration becomes equal to C_E. This extra amount of pollutant is:

$$m = \int_{V_B}^{V_E} \left(C_o - C \right) dV$$

This amount is only a fraction of that which could be removed if the adsorption zone was not at the end of the column, in which case it would be:

$$m_s = C_o \left(V_E - V_B \right)$$

Fractional Pollutant Removed in the Adsorption Zone

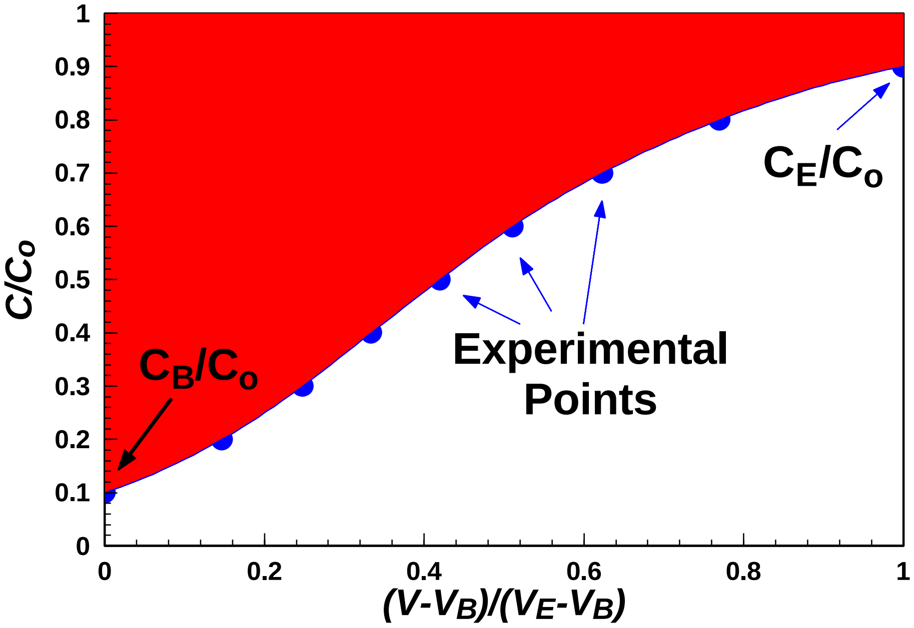
The fractional pollutant removal capacity at the end of the column, *f*, is then:

$$f = \frac{m}{m_s} = \frac{\int_{V_B}^{V_E} \left(C_o - C \right) dV}{C_o \left(V_E - V_B \right)}$$

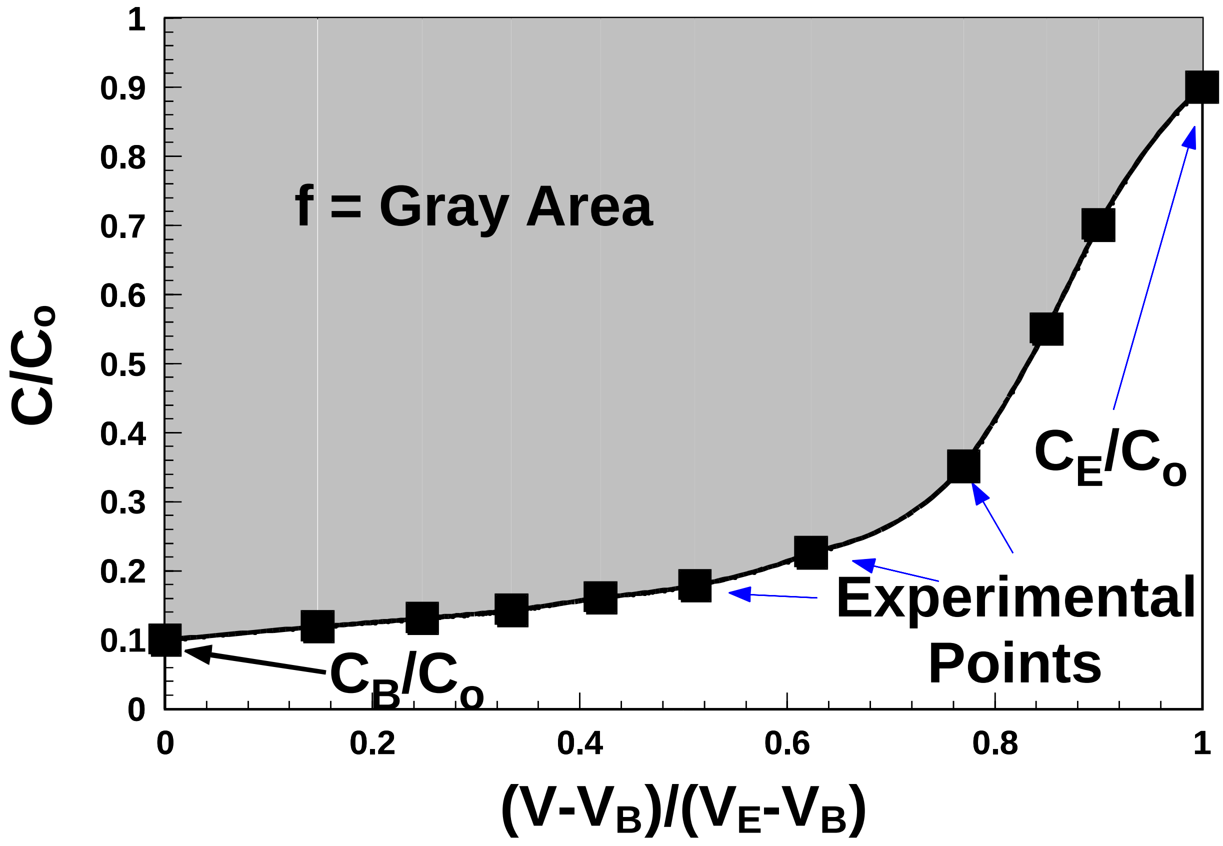
The fractional pollutant removal capacity, *f*, can be determined experimentally by monitoring the effluent concentration (after the breakpoint) as a function of the effluent cumulative volume.

Fractional Pollutant Removed in the Adsorption Zone

$$f = \frac{m}{m_s} = \int_0^1 \left(1 - \frac{C}{C_o}\right) d\left(\frac{V - V_B}{V_E - V_B}\right)$$



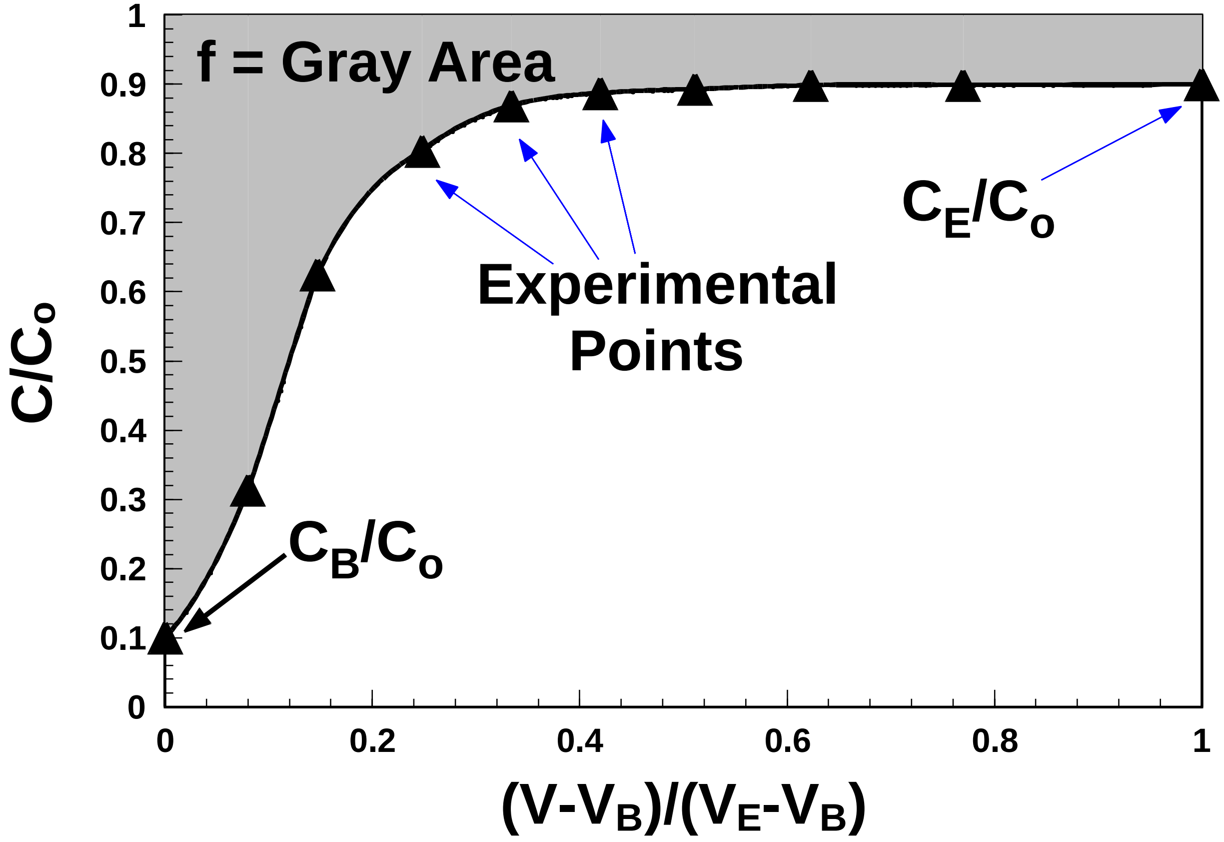
Pollutant Removed in the Adsorption Zone: Large *f* Value (*f* ® 1)



Pollutant Removed in the Adsorption Zone: Large *f* Value (*f*® 1)

- **If *f*® 1, then the adsorption zone at the end of the column already contains a significant amount of the adsorbate and has the potential for adsorbing very little extra pollutant.**
- **This implies that, in general, the wastewater saturates the carbon “layer by layer” and that the transition zone from the fully saturated carbon zone to the unsaturated zone is short. This typically occurs when the wastewater velocity is “low”.**
- **This also means that the adsorption zone is quite short and the *time required for its formation is close to zero.***

Pollutant Removed in the Adsorption Zone: Small *f* Value (*f*® 0)



Pollutant Removed in the Adsorption Zone: Small *f* Value (*f*® 0)

- **If *f*® 0, then the adsorption zone at the end of the column contains little adsorbate in the carbon. Hence it has the potential for adsorbing nearly as much as a similar zone made of fresh carbon.**

- **This implies that, in general, the wastewater does not saturate the carbon “layer by layer,” but that the transition zone from the fully saturated carbon zone to the unsaturated zone is gradual. This typically occurs when the wastewater velocity is “high”.**

- **This also means that the adsorption zone is quite deep and the *time required for its formation is “large” and nearly equal to that needed for the adsorption zone to move a distance equal to its depth.***

Time Required for the Formation of the Adsorption Zone

- **As the wastewater first enters a column containing fresh (or regenerated) activated carbon the adsorption zone is not established. The time required for the formation of the adsorption zone can be estimated from:**

$$t_F = \left(1 - f\right) t_A$$

- **When f® 1, the length of the adsorption zone is quite small and the time for the formation of the adsorption zone, t_F, is nearly zero ("layer-by-layer" buildup);**

- **When f® 0, the length of the adsorption zone is quite extended and the time for the formation of the adsorption zone, t_F, is significant.**

Height of Adsorption Zone

Recalling that it is:

$$\frac{L_A}{L} = \frac{t_A}{t_L} = \frac{t_A}{t_E - t_F}$$

it is possible now to eliminate t_F from the expression of the L_A/L ratio to get:

$$\frac{L_A}{L} = \frac{t_A}{t_L} = \frac{t_A}{t_E - (1 - f)\,t_A}$$

which can also be expressed in terms of the corresponding cumulative volumes as:

$$\boxed{\frac{L_A}{L} = \frac{V_E - V_B}{V_E - (1 - f)(V_E - V_B)}}$$

Height of Adsorption Zone

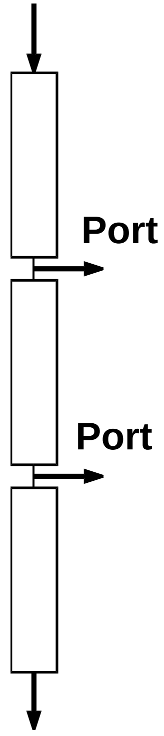
The equation:

$$\frac{L_A}{L'} = \frac{V_E - V_B}{V_E - (1-f)(V_E - V_B)} = \frac{\dfrac{V_E}{S} - \dfrac{V_B}{S}}{\dfrac{V_E}{S} - (1-f)\left(\dfrac{V_E}{S} - \dfrac{V_B}{S}\right)}$$

can be use to experimentally determine the height of the adsorption zone, L_A, from experimental lab data (since only the ratios V_i/S are important). The experiments should be conducted for the same value of the ratio Q/S. Then the value of L_A can be determined provided the height of the test column (L') is known.

Interpretation of Experimental Data

- **A common way to collect information on the performance of an adsorption column and to scale up the results consists in setting up a column as high as that eventually to be used in the full scale application, but of much smaller diameter**
- **Data are then collected by determining the time at breakpoint, t_B, at different points (ports) along the column**



Experimental Determination of the *f* Value

The *f* value can be determined experimentally by obtaining *C* vs. *V* data as the adsorption zone passes through the sampling port. Since V_B and V_E can also be determined with this approach then *f* can be calculated from its definition:

$$\boxed{f = \frac{m}{m_s} = \frac{\int_{V_B}^{V_E} \left(C_o - C\right) dV}{C_o \left(V_E - V_B\right)}}$$

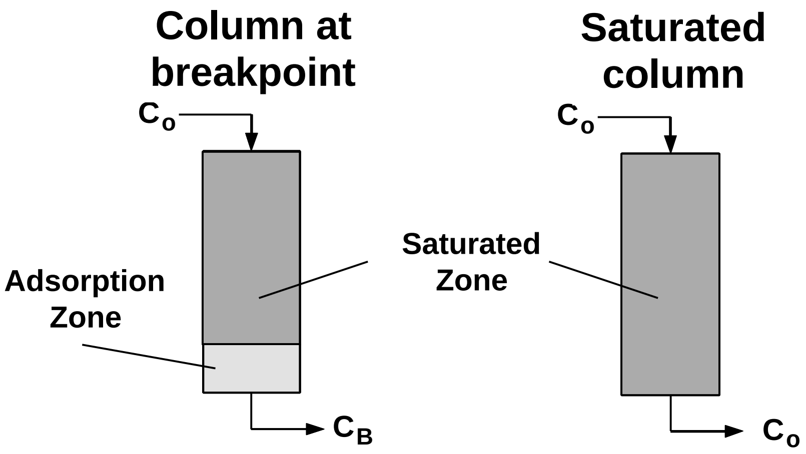
Degree of Column Saturation at Breakpoint

The degree of column saturation at breakpoint, x, is defined as the fraction of column saturation at breakpoint, i.e.:

$$x = \frac{\text{Amount of pollutant in column at breakpoint}}{\text{Maximum theoretical amount of pollutant in column}}$$

The value of x is within the range 0 - 1, and is proportional to the degree of utilization of the activated carbon packing at breakpoint, i.e., before the column must be shut down for carbon replacement or regeneration.

Degree of Column Saturation at Breakpoint (continued)


Column at breakpoint

Saturated column

C_o

C_o

Adsorption Zone

Saturated Zone

C_B

C_o

$$x = \frac{M}{M_S} = \frac{S\left(L - L_A\right) r_s \left(1 - e\right) q_{So} + S\,L_A \left(1 - f\right) r_s \left(1 - e\right) q_{So}}{S\,L\; r_s \left(1 - e\right) q_{So}} =$$

$$= \frac{S\left(L - L_A\right) r_{s\ app}\, q_{So} + S\,L_A \left(1 - f\right) r_{s\ app}\, q_{So}}{S\,L\; r_{s\ app}\, q_{So}}$$

Degree of Column Saturation at Breakpoint (continued)

By simplification one can obtain the following equation for x:

$$x = \frac{M}{M_S} = \frac{\left(L - L_A\right) + L_A\left(1 - f\right)}{L}$$

i.e.:

$$\boxed{x = \frac{M}{M_S} = \frac{L - f\,L_A}{L}}$$

If *f* and *L*$_A$ have been determined x can be calculated for any column of length *L*.

Calculation of Cumulative Pollutant Removal at Breakpoint

Once x is known it is possible to determine the cumulative amount of pollutant, *M*, removed by the time the breakpoint is reached (and the column must be taken off line):

$$\boxed{M = x M_S = x q_{So}\, r_{s\,app} S L = x K_F C_o^{1/n}\, r_{s\,app} S L}$$

where C_o is the pollutant concentration in the incoming wastewater.

Calculation of Breakpoint Time

The breakpoint time, t_B, can be calculated as:

$$t_B = \frac{\text{cumulative amount of pollutant adsorbed at breakpoint}}{\text{rate of pollutant fed to column}}$$

i.e.:

$$\boxed{t_B = \frac{M}{Q\,C_o}}$$

at which time the column must be taken off line.

The cumulative volume of wastewater, V_B, treated at breakpoint is given by:

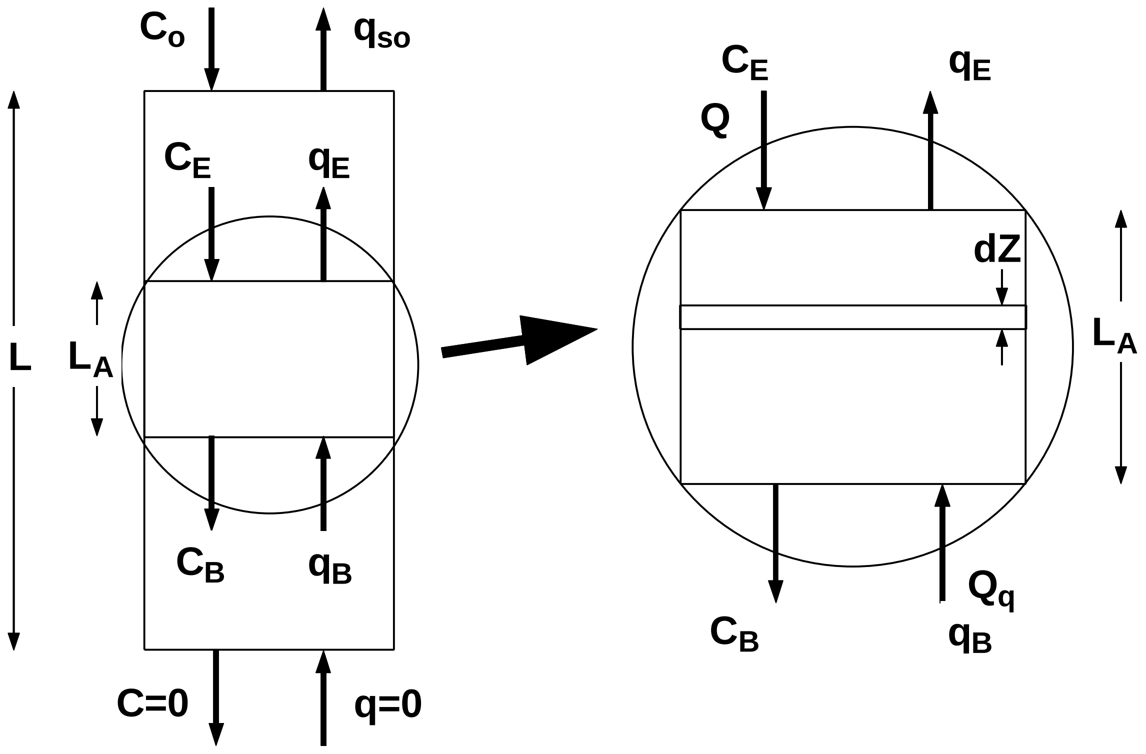
$$\boxed{V_B = Q\,t_B}$$

Alternative Determination of the Adsorption Zone Profile

An alternative method to determine the profile and length of the adsorption zone (and hence the *f* value and L_A) is to model the adsorption zone as if it were an *independent* column operating at steady state and having a *continuous* input of both solid activated carbon and wastewater.

This approach is equivalent to assume that the frame of reference moves with the adsorption wave.

Alternative Determination of the Adsorption Zone Profile



Alternative Determination of the Adsorption Zone Profile: Mass Balance

- **In performing a mass balance for such a continuous column the assumption is made that the incoming and outgoing streams are *nearly* in equilibrium (if they were really in equilibrium the column will be infinitely high).**
- **This implies that the incoming wastewater (pollutant concentration: C_o) encounters a carbon which is practically saturated with the pollutant at that concentration (q_{So}).**
- **Similarly the wastewater leaving the column contains practically no pollutant, and so does the fresh incoming carbon.**

Alternative Determination of the Adsorption Zone Profile: Mass Balance

A material balance around the entire continuous column gives:

$$Q\left(C_o - 0\right) \cong Q_q\left(q_{So} - 0\right)$$

where:

Q = wastewater flow rate

Q_P = carbon flow rate

C_o = pollutant concentration in incoming wastewater

q_{So} = pollutant concentration in spent carbon

Alternative Determination of the Adsorption Zone Profile: Mass Balance

Similarly, a material balance between the bottom of the column and a generic section gives:

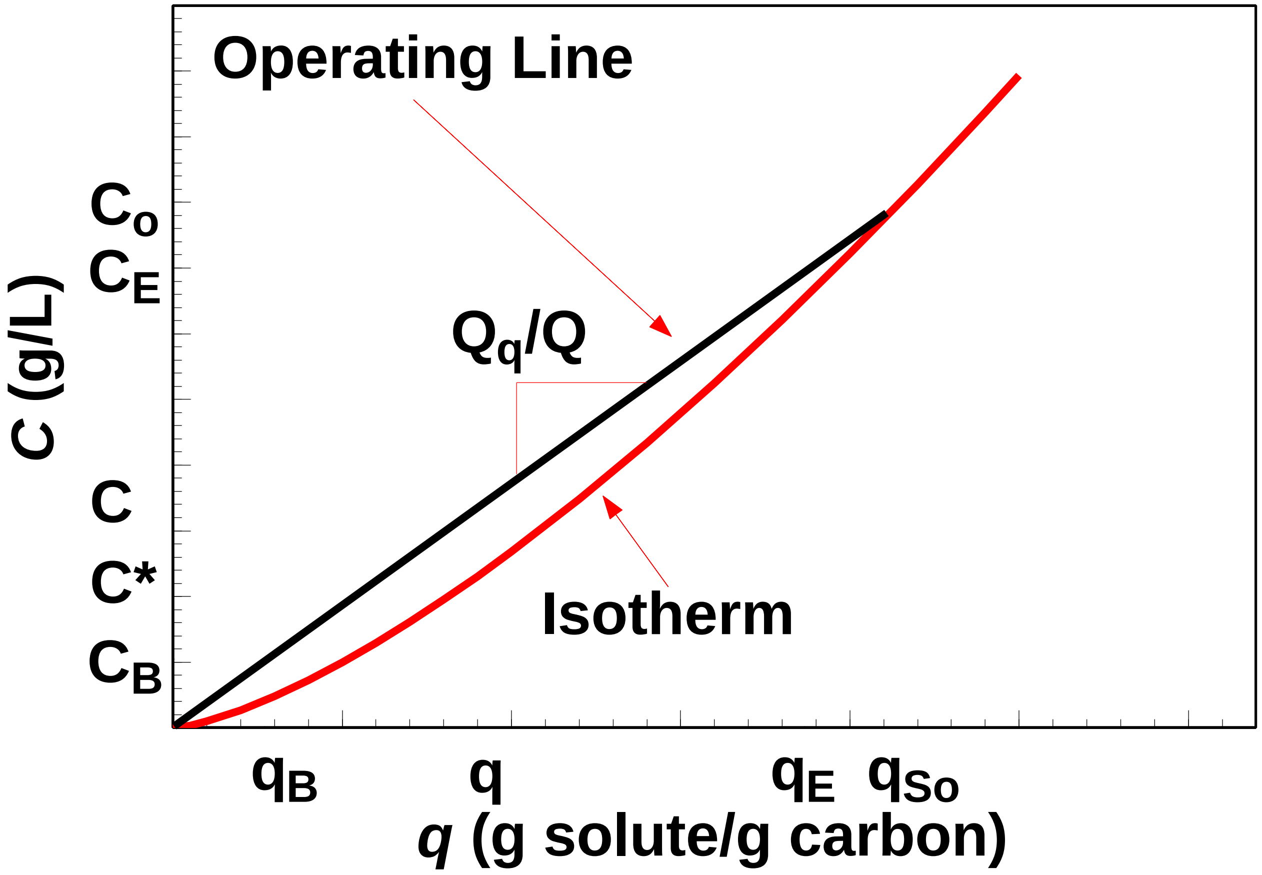
$$Q\left(C-0\right)\cong Q_q\left(q-0\right)$$

Hence, the operating line (mass balance) for the continuous column is:

$$\frac{C}{q}=\frac{C_o}{q_{So}}=\frac{Q_q}{Q}$$

Remark: the points (C_E, q_E) and (C_B, q_B) must lie on the operating line.

Alternative Determination of the Adsorption Zone Profile: Mass Balance



Alternative Determination of the Adsorption Zone Profile: Mass Balance in a Differential Section of the Column

Assuming that external (or external-internal) mass transfer dominates the overall adsorption phenomenon a differential balance for the pollutant in an infinitesimally thin layer of the column yields:

Rate of pollutant removal from the wastewater =

Rate of pollutant transfer to the carbon

Alternative Determination of the Adsorption Zone Profile: Mass Balance in a Differential Section of the Column

In mathematical terms the previous equation can be written as:

$$\frac{Q}{S}\,dC = u_s\,dC = K_L\,a\left(C - C^*\right)dz$$

- **K_L = mass transfer coefficient between the bulk of the wastewater and the surface of the carbon (m/s)**
- **a = external surface area of carbon particles per unit bed volume**
- **C^* = concentration of pollutant in the wastewater that would be in equilibrium with the adsorbed concentration, q**

Alternative Determination of the Adsorption Zone Profile: Integration of Mass Balance Equation

Integration of the previous equation yields:

$$z = \frac{u_s}{K_L\, a} \int_{C_B}^{C} \frac{dC'}{C' - C'^*} \qquad \text{for } C_B \le C \le C_E$$

In addition it is:

$$L_A = \frac{u_s}{K_L\, a} \int_{C_B}^{C_E} \frac{dC'}{C' - C'^*}$$

Alternative Determination of the Adsorption Zone Profile: Calculation of *f*

From the previous equations it is:

$$\frac{z}{L_A} = \frac{V - V_B}{V_E - V_B} = \frac{\displaystyle\int_{C_B}^{C} \frac{dC'}{C' - C'^*}}{\displaystyle\int_{C_B}^{C_E} \frac{dC'}{C' - C'^*}} \quad \text{with } 0 < z < L_A \text{ and } V_B < V < V_E$$

From this equation and recalling that:

$$f = \frac{m}{m_s} = \int_0^1 \left(1 - \frac{C}{C_o}\right) d\left(\frac{V - V_B}{V_E - V_B}\right)$$

the value of *f* can be calculated knowing only C_B, C_E and the adsorption isotherm.

Design of Adsorption Columns Based on Bed Depth Service Time (BDST) Method (Surface Reaction Model)

This method is based on the used of experimental data from columns of different depths (or a single column with ports) and the determination of the breakthrough curves as a function of time. These data provide information on the service time for each bed-depth (from which the name). Equations can be used to analyze these data to produce design relationships.

This method is an extension of a surface reaction model derived by a number of investigators.

Breakpoint Time vs. Column Length

The breakpoint time for an adsorption column is:

$$t_B = t_F + \left(t_L - t_A\right)$$

where:

t_F = time required for the adsorption zone to form

t_L = time required for the adsorption zone to travel down the column

t_A = time required for the adsorption zone to travel its own height

(compare this with definition of t_E)

Breakpoint Time vs. Column Length (continued)

Recalling that u_W is the velocity of the adsorption wave (and hence of the adsorption zone, u_A) the previous equation becomes:

$$t_B = t_F + \left(\frac{L}{u_W} - t_A \right)$$

Recalling that $t_F = (1 - f)\,t_A$ **then it is:**

$$t_B = (1 - f)\,t_A + \frac{L}{u_W} - t_A$$

Breakpoint Time vs. Column Length (continued)

By rearranging the previous equation one finds:

$$t_B = \frac{1}{u_W} L - \frac{f\,L_A}{u_W}$$

which implies that the breakpoint time increases linearly with the length of the column, ***L.***

This also means that a plot of t_B vs. *L* (for example using an experimental column in which *L* is the height of the different ports) should give a straight line.

Breakpoint Time vs. Column Length (continued)

The rate of advancement of the saturated zone in the column is equal to the wave velocity, u_W. As a result, each layer of upstream of the adsorption zone will become progressively saturated as the adsorption zone moves. Hence a mass balance for the pollutant gives:

$$QC_o = q_{so}\ r_{s\ app}\,S\,u_W$$

pollutant removed from wastewater = pollutant adsorbed

Breakpoint Time vs. Column Length (continued)

The previous equation provides us with an expression for u_W:

$$u_W = \frac{Q}{S} \frac{C_o}{r_{s\ app}\, q_{so}}$$

which can be used in the equation for t_B to give:

$$t_B = \frac{r_{s\ app}\, q_{so}}{u_S\, C_o} L - \frac{r_{s\ app}\, q_{so}\, f}{u_S\, C_o} L_A$$

since $u_S = Q/S$.

Breakpoint Time vs. Column Length (continued)

Finally, experimental data from test columns can be interpreted using this equation:

$$\boxed{t_B = \frac{r_{app}\, q_{so}}{u_S\, C_o} L - \frac{r_{app}\, q_{so}}{u_S\, C_o} f\, L_A}$$

$$\boxed{t_B = a\, L - b}$$

A plot of the breakpoint times, t_B's at different column heights, L's, should give a straight line.

<u>Remark</u>: The parameter ($r_{s\ app}\, q_{so}$) is more reliably obtained from experiments than equilibrium data.

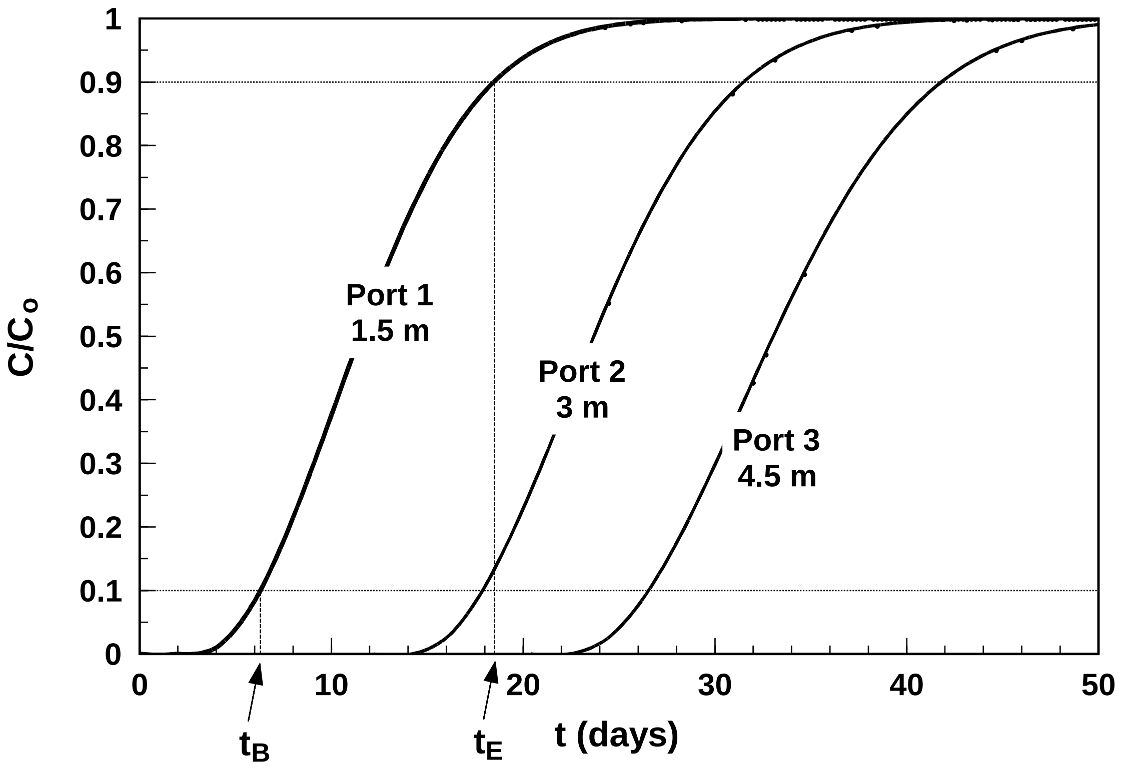
Bohart and Adams Equation

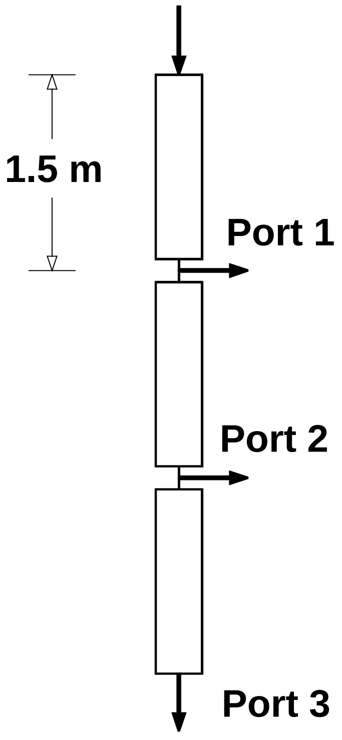
Using a completely different approach Bohart and Adams (1920) proposed an equation very similar to the previous one:

$$\boxed{t_B = \frac{r_{s\ app}\, q_{so}}{u_S\, C_o} L - \frac{1}{k_r\, C_o}\left(\ln\frac{C_o}{C_B} - 1\right)}$$

which can also be used to interpret the experimental data from test columns.

Interpretation of Experimental Data from Test Columns of Different Lengths

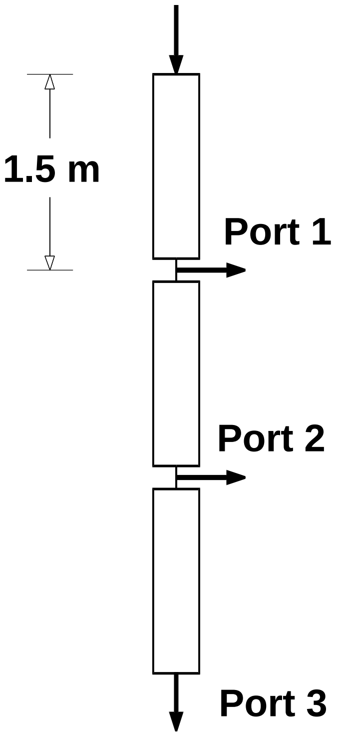




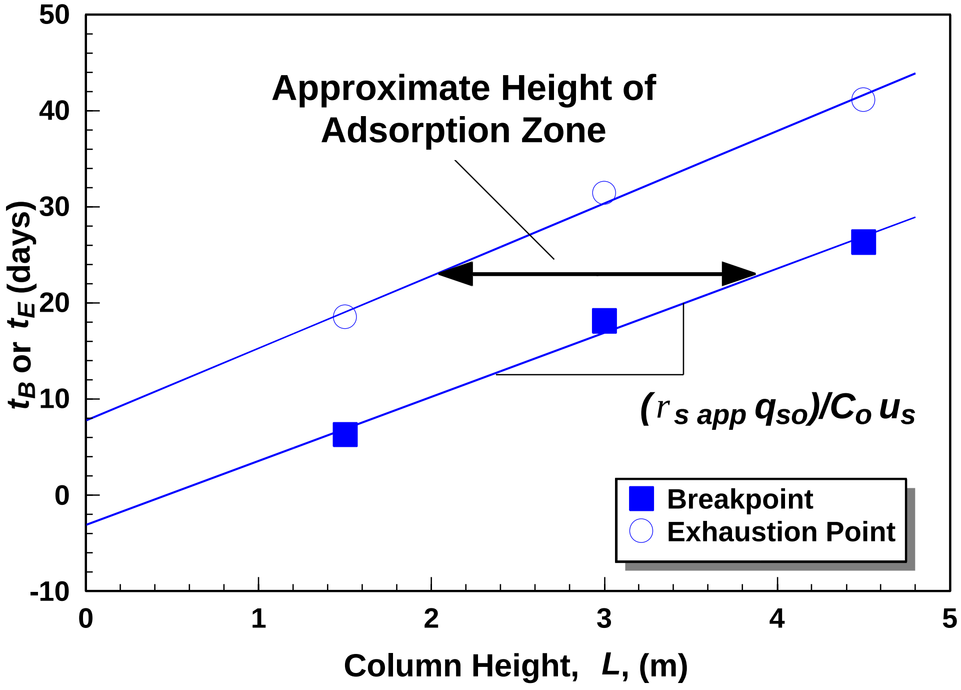
Interpretation of Experimental Data from Test Columns of Different Lengths

Example of experimental data:

Height of Column (m)	t_B (days)	t_E (days)
1.5	6.3	18.5
3	18.1	31.5
4.5	26.3	41.1



Interpretation of Experimental Data from Test Columns of Different Lengths



Pollutant Concentration in Wastewater at Breakpoint = 10% C_o

Pollutant Concentration in Wastewater at Exhaustion Point = 90% C_o

Design Method for BDST Method

- **Obtain experimental t_B vs. L data at breakpoint for columns of different depths. Possibly (but not necessarily) use same flow velocity (u_S) in the experimental and in the full scale column;**
- **Interpret the data using the expression for $t_B=f(L)$ or the Bohart and Adams equation and obtain equation parameters ($r_{s\,app}$ q_{so} and intercept);**
- **Determine service time (t_B) for the a full scale column of a fixed depth (or the column depth for a given time).**

Determination of Moving-Bed Adsorption Performance

The same equations that were used above for the alternative determination of the adsorption zone profile can be used also for sizing and determining the pollutant removal efficiency of a continuous moving bed adsorber in which carbon is continuously added to the column.

Monitoring of Adsorption Columns to Detect Breakpoint

By monitoring the pollutant concentration in the wastewater at different sampling ports along the column the progression of the adsorption wave can be monitored and the breakpoint anticipated

Regeneration of Carbon Beds

Depending on the type of pollutant adsorbed on the bed spent activated carbon beds can be regenerated using two different methods, i.e.:

- **chemical regeneration**
- **thermal regeneration**

Thermal regeneration is by far the most common method.

Chemical Regeneration

- Chemical regeneration relies on the use of chemicals to produce dissolution or oxidation of the adsorbate
- Chemical regeneration agents that have been used include:
  - NaOH
  - HCl
  - CCl_4
  - NaOCl
  - H_2O_2
- Chemical regeneration is only partially effective and is not as commonly used as thermal regeneration

Thermal Regeneration

- Thermal regeneration consists of processing the spent carbon at high temperature to volatilize and/or burn the adsorbed materials.
- Thermal regeneration typically involves some loss of carbon (typically between 5 and 10%) and some changes in the adsorption characteristics of the carbon itself (mainly caused by the reactivation process producing larger pores than those present in the original material).
- Thermal regeneration can be conducted on site or, more often, off-site.

Thermal Regeneration

- Thermal regeneration is typically conducted in a furnace (e.g., rotary hearth, fluidized bed).
- In those cases in which only or mainly volatile compounds have been adsorbed on the bed steam stripping can be effectively used at temperature high enough to produce volatilization of the adsorbate, but low enough to minimize degradation of the activated carbon. The stripped volatile organics can then be condensed separately.
- If non-volatile compounds are also present they will stay in the carbon and accumulate.

Thermal Regeneration

Thermal regeneration typically includes the following steps:

- **Drying at 100 to 150 °C (212 to 300 °F) to remove the water**
- **Volatilization of the light organic compounds at 150 to 315 °C (300 to 600 °F)**
- **Pyrolysis of the heavier organic compounds at temperatures as high as 800 °C (1500 °F)**
- **Re-activation of the carbon at temperatures as high as 1040 °C (1900 °F) in the presence of an oxidizer (steam, carbon monoxide, or oxygen)**

Additional Information and Examples on Adsorption

Additional information and examples can be found in the following references:

- **Corbitt, R. A. 1990, *The Standard Handbook of Environmental Engineering*, McGraw-Hill, New York, pp. 5.140-5.146; 6.195-6.202.**
- **Droste, R. L., 1997, *Theory and Practice of Water and Wastewater Treatment*, John Wiley & Sons, New York, pp. 484-507.**
- **Eckenfelder, W. W., Jr., 1989, *Industrial Water Pollution Control*, McGraw-Hill, New York, pp. 263-284.**

Additional Information and Examples on Adsorption

- **Freeman, H. M. (ed.), 1989, *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill, New York, pp. 6.3-6.21.**
- **LaGrega, M. D., Buckingham, P. L., Evans, J. C., 1994, *Hazardous Waste Management*, McGraw-Hill, New York, pp. 476-486.**
- **Metcalf & Eddy, 1991, *Wastewater Engineering: Treatment, Disposal, and Reuse*, McGraw-Hill, New York, pp. 314-324; 751-755.**
- **Sundstrom, D. W. and Klei, H. E., 1979, *Wastewater Treatment*, Prentice Hall, Englewood Cliffs, NJ, pp. 241-273.**

Additional Information and Examples on Adsorption

- **Treybal, R. E., 1968, *Mass Transfer Operation*, McGraw-Hill, New York, pp. 490-568.**
- **Weber, W. J., Jr., 1972, *Physicochemical Process for Water Quality Control*, Wiley-Interscience, John Wiley & Sons, New York, pp. 199-259.**
- **Wentz, C. W., 1995, *Hazardous Waste Management*, Second Edition, McGraw-Hill, New York, pp. 201-202.**