Lecture 6: Adsorption

Water Treatment Technology

Water Resources Engineering
Civil Engineering
ENGC 6305

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1. Principles of Adsorption

A. <u>Definition of Adsorption:</u>

- Adsorption is a natural process by which molecules of a dissolved substance collect on and adhere to the surface of an adsorbent solid.
- The *adsorbent* is the solid material onto which the adsorbate accumulates.
- The *adsorbate* is the dissolved substance that is being removed from liquid phase to the solid surface of the adsorbent.
- Adsorption may occur at the outer surface of the adsorbent and in the macropores, mesopores and micropores in the inner cracks of the adsorbent see Figures (6.1) and (6.2).

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macropores >25 nm (1 \text{ nm} = 10^{-6} \mu\text{m}) mesopores >1 nm and < 25nm micropores >1 nm
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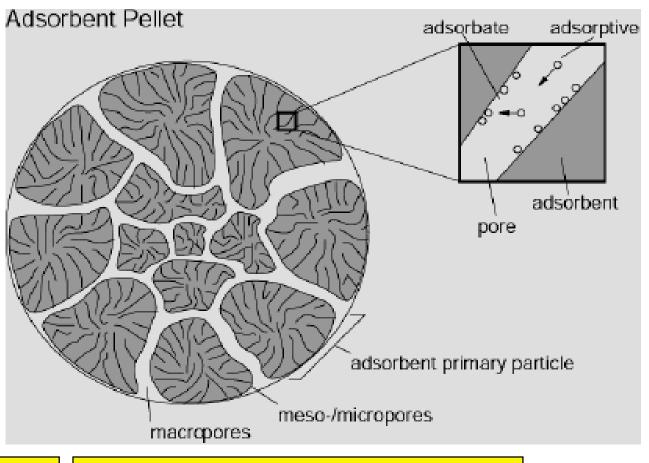
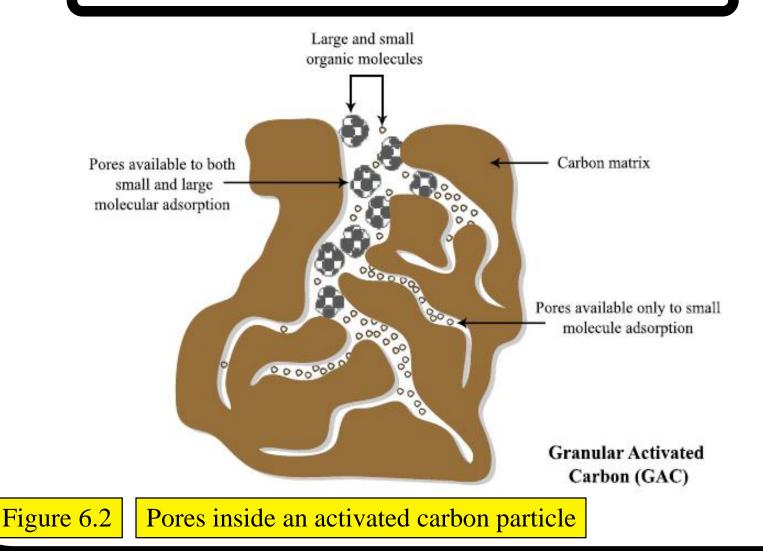


Figure 6.1

Pores inside an activated carbon particle



B. Use of adsorption in water treatment:

Adsorption is used in water treatment to remove dissolved organic chemicals such as:

- taste and odor causing chemicals
- synthetic organic chemicals
- color forming organics
- some disinfection organic by-products

Some of the organic chemicals that can be removed by adsorption is given in Table 6.1.

• Forces affecting adsorption:

The principal forces leading to sticking the adsorbate to the surface of the adsorbent solid are:

- Van der Waals forces
- Hydrogen bonding
- Dipole-dipole interactions

Table 6.1

Readily and poorly adsorbed organics

Readily adsorbed organics

Aromatic solvents

Benzene

Toluene Nitrobenzenes

Chlorinated aromatics

PCBs

Chlorophenols

Polynuclear aromatics

Acenaphthene

Benzopyrenes

Pesticides and herbicides

DDT

Aldrin

Chlordane

Atrazine

Chlorinated nonaromatics

Carbon tetrachloride

Chloroalkyl ethers

Trichloroethene

Chloroform

Bromoform

High-MW hydrocarbons

Dyes

Gasoline

Amines

Humics

Poorly adsorbed organics

Low-MW ketones, acids, and aldehydes

Sugars and starches

Very-high-MW or colloidal organics

Low-MW aliphatics

D. Types of Adsorbents:

The following are the main materials that are used as adsorbents:

- Activated carbon
- Silica
- Synthetic polymers

Activated carbon (AC) is the mostly used adsorbent in water treatment, that's why we will limit our study to <u>Activated Carbon Adsorption</u>.

2. Activated Carbon Characteristics:

- A. Production of activated carbon:
 - i) Activated carbon is prepared by two steps:
 - a) <u>Carbonization</u>: carbonaceous material such as wood, almond, coal, coconut shells, is first heated to red heat (to less than 700 °C) to produce char. Heating is applied under controlled oxygen supply to prevent the destruction of the carbonaceous material.
 - b) <u>Activation:</u> the carbonized material is exposed to steam or hot CO₂ to cause pores and cracks to form.
 - ii) After the preparation of (AC), it is produced in two diameter sizes:
 - a) Powdered activated carbon (PAC): particles size < 0.074 mm
 - b) Granular activated carbon (GAC): particles size > 0.1 mm the characteristics of PAC and GAC are in Table 6.2. see also Figures 6.3, 6.4, and 6.5 showing photos of GAC and PAC.



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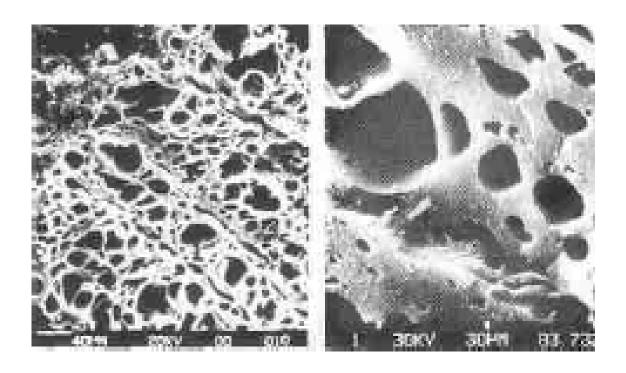


Figure 6.5

Microscopic photo showing the pores at the surface of GAC particle

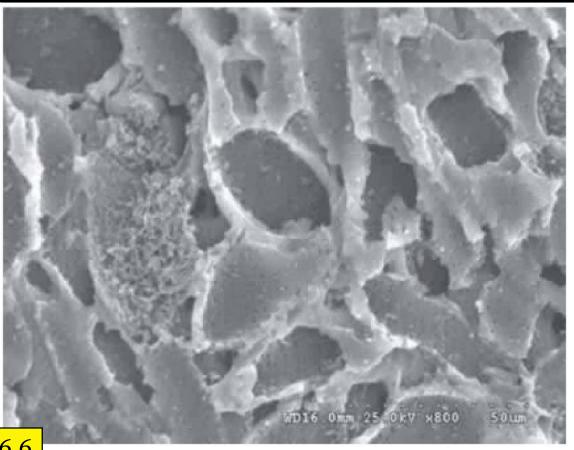


Figure 6.6

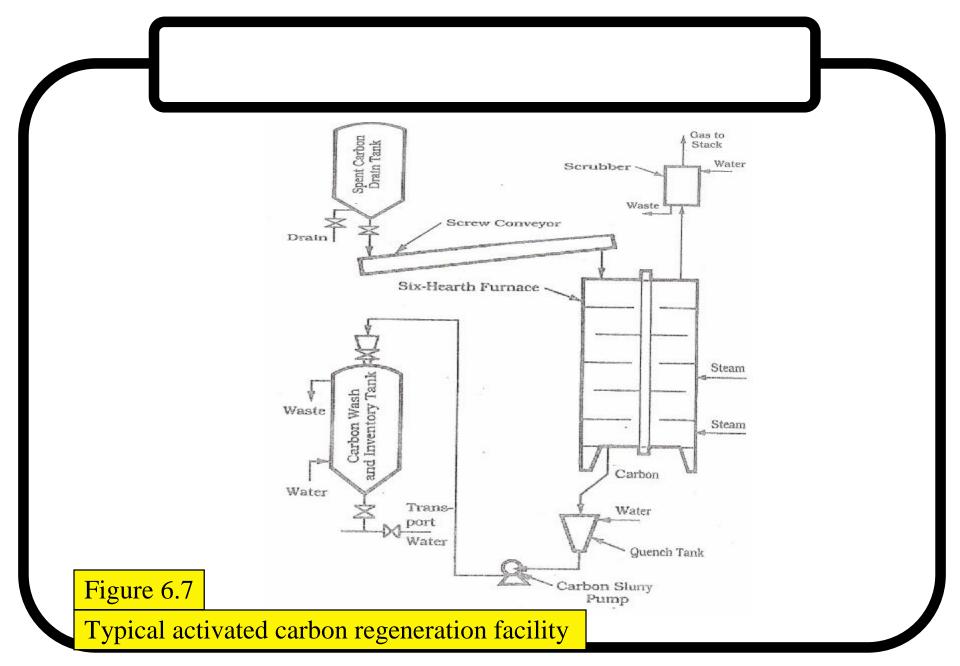
Microscopic photo showing the surface of an exhausted GAC particle

Table 6.2 Comparison between granular and powdered activated carbon

	**	Type of activated carbona		
Parameter	Unit	GAC	PAC	
Total surface area	m²/g	700-1300	800-1800	
Bulk density	kg/m³	400-500	360-740	
Particle density, wetted in water	kg/L	1.0-1.5	1.3-1.4	
Particle size range	mm (μm)	0.1-2.36	(5-50)	
Effective size	mm	0.6-0.9	na	
Uniformity coefficient	UC	≤1.9	na :	
Mean pore radius	Â	16-30	20-40	
lodine number		600-1100	800-1200	
Abrasion number	minimum	75-85	70-80	
Ash ·	%	≤8	≤6	
Moisture as packed	%	2-8	3-10	

B. Regeneration of activated carbon:

- After using the activated carbon for adsorbing the dissolved organic matter it eventually reaches its maximum adsorptive capacity. It is called in this state as spent activated carbon.
- To recycle the spent activated carbon its adsorptive capacity should be first restored by a process called regeneration.
- Regeneration is achieved by taking the spent activated carbon out of the treatment tanks and exposing it to different materials such as:
 - i) Adding oxidizing chemicals to oxidize the adsorbed organics.
 - ii) Steam to drive off the adsorbed materials.
 - iii) Some solvents. See a typical regeneration facility in Figure 6.7.
- After regeneration, the spent carbon is reactivated by the same way by which the original carbonaceous was activated.
- Some of the adsorptive capacity (2-5 %) of the AC is lost permanently during regeneration. Some carbon (4-8 %) is lost due to mishandling. So a makeup amount of carbon should be added to the system.



3. Adsorptive capacity of activated carbon:

- The quantity of the adsorbate (i.e. dissolved organics) that can be taken up by an absorbent (i.e. activated carbon) is a function of the characteristics and concentration of the adsorbate, characteristics of the adsorbent and temperature.
- The amount of material adsorbed is determined as a function of the concentration at constant temperature, and the resulting function is called adsorption isotherms.
- Many equations (adsorption isotherms) were developed to determine amount of material adsorbed. The most famous isotherms are:
 - a) Freundlich isotherm
 - b) Langmuir isotherm

The following slides will illustrate both of these isotherms.

4. Freundlich isotherm

The Freundlich isotherm is presented by the following equations:

$$q_e = \frac{X}{m} = K_f C_e^{1/n}$$
, or $\log \left(\frac{x}{m}\right) = \log K_f + \frac{1}{n} \log C_e$(6.1)

 $q_e = mass of materil adsorbed (X) per unit mass (m) of adsobent at equilibrium, mg/g$

 $K_f = Freundlich capacity factor, (L/mg)^{1/n}$

C_e = equilibrium concentration of adsorbate in liquid phase after adsorption, mg/L

1/n = Freundlich intensity parameter

This form of the equation $\left| \log \left(\frac{x}{m} \right) \right| = \log K_f + \frac{1}{n} \log C_e$ is linear.

The constants in the Freundlich isotherm can be determined by plotting $\log \left(\frac{x}{m}\right)$ versus $\log C_e$, the Y-intercept is $\log K_f$, and the slope is $\frac{1}{n}$.

The constants in Freundlich isotherm for different organics is in Table 6.3

Table 6.3

Freundlich
Adsorption
isotherm
Constant for
Selected
organic
compounds

Compound	рН	pH $K_f(mg/g)(L/mg)^{1/n}$	
Benzene	5.3	1.0	1.6-2.9
Bromoform	5.3	19.6	. 0.52
Carbon tetrachloride	5.3	11	0.83
Chlorobenzene	7.4	91	0.99
Chloroethane	5.3	0.59	0.95
Chloroform	5.3	2.6	0.73
DDT	5.3	322	0.50
Dibromochloromethane	5.3	4.8	0.34
Dichlorobromomethane	5,3	7.9	0.61
1,2-Dichloroethane	5,3	3.6	0.83
Ethylbenzene	7.3	53	0.79
Heptachlor	5.3	1,220	0.95
Hexachloraethane	5.3	96.5	0.38
Methylene chloride	5.3	1.3	1.16
N-Dimethylnitrosamine	па	6.8×10^{-5}	6.60
N-Nitrosodi-n-propylamine	na	24	0.26
N-Nitrosodiphenylamine	3-9	220	0.37
PCB	5.3	14,100	1.03
PCB 1221	5.3	242	0.70
PCB 1232	5.3	630	0.73
Phenol	3-9	21	0.54
Tetrachloroethylene	5.3	51	0.56
Toluene	5.3	26.1	0.44
1,1,1-Trichloroethane	5.3	2-2.48	0.34
Trichloroethylene	5.3	28	0.62

5. Langmuir isotherm

The Langmuir isotherm is presented by the following equations:

$$\frac{X}{m} = \frac{abC_e}{1 + bC_e}$$
, or $\frac{C_e}{(x/m)} = \frac{1}{ab} + \frac{1}{a}C_e$ (6.2)

 $\frac{X}{m}$ = mass of materil adsorbed (X)per unit mass (m)of adsobent at equilibrium, mg/g

 C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L a, b = empirical constants

This form of the equation $\left| \frac{C_e}{(x/m)} = \frac{1}{ab} + \frac{1}{a}C_e \right|$ is linear.

The constants in the Langmuir isotherm can be determined by plotting versus C_e , the Y-intercept is $\frac{1}{ab}$, and the slope is $\frac{1}{a}$.

- 6. <u>Laboratory tests for determining the coefficients of the Freundlich and Langmuir isotherms:</u>
 - The coefficients in the isotherms are found using batch tests.
 - Typically more than ten beakers (with one liter volume each) are filled with polluted water that has an initial concentration of \mathbf{C}_0 .
 - Different masses of GAC or PAC are added to the beakers.
 - The test time is at least 7 days after which the concentration of the pollutant is reduced to an equilibrium concentration of C_e .
 - Equilibrium concentration is that concentration after which no more adsorption is observed.

Example 6.1 illustrates this test and its importance.

Example 6.1:

Analysis of Activated-Carbon Adsorption Data Determine the Freundlich and Langmuir isotherm coefficients for the following GAC adsorption test data. The liquid volume used in the batch adsorption tests was 1 L. The initial concentration of the adsorbate in solution was 3.37 mg/L. Equilibrium was obtained after 7 days.

Mass of GAC, m, g	Equilibrium concentration of adsorbate in solution, C_c , mg/L		
0.0	3.37		
0.001	3.27		
0.010	2.77		
0.100	1.86		
0.500	1.33		

Example 6.1 ... Cont'd:

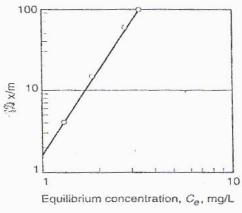
Solution:

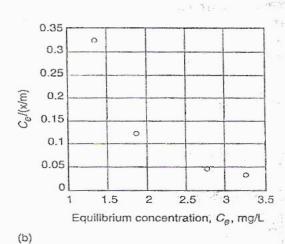
1. Derive the values needed to plot the Freundlich and Langmuir adsorption isotherms using the batch adsorption test data

mg/L			x/m,a	a - The way	
C _o	C _e	$C_{\circ} - C_{e}$	m, g	mg/g	$C_e/(x/m)$
3.37	3.37	0.00	0.000	_	1
3.37	3.27	0.10	0.001	100	0.0327
3.37	2.77	0.60	0.010	60	0.0462
3.37	1.86	1.51	0.100	15.1	0.1232
3.37	1.33	2.04	0.500	4.08	0.3260

Example 6.1 ... Cont'd:

2. Plot the Freundlich and Langmuir adsorption isotherms using the data developed in Step 1 (see following figures).





(a)

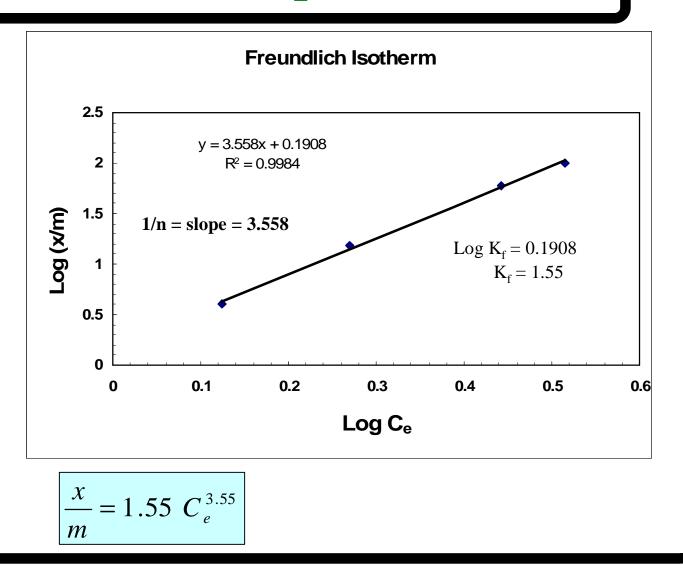
- 3. Determine the adsorption isotherm coefficients.
 - a. Freundlich

When x/m versus C_e is plotted on log-log paper, the intercept when $C_e = 1.0$ is the value of (x/m) and the slope of the line is equal to 1/n. Thus, x/m = 1.55, and $K_f = 1.55$. When x/m = 1.0, $C_e = 0.9$, and 1/n = 0.25. Thus,

$$\frac{x}{m} = 1.5 C_e^{3.285}$$

b. Langmuir

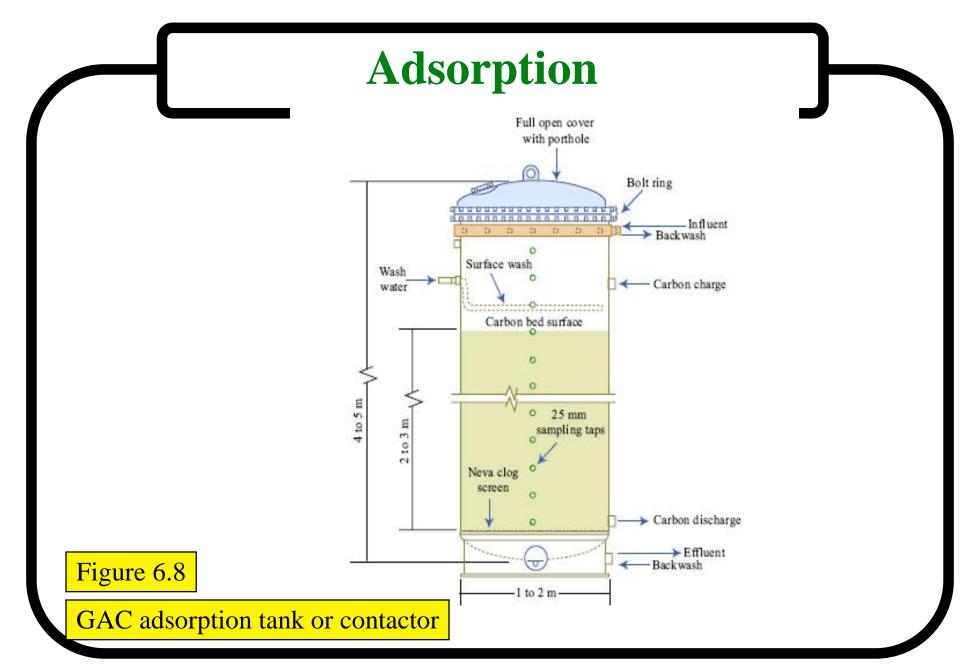
Because the plot for the Langmuir isotherm is curvilinear, use of the Langmuir adsorption isotherm is inappropriate.



7. Systems of PAC and GAC in water treatment:

- Powdered activated carbon (PAC) treatment is mostly performed in contact basins where it is added and continuously mixed for a specified time then it is allowed to settle and the treated water is withdrawn. The process is similar to that described in the batch experiments in the lab mentioned previously and as in Example 6.1.
- Granular activated carbon (GAC) treatment is mostly performed in cylindrical metallic tanks called columns or bed contactor. Several types of GAC contactors are used such as Fixed Bed, and Fluidized Bed Contactors. See Figures 6.8, 6.9 and 6.10.

The most used type in water treatment is the fixed bed contactor that's why the next discussion will concentrate on this type.



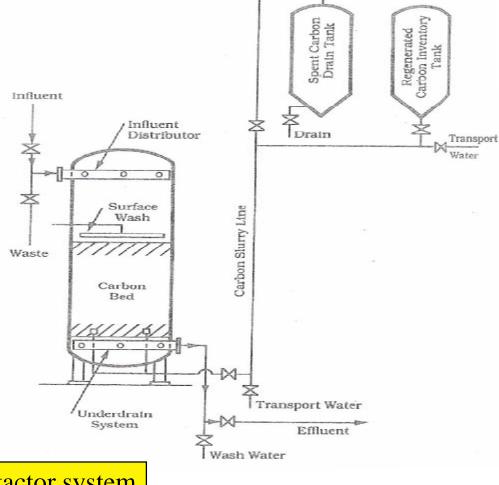


Figure 6.9

GAC adsorption contactor system



Figure 6.10 GAC adsorption tanks

8. Fixed bed GAC contactors:

- a) Configuration of The GAC contactor (Figures 6.8,6.9 & 6.10):
 - The main component of the contactor is a cylindrical steel tank with the following typical dimensions:

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Diameter 1-2 m (maximum available diameter is 3.7m)
Height 4-5 m
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- The GAC bed occupies 2-3 meters of the contactor height and supported from the bottom with an under drain system.
- The water inters from the top (downflow) by an influent distributor piping system and applied at the rate of 1.4 to 3.4 L/s.m². When the headless in the contactor becomes excessive due to the accumulation of suspended solids the tank is taken off-line and backwashed by applying water form the bottom upwards at the rate of 6.8 to 13.6 L/s.m². The same influent distributor is used to drain the upflow backwash water .
- A surface whishing system is used to clean the surface of the GAC bed.
- An under drain piping system is installed at the bottom to collect the treated water. This piping system is used to pump the upflow backwash water.
- Piping system to remove the spent GAC and to add the new or regenerated GAC to the tank.

b) Sizing The GAC contactor (Figure 6.7):

- The sizing of the GAC contactor depends on the following factors:
 - i) Contact time
 - ii) Hydraulic loading rate
- iii) carbon depth
- iv) number of contactors.

Table 6.4 shows typical design values for GAC contactors, and Table 6.5 shows typical specifications of GAC material used in GAC contactors.

c) Multiple tanks Operation:

- GAC tanks can be operated in parallel or in series. See Figures 6.11 and 6.12.
- A minimum of two parallel carbon contactors is recommended for design.
- Multiple units permit one or more units to remain in operation while one unit is taken out of service for removal and generation of spent carbon or maintenance.

Table 6.4

Typical design values of GAC contactors

Parameter	Symbol	Unit	Value
Volumetric flowrate	V	m^3/h	50-400
Bed volume	V_b	m ³	10-50
Cross-sectional area	A_b	m^2	5-30
Length	D	m	1.8-4
Void fraction	α	m^3/m^3	0.38-0.42
GAC density	ρ	kg/m³	350-550
Approach velocity	V_i	m/h	5-15
Effective contact time	1	min	2-10
Empty bed contact time	EBCT	min	5-30
Operation time	t	d	100-600
Throughput volume	V_{L}	m^3	10-100
Specific throughput	V_{sp}	m³/kg	50-200
Bed volumes	BV	m^3/m^3	2,000 20,000

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Typical specifications for GAC

Parameter	Unit Value		
Total surface area	m²/g	700-1300°	
Bulk density	kg/m³	400-440°	
Particle density, wetted in water	kg/L	1.3–1.5°	
Effective size	mm	0.8-0.9°	
Uniformity coefficient	UC	≤1.9	
Mean particle diameter	mm	1.5-1.7	
lodine number		850 min	
Abrasion number	•	70 min	
Ash	%	8 max	
Moisture	%	4-6 max	
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 $[\]ensuremath{^{\alpha}}\xspace\ensuremath{\text{Depends}}\xspace$ on the source material for the carbon.

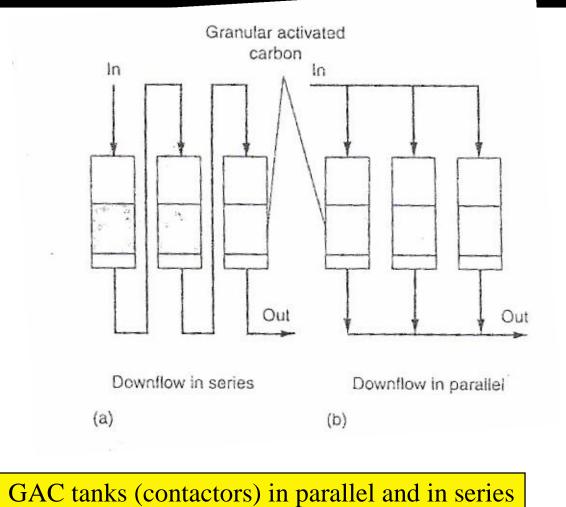


Figure 6.11

Columns containing activated carbon

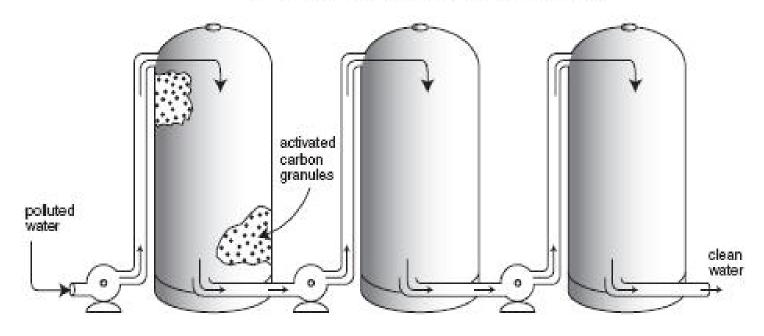


Figure 6.12

GAC tanks (contactors) in series

- 9. Adsorption process analysis in the Fixed bed GAC contactors:
- a) Mass transfer inside the GAC bed:

When the polluted water is pumped on the GAC bed the, the dissolved organic matter start to adsorb on the carbon. The area of the GAC bed in which sorption (adsorption) occurs is called the mass transfer zone (MTZ) See Figure 6.13.

- -No further adsorption occurs below the MTZ and the water leaving the MTZ zone contains the minimum concentration value of the pollutant that the bed can produce.
- -With time a zone of saturation is created above the MTZ in which the carbon has reached its maximum adsorption capacity and no further adsorption occurs. The equilibrium concentration C_e of the pollutant in water in this zone is the same as C_0 .

- -The Zone below the MTZ essentially clean zone and no adsorbed material on it.
- -With time the saturation zone depth increases and the MTZ is pushed down until we reach to a point where the clean zone disappears and breakthrough occurs.
- Breakthrough is said to have occurred when the effluent concentration reaches to 5% of the influent concentration (i.e, $C_b = 0.05C_0$).
- -After additional time the MTZ start to decrease until it disappears and the bed is called exhausted. Exhaustion of the bed is assumed to have occurred when the effluent Concentration is equal to 95% of the influent concentration (i.e, $C = 0.95C_0$)

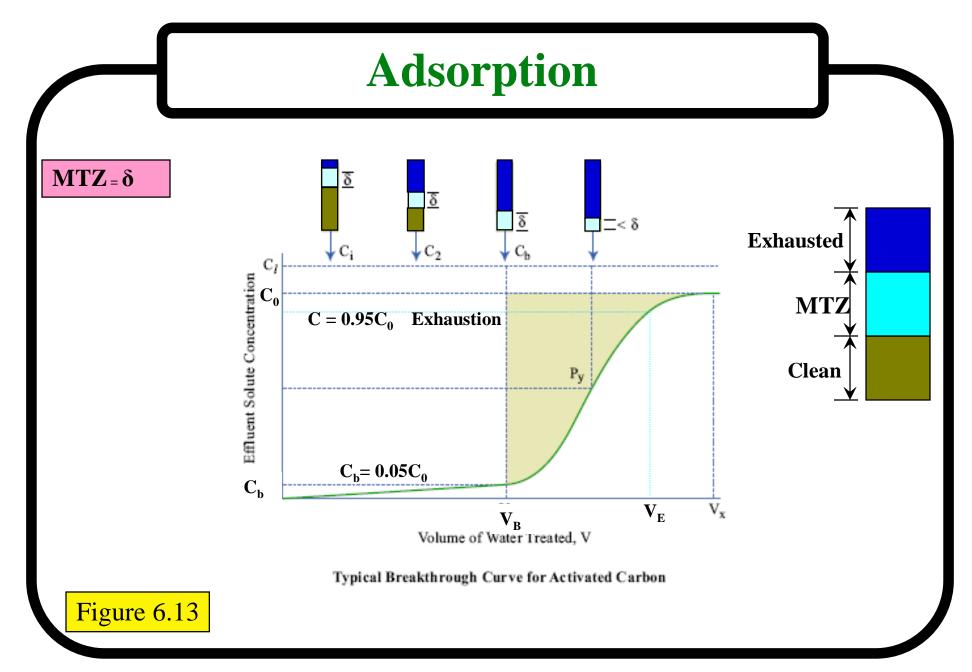
-The length of the MTZ is calculated from the following equation (6.3):

$$H_{MTZ} = Z \left[\frac{V_E - V_B}{V_E - 0.5(V_E - V_B)} \right](6.3)$$
where H_{MTZ} = length of mass transfer zone, (m)
$$Z = \text{height of the adsorption column, (m)}$$

$$V_E = \text{throughput volume to exhaustion, m}^3$$

$$V_B = \text{throughput volume to breakthrough, m}^3$$

-The area above the breakthrough curve is equal to the mass of the pollutant adsorbed in the column and equal to: $X = \int_0^V (C_0 - C) dV$(6.4)



b) Quantification of the operational performance of the GAC bed:

Many parameters were developed to quantify the performance of the GAC contactor as follows:

1. Empty bed contact time (EBCT):

$$EBCT = \frac{V_b}{Q} = \frac{A_b D}{v_f A_b} = \frac{D}{v_f}$$
.....(6.5)
where EBCT = empty bed contact time,(h)
$$Q = \text{flowrate, (m}^3/\text{h})$$

$$A_b = \text{cross-sectional area of GAC bed, (m}^2)$$

$$D = \text{length of GAC incontactor, (m)}$$

$$v_f = \text{linearapproachvelocity, (m/h)}$$

2. Activated carbon density:

3. Specific throughput (ST):

The specific throughput is defined as the volume of water treated per unit

weight of the carbon (m^3/g) :

specific throughput =
$$\frac{Qt}{m_{GAC}} = \frac{V_b t}{EBCT^* m_{GAC}} = \frac{t}{EBCT^* \rho_{GAC}}$$
(6.7)

4. Carbon usage rate (CUR):

The carbon usage rate is the reciprocal of (ST) and is defined the carbon needed to treat a unit weight of water (g/m^3) :

$$CUR = \frac{m_{GAC}}{Qt} = \frac{1}{\text{specific throughput}} \dots (6.8)$$

5. Mass of organic material adsorbed at breakthrough:

$$\left(\frac{x}{m}\right)_{b} = \frac{x_{b}}{m_{GAC}} = Q\left(C_{0} - \frac{C_{b}}{2}\right) \frac{t_{b}}{m_{GAC}}...(6.9)$$

wher $\left(\frac{x}{m}\right)_b$ = field breakthruogh adsorption capacity, (g/g)

 $x_b = \text{mass of organic material adsorbed in the GAC column at breakthrough, (g)}$

 $m_{GAC} = mass of carbon in the column, (g)$

 $Q = flowrate, (m^3/d)$

 $C_0 = \text{influent organic concentration}, (g/m^3)$

 C_b = breakthrough organic concentration, (g/m^3)

 $|t_b| = time to breakthrough, (d)$

6. Time to breakthrough:

$$t_{b} = \frac{\left[\frac{x}{m}\right]_{b} * m_{GAC}}{Q\left[C_{0} - \frac{C_{b}}{2}\right]}....(6.10)$$

Example 6.2:

Estimation of Activated Carbon Adsorption Breakthrough Time A fixed-bed activated carbon adsorber has a fast mass transfer rate, and the mass transfer zone is essentially a sharp wavefront. Assuming the following data apply, determine the carbon requirements to treat a flow of 1000 L/min, and the bed life.

- 1. Compound = trichloroethylene (TCE)
- 2. Initial concentration, $C_o = 1.0 \text{ mg/L}$
- 3. Final concentration $C_e = 0.005 \text{ mg/L}$
- GAC density = 450 g/L
- 5. Freundlich capacity factor $K_f = 28 \,(\text{mg/g})(\text{L/mg})^{1/n}$ (see Table 6.3)
- 6. Freundlich intensity parameter, 1/n = 0.62 (see Table 6.3)
- 7. EBCT = 10 min

Example 6.2 ... Cont'd:

Solution:

 Estimate the GAC usage rate for toluene. The GAD usage rate is estimated using Eq. 6.8

$$\frac{m_{\text{GAC}}}{Qt} = \frac{C_o - C_e}{q_e} = \frac{C_o - C_e}{K_f C_o^{1/n}}$$

$$= \frac{(1.0 \text{ mg/L})}{28 (\text{mg/g}) (\text{L/mg})^{0.62} (1.0 \text{ mg/L})^{0.62}}$$

$$= 0.036 \text{ g GAC/L}$$

Determine the mass of carbon required for a 10 min EBCT.

The mass of GAC in the bed = $V_b \rho_{GAC}$ = EBCT \times $Q \times \rho_{GAC} \longrightarrow$ From Eq. 6.5 & 6.6

 $m_{GAC} = Carbon required = 10 min (1000 L/min) (450 g/L) = 4.5 \times 10^6 g$

3. Determine the volume of water treated using a 10 min EBCT.

Volume of water treated =
$$\frac{\text{mass of GAC for given EBCT}}{\text{GAC usage rate}}$$

Volume of water treated =
$$\frac{4.5 \times 10^6 \text{ g}}{(0.036 \text{ g GAC/L})} = 1.26 \times 10^8 \text{ L}$$

Example 6.2 ... Cont'd:

4. Determine the bed life.

Bed life =
$$\frac{\text{volume of water treated for given EBCT}}{Q}$$

Bed life =
$$\frac{1.26 \times 10^8 \text{ L}}{(1000 \text{ L/min})(1440 \text{ min/d})} = 87.5 \text{ d}$$

Comment

In this example, the full capacity of the carbon in the contactor was utilized based on the assumption that two columns in series will be used. If a single column is to be used, a breakthough curve must be used to arrive at the bed life. Biological activity within the column was not considered.

Example 6.3:

Estimation of Powdered Activated Carbon (PAC) Adsorption Dose and Cost

A treated wastewater with a flowrate of 1000 L/min is to be treated with PAC to reduce the concentration of residual organics measured as TOC from 5 to 1 mg/L. The Freundlich adsorption isotherm parameters were developed as discussed previously. Assuming the following data apply, determine the PAC requirements to treat the wastewater flow. If PAC costs \$0.50/kg, estimate the annual cost for treatment, assuming the PAC will not be regenerated.

- Compound = mixed organics
- 2. Initial concentration, $C_o = 5.0 \text{ mg/L}$
- 3. Final concentration, $C_e = 1.0 \text{ mg/L}$
- 4. GAC density = 450 g/L
- 5. Freundlich capacity factor, $K_f = 150 \,(\text{mg/g})(\text{L/mg})^{1/n}$
- 6. Freundlich intensity parameter, 1/n = 0.5

Example 6.3 ... Cont'd:

Solution:

1. Estimate the PAC dose based on the isotherm data. The PAC dose can be estimated by writing Eq. (11-71) as follows:

$$\frac{\mathbf{m}}{\mathbf{V}} = \frac{(\mathbf{C}_0 - \mathbf{C}_e)}{\mathbf{q}_e} = \frac{(\mathbf{C}_0 - \mathbf{C}_e)}{K_f C_e^{1/n}}$$

Substituting Eq. (11–15) for q_e and using the given values in the above expression yields

$$\frac{m}{V} = \frac{[(5-1) \text{ mg/L}]}{(150 \text{ mg/g})(\text{L/mg})^{0.5}(1.0 \text{ mg/L})^{0.5}} = 0.0267 \text{ g/L}$$

2. Estimate the annual cost for the PAC treatment.

Annual cost

$$= \frac{(0.0267 \text{ g/L})(1000 \text{ L/min})(1440 \text{ min/d})(365 \text{ d/yr})(\$0.50/\text{kg})}{(10^3 \text{ g/kg})}$$

Annual cost = \$7008/year