Example

An industrial wastewater contains 10 mg/L chlorophenol, and is going to be treated by carbon adsorption. 90% removal is desired. The wastewater is discharged at a rate of 0.1 MGD. Calculate the carbon requirement for

- a) a single, mixed contactor (CMFR)
- b) two mixed (CMFR) contactors in series
- c) a column contactor.

Freundlich isoherm
$$\begin{array}{c} q = 6.74 x C^{0.41} \\ \downarrow & \downarrow \\ mg/g C & mg/L \end{array}$$



Carbon requirement =

$$3.4 \times 10^{6} \text{ mg/day x } \frac{\text{g C}}{6.74 \text{ mg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 505 \text{ kg/day}$$

b) Two CSTRs connected in series



you will calculate a different value.

Contactor 1

$$C_{inf} = 10 mg/L$$

 $C_{eff} = 5 mg/L$
 $q = 6.74x5^{0.41} = 13.0 mg/g C$

Organic Load = (10-5) mg/L x $(3.78 \times 10^5 \text{ L/d}) = 1.89 \times 10^6$ mg/day

Carbon requirement =

$$1.89 \times 10^{6} \text{ mg/day x } \frac{\text{g C}}{13.0 \text{ mg}} \text{x} \frac{1 \text{ kg}}{1000 \text{ g}} = 145 \text{ kg / day}$$

Contactor 2

$$C_{inf} = 5 mg/L$$

 $C_{eff} = 1 mg/L$

$$q = 6.74 x 1^{0.41} = 6.74 mg/g C$$

Organic Load = (5-1) mg/L x $(3.78 \times 10^5 \text{ L/d})$ = **1.51x10⁶ mg/day**

Carbon requirement =

$$1.51 \times 10^{6} \text{ mg/day x } \frac{\text{g C}}{6.74 \text{ mg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 224 \text{ kg/day}$$



Total C requirement = 145+224=369 kg/day

a) a single, mixed contactor (CMFR) =505 kg/day

b) two mixed (CMFR) contactors in =369 kg/day series

C requirement decreased because, in the 1st contactor, we are able to put more on the surface of the carbon.



Flow Direction

Column Height



Everything happens in the primary adsorption zone (or mass transfer zone, MTZ). This layer is in contact with the solution at its highest concentration level, C_o. As time passes, this layer will start saturating. Whatever escapes this zone will than be trapped in the next zones. As the polluted feed water continues to flow into the column, the top layers of carbon become, practically, saturated with solute and less effective for further adsorption. Thus the primary adsorption zone moves downward through the column to regions of fresher adsorbent.

Concentration (mg/L)

Here you start observing your breakthrough curve when the last layer starts getting saturated.



Last primary adsorption zone. It is called **primary** because the upper layers are not doing any removal job. They are saturated.

When breakthrough occurs there is some amount of carbon in the column still not used. Generally, this is accepted to be 10-15%.

Primary adsorption zone

Region where the solute is most effectively and rapidly adsorbed.

This zone moves downward with a constant velocity as the upper regions become saturated.



Active zones at various times during adsorption and the breakthrough curve..

Ref: <u>http://web.deu.edu.tr/atiksu/ana07/arit4.html</u>

Column Contactor

 $C_{inf} = 10 \text{ mg/L}$ $C_{eff} = 1 \text{ mg/L}$ $q = 6.74 \times 10^{0.41} = 17.3 \text{ mg/g C}$

Organic Load = (10-1) mg/L x $(3.78 \times 10^5 \text{ L/d})$ =**3.4x10⁶ mg/day**

Assume that the breakthrough occurs while 10% of the carbon in the column is still not used.

Carbon requirement =

$$3.4 \times 10^{6} \text{ mg/day x } \frac{\text{g C}}{17.3 \text{ mg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{100\%}{90\%} = 218.4 \text{ kg/day}$$

- It is not possible to design a column accurately without a
- test column breakthrough curve for the liquid of interest
- and the adsorbent solid to be used.



Theoretical Breakthrough Curve

i. Scale – up procedure

and

ii. Kinetic approach

are available to design adsorption columns . In both of the approaches a breakthrough curve from a test column, either laboratory or pilot scale, is required, and the column should be as large as possible to minimize side – wall effects. Neither of the procedures requires the adsorption to be represented by an isotherm such as the Freundlich equation.

<u>Scale – up Procedure for Packed Columns</u>

- Use a pilot test column filled with the carbon to be used in full scale application.
- Apply a filtration rate and contact time (EBCT) which will be the same for full – scale application (to obtain similar mass transfer characteristics).
- Obtain the breakthrough curve.
- Work on the curve for scale up.

Example

An industrial wastewater having a TOC of 200 mg/L will be treated by GAC for a flowrate of 150 m³/day. Allowable TOC in the effluent is 10 mg/L.

Pilot Plant Data

- Q = 50 L/hr
- Column diameter = 9.5 cm
- Column depth (packed bed) = 175 cm
- Packed bed carbon density = 400 kg/m^3
- V_{breakthrough} = 8400 L
- $V_{exhaustion} = 9500 L$



Breakthrough Curve of the Pilot Plant

a) Filtration rate of the pilot plant

FR =
$$\frac{Q}{A} = 50 \frac{L}{hr} x \frac{1}{\pi \left(\frac{d}{2}\right)^2} x \frac{1000 \text{ cm}^3}{1L} = 705 \frac{\text{ cm}^3}{\text{ hr.cm}^2}$$

d = 9.5 cm

The same FR applies to Packed Column.

b) Area of the Packed Column

$$\mathsf{FR} = \frac{\mathsf{Q}}{\mathsf{A}} \qquad \mathsf{A} = \frac{\mathsf{Q}}{\mathsf{FR}}$$

$$A = \left(150 \frac{m^2}{d}\right) x \left(\frac{1}{705} \cdot \frac{h.cm^2}{cm^3}\right) x \left(\frac{1}{24} \frac{d}{h}\right) x \left(\frac{10^6 cm^3}{1 m^3}\right) = 8865 cm^2$$

$$d = \sqrt{\frac{4 \times 8865}{\pi}} = 106cm$$

c) Empty Bed Contact Time of the Pilot Plant

$$\tau = \frac{\forall}{Q}$$
$$\forall = A \text{ x Height} = \pi \left(\frac{d}{2}\right)^2 \text{ x H} = (3.14) \text{ x} \left(\frac{9.5}{2}\right)^2 \text{ x175} = 12,404 \text{ cm}^3 = 12.4 \text{ L}$$

$$\tau = \frac{12.4 \text{ L}}{50 \text{ L/hr}} = 0.248 \text{ hr} = 14.88 \cong 15 \text{ min}$$

15 mins.is the EBCT of the Packed Column.

d) <u>Height of the Packed Column</u>

$$\tau \propto \frac{Q}{A} = (15 \text{ min}) \times \left(705 \frac{\text{cm}^3}{\text{hr.cm}^2}\right) \times \left(\frac{1 \text{ hr}}{60 \text{ min}}\right) = 176 \text{ cm}$$

The same as the height of the Pilot Plant. Because height is set by τ and Q/A , and these are the same for Pilot Plant and the Packed Column.

e) Mass of Carbon required in the Packed Column

$$\forall = 1.76 \text{ m x} \left(\frac{\pi}{4} \text{ x } 1.06^2\right) = 1.553 \text{ m}^3$$

Packed bed carbon density is given by the supplier.

density = 400 kg/m^3

$$(1.553 \text{ m}^3) \ge 400 \frac{\text{kg}}{\text{m}^3} = 621 \text{kg}$$

f) <u>Determination of q_e</u>

Mass of carbon in the pilot column =

Volume of the pilot column = 12.4 L $\forall x \text{ density} = 0.0124 \text{ m}^3 \text{ x } 400 \frac{\text{kg}}{\text{m}^3} = 4.96 \cong 5 \text{ kg}$

TOC removed by 5 kg of carbon =

(200 mg/L) x 9500 L = **1.9x10⁶ mg** $q_{e} = \frac{1.9x10^{6} \text{ mg TOC}}{5 \text{ kg C}} = 380 \frac{\text{mg}}{\text{g}} \text{ C}$

g) Fraction of Capacity Left Unused (Pilot Plant)

Total capacity =
$$(9500 \text{ L}) \times (200 \frac{\text{mg}}{\text{L}}) = 1.9 \times 10^6 \text{ mg}$$

TOC removed before breakthrough =

(8400 L) x
$$\left(200 \ \frac{\text{mg}}{\text{L}}\right) = 1.68 \text{x} 10^6 \text{ mg}$$

Fraction of capacity left unused = $f = \frac{(1.9-1.68) \times 10^6}{1.9 \times 10^6} \times 100 \cong 12\%$

This fraction of capacity left unused will apply to the Packed Column also.

h) Breakthrough time of the Packed Column

Organic Loading =
$$\left(200 \ \frac{\text{mg}}{\text{L}}\right) \text{x} \left(150 \ \frac{\text{m}^3}{\text{d}}\right) \text{x} \left(\frac{1000 \ \text{L}}{1 \ \text{m}^3}\right) = 30\text{x}10^6 \ \text{mg/d}$$

arbon consumption rate = $\left(30\text{x}10^6 \ \frac{\text{mg}}{\text{d}}\right) \text{x} \left(\frac{1}{380 \ \text{mg/g C}}\right) = 78.9 \ \text{kg/d}$

Amount of carbon consumed = $(621 \text{ kg}) \times (1-0.12) = 546.5 \text{ kg}$

Breakthrough time = $\frac{546.5 \text{ kg}}{78.9 \text{ kg/d}} \cong 7 \text{ days}$

The same as the Packed Column :

(8400 L) x
$$\left(\frac{1 \text{ hr}}{50 \text{ L}}\right)$$
 x $\left(\frac{1 \text{ d}}{24 \text{ hr}}\right)$ = 7 days



i) Volume Treated Before Breakthrough

$$\forall_{\text{treated}} = 150 \ \frac{\text{m}^3}{\text{d}} \ \text{x 7 days} = 1050 \ \text{m}^3$$

Kinetic Approach

This method utilizes the following kinetic equation.



where

- C = effluent solute concentration
- C_o = influent solute concentration
- k_1 = rate constant
- q_o = maximum solid phase concentration of the sorbed solute, e.g. g/g
- M = mass of the adsorbent. For example, g
- V = throughput volume. For example, liters
- Q = flow rate. For example, liters per hour

Kinetic Approach

The principal experimental information required is a breakthrough curve from a test column, either laboratory or pilot scale.

One advantage of the kinetic approach is that the breakthrough volume, V, may be selected in the design of a column.

Assuming the left side equals the rigth side, cross multiplying gives

$$1 + e^{\frac{k_t}{Q}(q_o M - C_o V)} = \frac{C_o}{C}$$

Rearranging and taking the natural logarithms of both sides yield the design equation

Rearranging and taking the natural logarithms of both sides yield the design equation.



Example

A phenolic wastewater having a TOC of 200 mg/L is to be treated by a fixed – bed granular carbon adsorption column for a wastewater flow of 150 m³/d, and the allowable effluent concentration, C_a , is 10 mg/L as TOC. A breakthrough curve has been obtained from an experimental pilot column operated at 1.67 BV/h. Other data concerning the pilot column are as follows: inside diameter = 9.5 cm, length = 1.04 m, mass of carbon = 2.98 kg, liquid flowrate = 12.39 L/h, unit liquid flowrate = 0.486 L/s.m^2 , and the packed carbon density = 400 kg/m^3 . The design column is to have a unit liquid flowrate of 2.04 $L/s.m^2$, and the allowable breakthrough volume is 1060 m³.

Example

Using the kinetic approach for design, determine :

- The design reaction constant, k_1 , L/s-kg.
- The design maximum solid phase concentration, q_o, kg/kg.
- The carbon required for the design column, kg.
- The diameter and height of the design column, m.
- The kilograms of carbon required per cubic meter of waste treated.

V (L)	C(mg/L)	C/Co	Co/C	Co/C-1	In(Co/C-1)
0	0	0,000			
378,0	9	0,045	22,222	21,222	3,06
984,0	11	0,055	18,182	17,182	2,84
1324,0	8	0,040	25,000	24,000	3,18
1930,0	9	0,045	22,222	21,222	3,06
2272,0	30	0,150	6,667	5,667	1,73
2520,0	100	0,500	2,000	1,000	0,00
2740,0	165	0,825	1,212	0,212	-1,55
2930,0	193	0,965	1,036	0,036	-3,32
3126,0	200	1,000	1,000	0,000	





Plot of Complete Data Set



Take the linear range only!

$$15.787 = \frac{q_0 \times k_1 \times M}{Q}$$

$$0.0064L^{-1} = \frac{k_1 \times C_0}{Q}$$

a)k₁ =
$$\frac{(0.0064L^{-1}) \times (12.39\frac{L}{h})}{200\frac{mg}{L}} = 3.96 \times 10^{-4} \frac{L}{mg \cdot h}$$

$$3.96 \times 10^{-4} \frac{L}{\text{mg} \cdot \text{h}} \times \frac{1\text{h}}{3600\text{s}} \times \frac{10^{6}\text{mg}}{1\text{kg}} = 0.11 \frac{L}{\text{kg} \cdot \text{s}}$$

b)15.787=
$$\frac{q_0 \times 0.11 \frac{L}{kg \cdot s} \times 2.98 kg}{12.39 \frac{L}{h} \times \frac{1h}{3600s}}$$

$$q_{0} = \frac{15.787 \times 12.39 \frac{L}{h} \times \frac{1h}{3600s}}{0.11 \frac{L}{kg \cdot s} \times 2.98 kg}$$

$$q_0 = 0.166 \frac{kg}{kg}$$

$$k_1 = 3.96 \times 10^{-4} \frac{L}{\text{mg} \cdot \text{h}}$$
$$q_0 = 0.166 \frac{\text{kg}}{\text{kg}}$$

Q = 6250 L/hV = 1050000 L C₀ = 200 mg/L

Using

$$\ln\left(\frac{C_{o}}{C}-1\right) = \frac{k_{1}q_{o}M}{Q} - \frac{k_{1}C_{o}V}{Q}$$
$$\ln\left(\frac{200}{10}-1\right) = \frac{3.96 \times 10^{-4} \frac{L}{mg \cdot h} \times 0.166 \frac{kg}{kg} \times M}{6250 \frac{L}{h}} - \frac{3.96 \times 10^{-4} \frac{L}{mg \cdot h} \times 200 \frac{mg}{L} \times 1050000 L}{6250 \frac{L}{h}}$$

M = 1545009487 mg = 1545 kg

M =1545 kg

Packet carbon density = $400 \text{ kg} / \text{m}^3$ (given)

Then, design bed volume is;

$$V = \frac{1545 \, kg}{400 \, \frac{kg}{m^3}} = 3.86 \, \mathrm{m}^3$$

Q = 6250 L / h = 1.736 L / s

Unit liquid flowrate =
$$2.04 \text{ L/s} \cdot \text{m}^2$$
 (given)
Cross section area = $\frac{1.736 \text{ L/s}}{2.04 \text{ L/s} \cdot \text{m}^2} = 0.85 \text{m}^2$
d = 1.04 m Column height = $\frac{3.86 \text{ m}^3}{0.85 \text{ m}^2} = 4.54 \text{ m}$
Breakthrough time is; $T_B = \frac{1050 \text{ m}^3}{150 \text{ m}^3/\text{d}} = 7 \text{ d}$

Scale-up approach:

1. The design bed volume (BV) is found as;

1.67 BV / h =
$$\frac{150 m^3 / d}{24 h / d}$$
 = 6.25 m³ / h

 $BV = 3.74 \text{ m}^3$

2. The mass of carbon required is;

$$M = BV \times \rho = 3.74 \text{ m}^3 \times 400 \text{ kg} / \text{m}^3 = 1500 \text{ kg}$$

From the breakthrough curve the volume treated at the allowable breakthrough (10 mg/L TOC) is 2080 L. So, the solution treated per kilogram of carbon is 2080 L/2.98 kg or 698 L/kg (pilot scale). The same applies to the design column; for a flow rate of 150 m^3/d .

3. The weight of carbon exhausted per hour (M_t) is

$$M_{t} = \frac{150 \text{ m}^{3} / \text{d}}{24 \text{ h}} \times \frac{\text{kg}}{698 \text{ L}} \times \frac{1000 \text{ L}}{\text{m}^{3}} = 8.954 \text{ kg/h}$$



4. The breakthrough time is;

$$T = \frac{1500 \text{ kg}}{8.954 \text{ kg} / \text{h}} = 168 \text{ h} = 7 \text{ d}$$

5. The breakthrough volume of the design column is;

$$V_{\rm B} = Q \times T = 150 \,{\rm m}^3 \,/\,d \times 7 \,d = 1050 \,{\rm m}^3$$

Comparing the results of two approaches:

Kinetic approachScale-up approachM=1545 kgM=1500 kg $V_B = 1050 \text{ m}^3$ $V_B = 1050 \text{ m}^3$ $T_B = 7 \text{ d}$ $T_B = 7 \text{ d}$ $V_{\text{Design}} = 3.86 \text{ m}^3$ $V_{\text{Design}} = 3.74 \text{ m}^3$

Example

A phenolic wastewater that has phenol concentration of 400 mg/L as TOC is to be treated by a fixed-bed granular carbon adsorption column for a wastewater flow of 227100 L/d, and the allowable effluent concentration, C_a , is 35 mg/L as TOC. A breakthrough curve has been obtained from an experimental pilot column operated at 1.67 BV/h. Other data concerning the pilot column are as follows: inside diameter = 9.5 cm, length = 1.04 m, mass of carbon = 2.98 kg, liquid flowrate = 17.42 L/h, unit liquid flowrate = 0.679 L/s.m^2 , and the packed carbon density = 401 kg/m^3 . The design column is to have a unit liquid flowrate of 2.38 $L/s.m^2$, and the allowable breakthrough volume is 850 m³.

V	С				
(L)	(mg/L)	C/Co	Co/C	Co/C - 1	In(Co/C - 1)
15	12	0.030	33.333	32.333	3.476
69	16	0.040	25.000	24.000	3.178
159	24	0.060	16.667	15.667	2.752
273	16	0.040	25.000	24.000	3.178
379	16	0.040	25.000	24.000	3.178
681	20	0.050	20.000	19.000	2.944
965	28	0.070	14.286	13.286	2.587
1105	32	0.080	12.500	11.500	2.442
1215	103	0.258	3.883	2.883	1.059
1287	211	0.528	1.896	0.896	-0.110
1408	350	0.875	1.143	0.143	-1.946
1548	400	1.000	1.000	0.000	







$$18.657 = \frac{q_0 \times k_1 \times M}{Q}$$

 $0.0146 \text{ L}^{-1} = \frac{k_1 \times C_0}{Q}$

$$k_{1} = \frac{(0.0146 \text{ L}^{-1}) \times (17.42 \frac{\text{L}}{\text{h}})}{400 \frac{\text{mg}}{\text{L}}} = 6.36 \times 10^{4} \frac{\text{L}}{\text{mg} \cdot \text{h}} = 0.177 \frac{\text{L}}{\text{kg} \cdot \text{s}}$$

$$q_0 = \frac{18.657 \times 17.42 \frac{L}{h} \times \frac{1h}{3600s}}{0.177 \frac{L}{kg \cdot s} \times 2.98 kg}$$

 $q_0 = 0.171 \frac{kg}{kg}$

$$k_1 = 6.36 \times 10^{-4} \frac{L}{\text{mg} \cdot \text{h}}$$
$$q_0 = 0.171 \frac{\text{kg}}{\text{kg}}$$

Q = 9462.5 L/h V = 850000 L $C_0 = 400 mg/L$

Using

$$\ln\left(\frac{C_{o}}{C}-1\right) = \frac{k_{1}q_{o}M}{Q} - \frac{k_{1}C_{o}V}{Q}$$
$$\ln\left(\frac{400}{35}-1\right) = \frac{6.36 \times 10^{-4} \frac{L}{mg \cdot h} \times 0.171 \frac{kg}{kg} \times M}{9462.5 \frac{L}{h}} - \frac{6.36 \times 10^{-4} \frac{L}{mg \cdot h} \times 400 \frac{mg}{L} \times 850000 L}{9462.5 \frac{L}{h}}$$

M = 2190 kg

M = 2190 kgPacket carbon density = $401 \text{ kg} / \text{m}^3$ (given)

Then, design bed volume is;

$$V = \frac{2190 \, kg}{401 \frac{kg}{m^3}} = 5.46 \, \mathrm{m^3}$$

Q = 9462.5 L / h = 2.63 L / s

Unit liquid flowrate =
$$2.38 \text{ L/s} \cdot \text{m}^2$$
 (given)
Cross section area = $\frac{5.46 \text{ L/s}}{2.38 \text{ L/s} \cdot \text{m}^2} = 2.29 \text{m}^2$
d = 1.71 m Column height = $\frac{5.46 \text{ m}^3}{2.29 \text{ m}^2} = 2.38 \text{ m}$
Breakthrough time is; $T_B = \frac{850 \text{ m}^3}{227.1 \text{ m}^3/\text{d}} = 3.74 \text{ d}$

Scale-up approach:

The design bed volume (BV) is found as;

1.67 BV / h =
$$\frac{227100 L/d}{24 h/d}$$
 = 9462.5 L / h

 $BV = 5666.17 L = 5.67 m^3$

The mass of carbon required is;

$$M = BV \times \rho = 5.67 \text{ m}^3 \times 401 \text{ kg} / \text{m}^3 = 2272 \text{ kg}$$

From the breakthrough curve the volume treated at the allowable breakthrough (35 mg/L TOC) is 1110 L. So, the solution treated per kilogram of carbon is 1110 L/2.98 kg or 372.5 L/kg (pilot scale). The same applies to the design column; for a flow rate of 227100 L/d, the weight of carbon exhausted per hour (M_t) is

$$M_{t} = \frac{227100 \text{ L/d}}{24 \text{ h/d}} \times \frac{\text{kg}}{372.5 \text{ L}} = 25.4 \text{ kg/h}$$



The breakthrough time is;

$$T = \frac{2272 \text{ kg}}{25.4 \text{ kg}/\text{h}} = 89.5 \text{ h} = 3.73 \text{ d}$$

The breakthrough volume of the design column is;

$$V_{\rm B} = Q \times T = 227.1 \,{\rm m}^3 \,/\, d \times 3.73 \,d = 846.5 \,{\rm m}^3$$

Comparing the results of two approaches: Kinetic approach Scale-up approach

$$\begin{split} M &= 2190 \text{ kg} & M &= 2272 \text{ kg} \\ V_B &= 850 \text{ m}^3 & V_B &= 846.5 \text{ m}^3 \\ T_B &= 3.74 \text{ d} & T_B &= 3.73 \text{ d} \\ V_{\text{Design}} &= 5.46 \text{ m}^3 & V_{\text{Design}} &= 5.67 \text{ m}^3 \end{split}$$