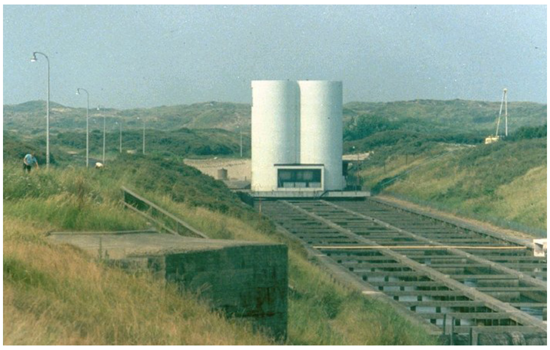
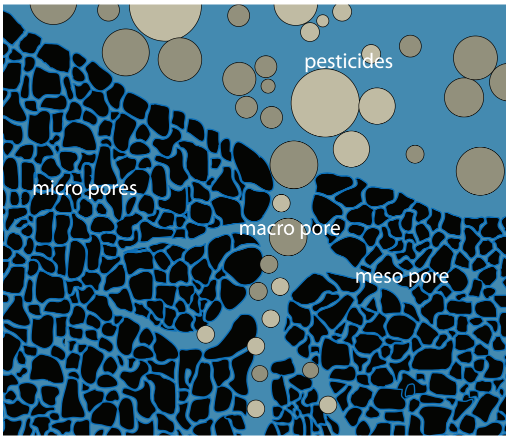
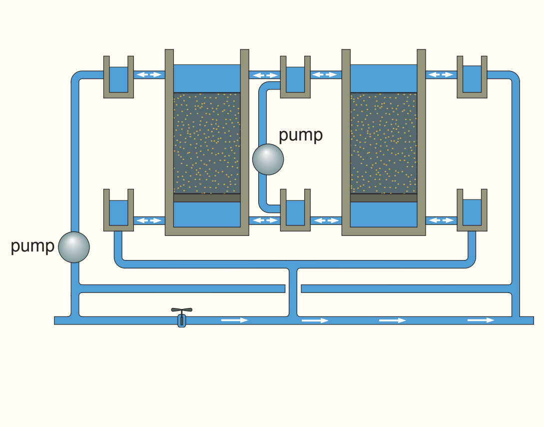
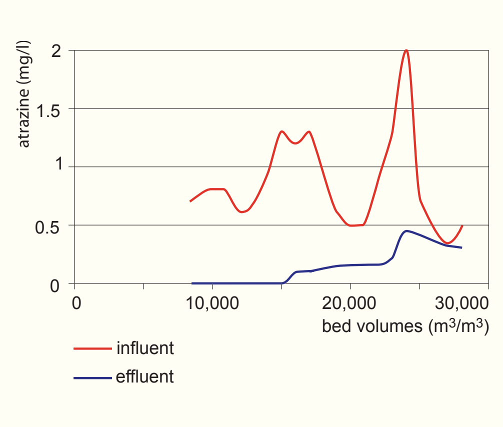
WATER TREATMENT

Adsorption









Framework
This module explains adsorption.

Contents
This module has the following contents:

1 Introduction

Water contains dissolved organic matter that cannot be removed with floc formation, floc removal or sand filtration. These dissolved organic compounds are:

- odor-, taste- and color-producing compounds
- organic micropollutants (pesticides, hydrocarbon compounds)

Activated carbon adsorbs (part of) the organic matter and is mainly used to treat drinking water produced from surface water.

In the past, drinking water produced from surface water would pass through the following steps: floc formation, floc removal (sedimentation and filtration) and disinfection with chlorine.
This was sufficient to comply with the drinking water guidelines for turbidity, odor, taste and hygienic reliability.

In 1987 Amsterdam Water Supply discovered the presence of pesticides (Bentazon) in drinking water. Due to this discovery, the traditional treatment of surface water was no longer satisfactory and an extension with activated carbon was required.

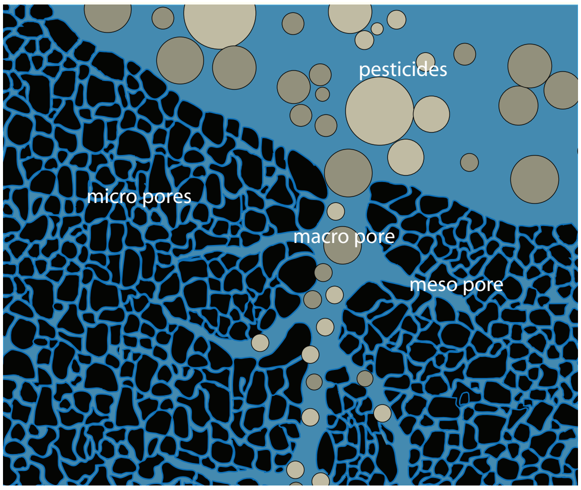
In addition, chlorine can react with organic matter (precursor), and trihalomethanes (THMs) can be formed. These THMs are toxic.
To reduce the concentration, the formed THMs can be removed with activated carbon. The problem, however, is that carbon is rapidly saturated with THMs and has to be regenerated frequently. It is preferable to prevent the THMs from being formed. This can be done by reducing the concentration of the precursor before adding chlorine.
Precursors cannot be measured directly, but the concentration of organic matter, expressed as TOC or DOC, is an indication.
The best way to prevent THM formation is to avoid the dosing of chlorine, but this requires another treatment setup.

The activated carbon filters of the drinking water production plant at Kralingen have the objective to improve the taste of the water, to reduce the regrowth of bacteria in the piped network, and to remove toxic substances from the water.
The carbon filters are placed after the floc formation, sedimentation and rapid sand filtration to avoid rapid clogging.

The installation is based on pressure filters, so the construction height can be limited and only an extra pumping phase (middle pressure) is needed.

The installation has the following characteristics:
Filter bed height: 4 m
Filtration surface area: 28 m^2
Number of filters: 12
Contact time (EBCT): 12 min
Type of carbon: Norit ROW 0.95
Regeneration frequency: 1.5 year

Activated carbon is a substance with a high carbon concentration (e.g., pit-coal, turf). Under high temperatures this material becomes carbonated, meaning that the carbon partly transforms into carbon monoxide and water. This is how the carbon gets its open structure (Figure 1).
The internal surface area of the activated carbon is several times larger than the external surface area.



macro pores	> 25 nm
meso pores	1 - 25 nm
micro pores	< 1 nm

Figure 1 - The open structure of activated carbon

Hence, a majority of the adsorbed substances is adsorbed inside the carbon.
The dissolved organic matter can be removed from the water by filtration through a bed of activated carbon.

Organic matter diffuses from the water phase to the surface of the carbon grains. The organic compounds are further transported into the carbon to be attached in the pores.
The adsorption of organic matter is not finite. There is equilibrium between the concentration of dissolved compounds in water and the quantity of substances that are adsorbed onto the carbon.
When different kinds of organic compounds are present in the water, competition will occur. Compounds that have been well-adsorbed will occupy adsorption places that cannot be used by compounds that are less adsorbable. Large organic molecules can also block micro pores, thus preventing the smaller organic molecules from entering these micro pores.

After some time the activated carbon is saturated with adsorbed organic matter and the carbon needs to be cleaned. This is done by removing the carbon from the installation and heating it to 1000 ^oC.
This regeneration process has to be carried out once every couple of years.

Activated carbon filters operate in the same way as rapid sand filters. Mostly downward flow, open filters are applied to prevent fine carbon grains from washing out (Figure 2).
Since the contact time is the most important parameter for good removal, the filter is often designed with high beds to reduce the construction surface area. Therefore, activated carbon filters cannot be operated under gravity, making an extra pumping phase necessary. After passing the filter bed, the water reaches the bottom construction of the filter and is then collected and transported to the clear water tank or the next treatment step.

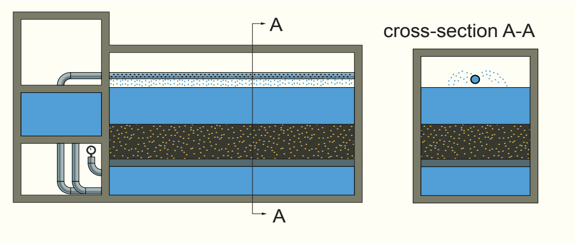


Figure 2 - Longitudinal and cross-section of an activated carbon filtration installation

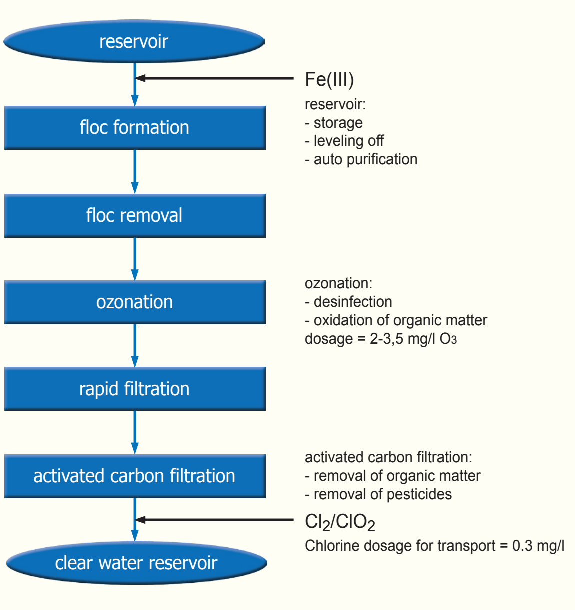


Figure 3 - Treatment process at Kralingen (Evides)

When the filter is clogged with suspended matter or biomass and the resistance is high, the filter bed is backwashed.
The backwash water is drained by troughs that are placed above the filters.
Clogging of the filter by suspended matter can lead to a higher regeneration frequency. Therefore, activated carbon filters are usually placed after floc formation, floc removal and rapid sand filtration (Figure 3).

Figure 4 - Activated carbon filtration at Andijk (treatment of surface water)

After activated carbon filtration, disinfection takes place to prevent biological growth in the piped network. This process can consist of slow sand filtration, UV-disinfection or dosing chlorine or chlorine dioxide.

2 Theory

2.1 Equilibrium

Similar to aeration, equilibrium is established during adsorption.

The maximum loading (loading capacity q_{max}) depends on the concentration of adsorbable matter in the bulk liquid (water). The higher this concentration, the higher the loading capacity is.

The relationship between the loading capacity and the concentration of adsorbable matter in the bulk liquid is called the adsorption-isotherm.

The best known is the Freundlich isotherm:

$$q_{max} = \frac{x}{m} = K \cdot c_s^{\,n}$$

in which:

q_{max} = loading capacity (g/kg)
c_s = equilibrium concentration (g/m^3)
x = adsorbed amount of compound (g)
m = mass of activated carbon (kg)
K = Freundlich constant ((g/kg)·(m^3/g)n)
n = Freundlich constant (-)

The Freundlich constants K and n are influenced by water temperature, pH, type of carbon and the concentration of other organic compounds.

Using laboratory experiments the Freundlich constants can be determined for a single substance with a specific type of activated carbon.

In Figure 5 the results of a laboratory experiment are represented.

When these graphs are plotted on a logarithmic scale (Figure 6), the Freundlich constant K can be determined from the intersection of the graph with the y-axis. The slope of the line is equal to the Freundlich constant n.

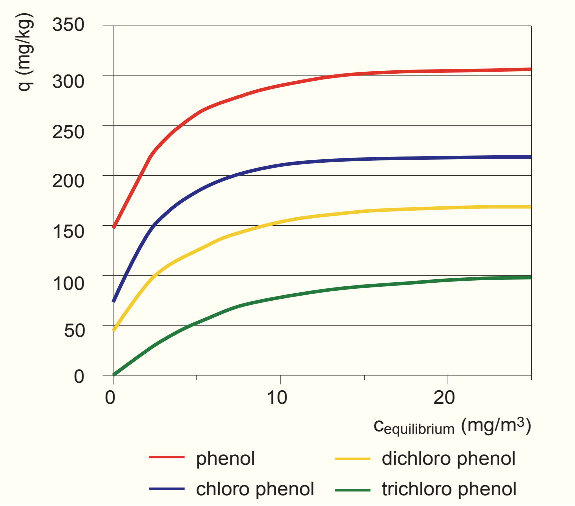


Figure 5 - Loading capacity as a function of equilibrium concentration

The higher the K-value, the better the adsorption.

In Table 1 the values of the constants K and n are given for some known substances.

From the structure formula of a substance, the adsorbability can be derived. In general, non-polar substances are better adsorbed than polar substances. Substances with double bonds will be better adsorbed than substances with single bonds.

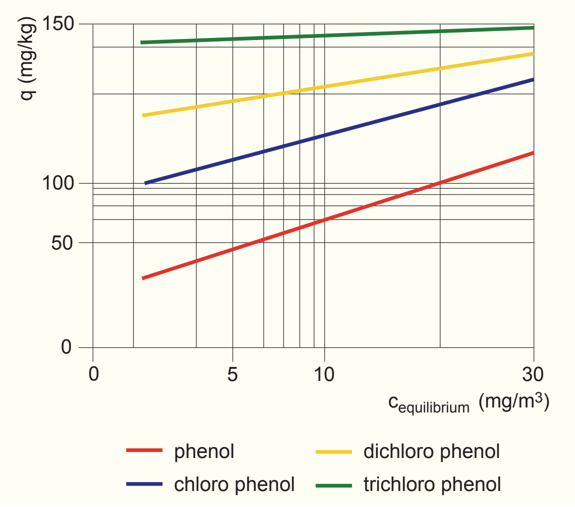


Figure 6 - Logarithm representation of the Freundlich isotherm

Compound	K. ((g/kg). $(m^3/g)^n$)	n (-)
alkanes		
CH_3Cl	6.2	0.80
CH_2Cl_2	12.7	12.7
CH_2Br	44.4	0.81
$CHCl_3$ (chloroform)	95.5	0.67
$CHBr_3$ (bromoform)	929	0.66
CH_2Cl - CH_2Cl (DCEA)	129	0.53
CH_2Br - CH_2Br (EDB)	888	0.47
CH_2Cl - CHCl - CH_3 (1,2 DCP)	313	0.59
CH_2Br - CHBr - CH_2Cl(DBCP)	6910	0.60
alkenes		
CCl_2 = CHCl (TCE)	2000	0.48
CCl_2 = CCl_2 (PCE)	4050	0.52
pesticides - organochlorides		
Dieldrin	17884	0.51
Lindane (HCH)	15000	0.43
Heptachlor	16196	0.92
Alachlor	81700	0.26
pesticides - organitrogenes		
atrazine	38700	0.29
simazine	31300	0.23
pesticides - fenolderivates		
dinoseb	30400	0.28
PCP	42600	0.34
pesticides - fenoxycarbonicacid		
2,4 D	10442	0.27
2,4,5 TP	15392	0.38
aromates		
C_6H_6 (benzene)	1260	0.53
C_6H_5Cl	9170	0.35
CH_5CH_3 (toluene)	5010	0.43
$C_6H_5NO_2$ (nitrobenzene)	3488	0.43
C_6H_5COOH	2802	0.42
C_6H_5OH (phenol)	503	0.54
$C_{10}H_8$ (naftalene)	7260	0.42

Table 1 - Freundlich constants K and n of several substances

2.2 *Kinetics*

The kinetics equation (equation of motion) for activated carbon filtration is as follows:

$$\frac{dc}{dt} = -u\frac{dc}{dy} - k_2 \cdot (c_0 - c_s)$$

in which:

k_2 = mass transfer coefficient (d^{-1})
c_0 = initial concentration of organic compound (mg/l)
u = pore velocity of the water (m/s)
c_s = equilibrium concentration of organic compound linked to a certain loading of the activated carbon (mg/l)

The kinetics equation consists of a convection term with which transport of the compound through the filter bed can be described:

$$u\frac{dc}{dy}$$

and a removal term:

$$k_2(c_0 - c_s)$$

The rate of mass transfer is similar to aeration proportional to the difference between the prevailing concentration and the equilibrium concentration.
The equilibrium concentration depends on the loading and is determined by the Freundlich isotherm.
The lower the loading of the carbon, the lower is the equilibrium concentration and the higher is the mass transfer rate.
The mass transfer coefficient depends on the compound to be adsorbed and the type of carbon (including the grain size).

In addition, the mass transfer coefficient can be influenced by the velocity of the water passing the carbon grains. The higher the velocity of the water, the better the mass transfer is between liquid and carbon.

2.3 *Mass balance*

In Figure 7 the activated carbon filter is schematized as a cube, in which:

Q = flow (m^3/h)
B = width of filter (m)
L = length of filter (m)

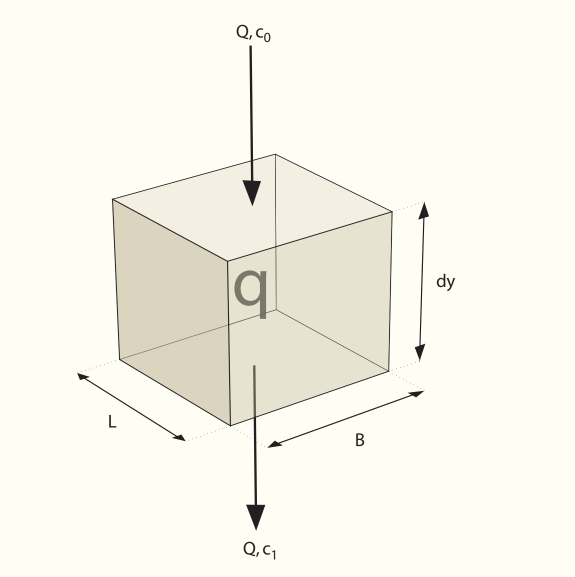


Figure 7 - Schematic representation of activated carbon filter

d_y = height of filter (m)
c = concentration of organic compound (g/m^3)

An organic compound with a concentration c_0 enters the system with a flow Q and leaves the system with a concentration c_1. The difference in concentration between in- and outflow is adsorbed on the activated carbon and increases the loading of the carbon.

The continuity equation or mass balance is:

$$\frac{dq}{dt} = -\frac{v}{\rho}\frac{dc}{dy}$$

in which:
v = filtration rate = Q/BL (m/h)
q = loading (g/g)
ρ = density of the carbon (g/m^3)

2.4 Solutions for the basic equations

The system of equations is non-linear and cannot be solved analytically.

When a stationary situation is assumed, and when the influent concentration and the flow are assumed to be constant, the effluent concentration of the activated carbon filter can be calculated using the Bohart-Adams equation. This equation is derived from the mass balance and the kinetics equation.

$$\frac{c_0}{c_e} = 1 + \exp\left(k_2 \cdot EBCT \cdot \left(1 - \frac{BV \cdot c_0}{q \cdot \rho}\right)\right)$$

$$EBCT = \frac{V}{Q}$$

$$BV = \frac{Q \cdot T}{V} = \frac{T}{EBCT}$$

in which:
EBCT = empty bed contact time (h)
BV = filtered water per bed volume (m^3/m^3)
T = filter run time (h)
V = volume filter (m^3)

Figure 8 shows the progress of the organic compound concentration in the activated carbon filtration.
Water with a concentration of organic compound c_0 is supplied. Since, in the beginning, the carbon is not yet loaded, the effluent concentration of the organic compound drops to zero.
After some time, the loading of the carbon increases, the available adsorption places are filled, and breakthrough of the organic compound in the effluent occurs.

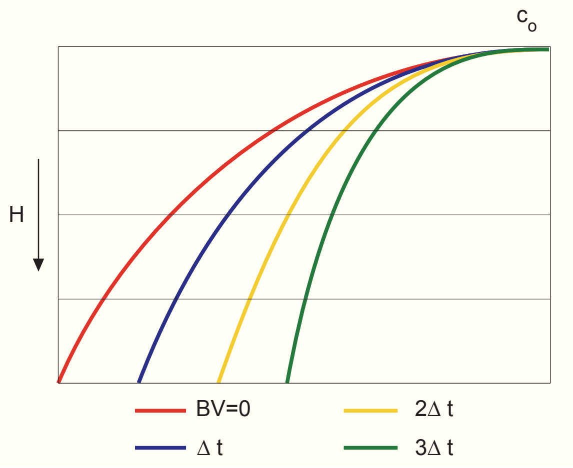


Figure 8 - Progress of the concentration in time and height

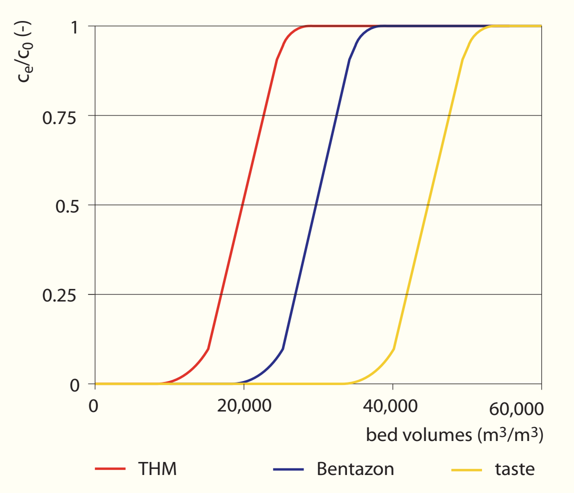


Figure 9 - Breakthrough curve

Finally, the activated carbon is saturated without any removal of organic matter.

In Figure 9 the effluent concentration is plotted against the filter run time (expressed in number of bed volumes). This curve is called the breakthrough curve.
In the beginning the effluent concentration is 0.
After time the effluent concentration increases until the activated carbon is saturated and the effluent concentration is equal to the influent concentration.
When the effluent concentration of the activated carbon filter no longer meets the standards, the filter must be regenerated.

The run time of activated carbon filters depends on the objective.
The breakthrough of THMs occurs relatively fast (15,000 BV); for the removal of taste substances, however, longer run times can be applied (50,000 BV) without intermediate regeneration (Figure 9).

Contact time
The correlation between contact time and filter run time depends on the adsorption characteristics of the compound to be removed.
In general the filter run time increases exponentially with increasing contact time (Figure 10). Hence, per cubic meter of activated carbon, a larger volume of water can be treated before regeneration is necessary.

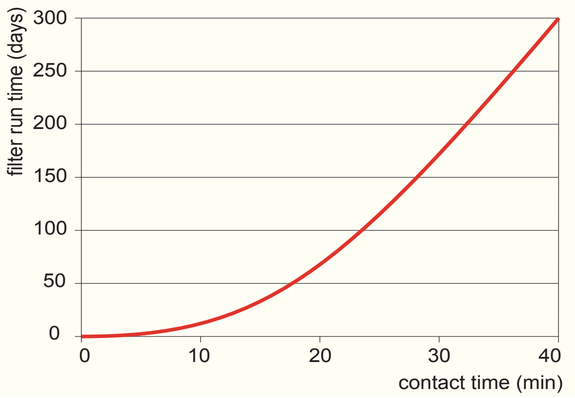


Figure 10 - Relationship between contact time and filter run time

Application of a shorter contact time indicates that a smaller volume of activated carbon is needed.
This leads to lower investment costs.
The regeneration costs, on the other hand, will increase.
An economical optimum depends on the adsorption behavior of the compound to be removed.

3 Practice

To solve the above-given basic equation, a stationary situation is assumed in which the influent concentration is considered to be constant.
In reality, the influent concentration is not constant but varies. Hence, the breakthrough curve will not describe a perfect “S”-form (Figure 11).
If the influent concentration is high, relatively large amounts of organic matter are adsorbed because

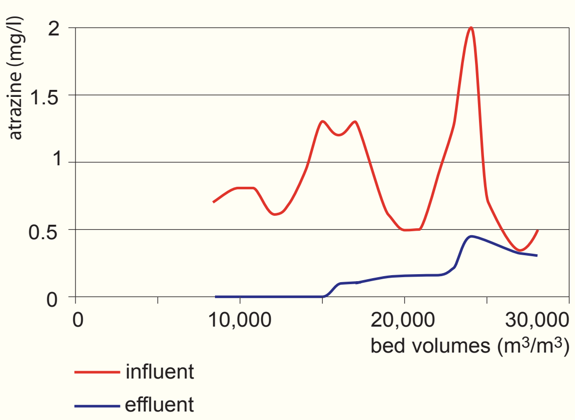


Figure 11 - Breakthrough curve measured in practice

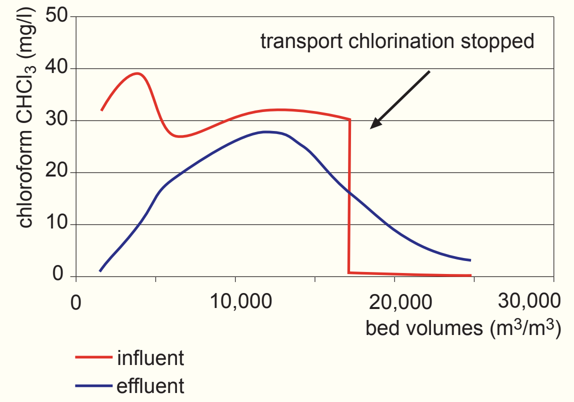


Figure 12 - Occurrence of desorption after termination of transport chlorination

of a large driving force. When, afterwards, a low influent concentration occurs and the loading of the carbon is already high, the saturation concentration can be almost equal to the influent concentration and adsorption is limited.

In extreme cases even desorption (higher concentrations of organic compounds in effluent than in influent) can occur.
This happens, for example, after terminating transport chlorination. Before termination, THMs were removed in the filters and accumulated in the activated carbon. After termination, THMs no longer form and the influent concentration is nil (Figure 12). In the effluent of the activated carbon filters, THMs are still present because of desorption.

3.1 Pseudo-moving-bed filtration

A special application for activated carbon filtration is the "pseudo-moving-bed" system (Figure 13), where two filters are placed in a series.

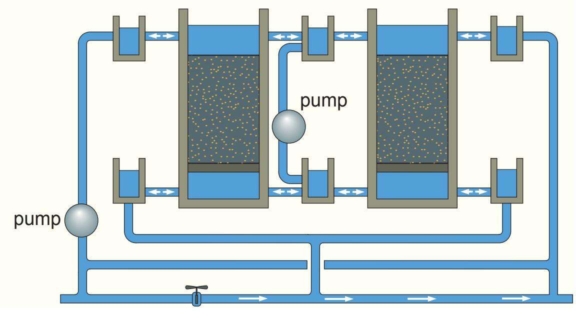


Figure 13 - Principle of pseudo-moving-bed filtration

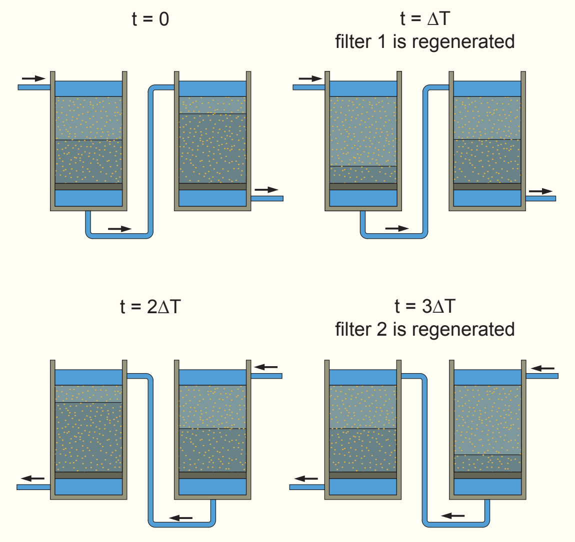


Figure 14 - Breakthrough curves for pseudo-moving-bed activated carbon filtration

After breakthrough occurs in the first filter, the second filter takes care of the polishing, and the effluent of the second filter still meets the guidelines.
The moment the second filter breaks through, the first filter is regenerated and then connected after the second filter.
The cleanest filter is thus always the last one (Figure 14).

The advantage of this setup is that the storage capacity of the filters is better used, resulting in longer run times.
Disadvantages of this setup are the high hydraulic loadings of the filters and the complex system of pipes and valves.

3.2 Pressure filtration

Figure 15 - Steel pressure filters with activated carbon

When activated carbon filters are placed in pressure vessels, an extra pumping phase can be avoided (Figure 15). The pressure is then sufficient to lead the water through the activated carbon filters to the clear water tanks.

3.3 Biological activated carbon filtration

Biological activity occurs in all carbon filters. Bacteria that grow on the carbon will decompose organic matter.
Even with pre-chlorination bacteria can grow, because the residual chlorine is adsorbed by the activated carbon.

When organic matter is pre-oxidized by ozone (a strong oxidizer), biological activity is stimulated, resulting in increased filter run times and increased removal of organic matter. This is called “biologically activated carbon filtration” (Figure 16).
Because of the increased biological activity on the carbon, the organic macropollutants (DOC) will occupy fewer adsorption places in the carbon. Hence, more space is left for the (persistent) organic micropollutants. Some persistent organic micropollutants like pesticides can even be (partially) biologically decomposed after ozonation.
In some seasons (e.g., summer), the biological activity will be greater than in other seasons (e.g., winter). Therefore, the adsorption process will be the dominant process in winter. The organic matter that is adsorbed in winter will be partially decomposed biologically in summer.
This phenomenon is called bio-regeneration.

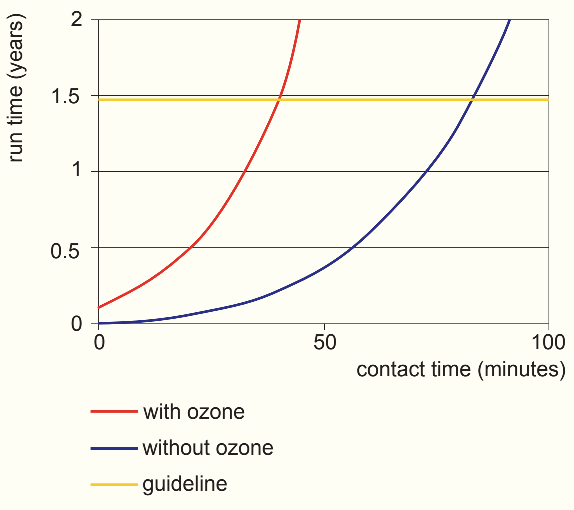


Figure 16 - Influence of pre-ozonation on required con-

With biologically activated carbon filtration, quickly degradable matter is formed that will stimulate bacterial growth.
Breakthrough of this degradable matter (expressed as Assimilable Organic Carbon(AOC)) must be avoided to prevent the regrowth of bacteria in the piped network.
In addition, bacteria can be eroded from the carbon and enter the effluent, thus increasing the colony counts.
A disinfection step with UV-radiation or chlorine will then be necessary.

3.4 Powdered activated carbon

In addition to granular activated carbon filtration (GAC), powdered activated carbon (PAC) dosing can be applied.

With powdered activated carbon, small carbon particles (1μm) are added to water.
These carbon particles are so small that during transport they do not settle.
When the water is in contact with the carbon particles (after some time), equilibrium between the organic matter in the water and on the powdered carbon will be established.
The particles will be removed afterwards by a sand filtration step.

For a powdered activated carbon dosing, a mass balance can be set up, schematically represented in Figure 17 :

$$c_0 \cdot V + q_0 \cdot m = c_e \cdot V + q_e \cdot m$$

$$q_e = 0 \Rightarrow W = \frac{m}{V} = \frac{c_0 - c_e}{q_e}$$

in which:
m = mass of activated carbon (g)

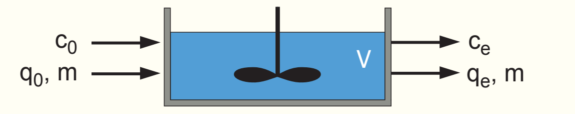


Figure 17 - Mass balance of powderd carbon dosage

V = volume filter (m^3)
W = dosing of activated carbon (g/m^3)

Starting with the Freundlich isotherm, the effluent concentration of an organic compound can be calculated, or the powdered activated carbon dosage can be calculated for a determined effluent concentration.

It is assumed that equilibrium occurs and the carbon is maximally loaded.

The loading capacity is determined by the prevailing concentration in the reactor, and in a completely mixed system this equals the effluent concentration.

For two ideal mixers placed in a series, the loading capacity of the powdered activated carbon in the second tank is lower than in the first tank because the concentration in the second tank is lower than in the first tank (Figure 18).

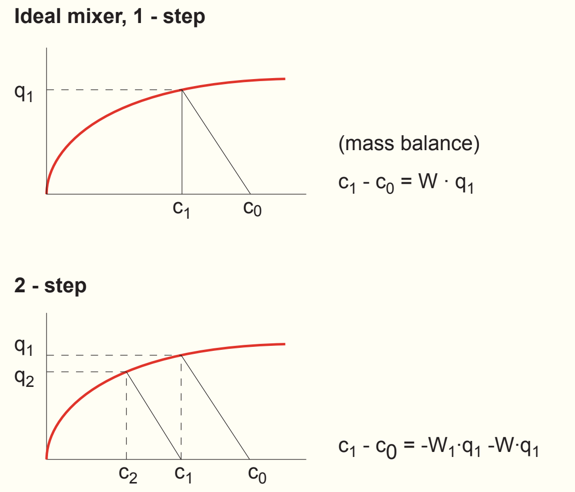


Figure 18 - One and two mixers in series

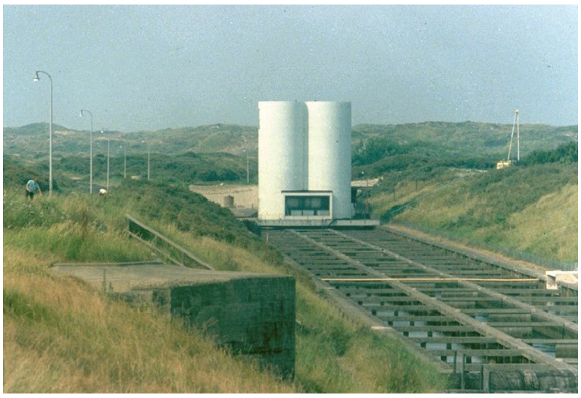


Figure 19 - Powdered activated carbon dosing unit at Scheveningen

A powdered activated carbon dosage has the advantage over granular activated carbon filtration that there are limited investment costs: there is no need for a filtration installation (with an extra pumping phase); a dosing unit for the powdered activated carbon together with a mixing tank is sufficient.

The removal of pesticides with powdered activated carbon, however, is limited and the rapid filters are quickly clogged. This results in a large backwash water loss.

Granular activated carbon filtration has a more intensive water/carbon contact, thus pesticides (and THMs) are removed more efficiently.

Further reading

- Water treatment: Principles and design, MWH (2005), (ISBN 0 471 11018 3) (1948 pgs)
- Unit processes in drinking water treatment, W. Masschelein (1992), (ISBN 0 8247 8678 5) (635 pgs)