Lecture 21

# ADSORPTION AND ION EXCHANGE (2)

Course: Water Reuse

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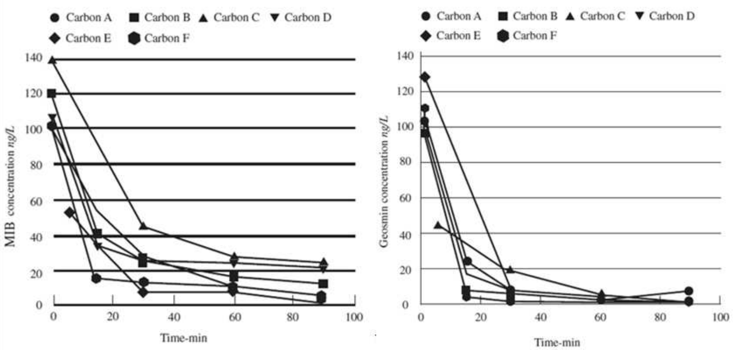
## Activated carbon

- Perhaps more than 50% of water and wastewater treatment plants around the world use activated carbon for taste and odor control.
- Odor and taste are mentioned together, because they are seldom separate. They usually arise due to deterioration of plants and microorganisms. More than being a health risk, they are an aesthetic problem.
- The AC bed can either be used continuously, or only brought into the process when color and odor problems arise (for example in the case of excess algae in the system)



## عملکرد متفاوت

- کربن های مختلف در حذف آلاینده های مختلف، متفاوت عمل می کنند




## Modeling

- When the mass transfer rate is fast and the mass transfer zone is a sharp wave front, a steady-state mass balance around a fixed bed carbon contactor may be written as:

$$\text{Accumulation} = \text{inflow} - \text{outflow} - \text{amount adsorbed}$$
$$0 = QC_o t - QC_e t - m_{GAC} q_e \quad (10\text{-}6)$$

where Q = volumetric flowrate, L/h
$C_o$ = initial concentration of adsorbate, mg/L
t = time, h
$C_e$ = final equilibrium concentration of adsorbate, mg/L
$m_{GAC}$ = mass of adsorbent, g
$q_e$ = adsorbent phase concentration after equilibrium, mg adsorbate/g adsorbent

From Eq. (10-6), the adsorbent usage rate is defined as:

$$\frac{m_{GAC}}{Qt} = \frac{C_o - C_e}{q_e} \quad (10\text{-}7)$$

# Modeling

If we are before breakthrough, we can assume no pollutant exists in the effluent:

$$\frac{m_{GAC}}{Qt} \approx \frac{C_o}{q_e} \quad (10\text{-}8)$$

1. Empty bed contact time (EBCT)

$$EBCT = \frac{V_b}{Q} = \frac{A_b D}{v_f A_b} = \frac{D}{v_f} \quad (10\text{-}9)$$

where EBCT = empty bed contact time, h
$V_b$ = volume of contactor occupied by GAC, $m^3$
Q = volumetric flowrate, $m^3/h$
$A_b$ = cross-sectional area of GAC filter bed, $m^2$
D = length of GAC in contactor, m
$v_f$ = linear approach velocity, m/h

2. Activated carbon density

The density of the activated carbon is defined as:

$$\rho_{GAC} = \frac{m_{GAC}}{V_b} \quad (10\text{-}10)$$

where $\rho_{GAC}$ = density of GAC, g/L
$m_{GAC}$ = mass of GAC, g
$V_b$ = volume of contactor occupied by GAC, L

3. Specific throughput, expressed as $m^3$ of water treated per gram of carbon:

$$\text{Specific throughput, } m^3/g = \frac{Qt}{m_{GAC}} = \frac{V_b t}{EBCT \times m_{GAC}} \quad (10\text{-}11)$$

Using Eq. (10-10), Eq. (10-11) can be written as:

$$\text{Specific throughput} = \frac{V_b t}{EBCT(\rho_{GAC} \times V_b)} = \frac{t}{EBCT \times \rho_{GAC}} \quad (10\text{-}12)$$

4. Carbon usage rate (CUR) expressed as gram of carbon per $m^3$ of water treated:

$$CUR, g/m^3 = \frac{m_{GAC}}{Qt} = \frac{1}{\text{Specific throughput}} \quad (10\text{-}13)$$

5. Volume of water treated expressed in liters, L:

$$\text{Volume of water treated, L} = \frac{\text{Mass of GAC}}{\text{GAC usage rate}} \quad (10\text{-}14)$$

6. Bed life, expressed in days, d:

$$\text{Bed life, d} = \frac{\text{Volume of water treated}}{Q} \quad (10\text{-}15)$$



# Typical design of GAC contactor

| Parameter | Symbol | Unit | Value |
|---|---|---|---|
| Volumetric flow rate | Q | $m^3/h$ | 50–400 |
| Bed volume | $V_b$ | $m^3$ | 10–50 |
| Cross-sectional area | $A_b$ | $m^2$ | 5–30 |
| Carbon depth | D | m | 1.8–4 |
| Void fraction | $\alpha$ | $m^3/m^3$ | 0.38–0.42 |
| GAC density | $\rho$ | $kg/m^3$ | 350–550 |
| Approach velocity | $V_f$ | m/h | 5–15 |
| Effective contact time | t | min | 2–10 |
| Empty bed contact time | EBCT | min | 5–30 |
| Operation time | t | d | 100–600 |
| Bed volumes | BV | $m^3/m^3$ | 2000–20,000 |

**EXAMPLE 10-2. 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 wave front. Assuming the following data apply, determine the carbon requirements to treat a flow of 1000 L/min, and the corresponding bed life.

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

Ignore the effects of biological activity within the column.



# Solution

**Comment**

In this example, the full capacity of the carbon in the contactor was utilized based on the assumption that two columns in series are used. If a single column is used, then a breakthrough curve must be used to determine the bed life.

1. Estimate the GAC usage rate for TCE. The GAC usage rate is estimated using Eq. (10-7) and Eq. (10-2).

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

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

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



2. Determine the mass of carbon

$$\text{The mass of GAC in the bed} = V_b \rho_{GAC} = \text{EBCT} \times Q \times \rho_{GAC}$$

$$= 10 \text{ min } (1000 \text{ L/min})\,(450 \text{ g/L}) = 4.5 \times 10^6 \text{ g}$$

3. Determine the volume of water treated

$$\text{Volume of water treated} = \frac{\text{Mass of GAC}}{\text{GAC usage rate}}$$

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

4. Determine the bed life.

$$\text{Bed life} = \frac{\text{Volume of water treated}}{Q}$$

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



# کربن فعال

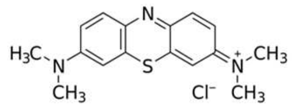
- اگر قرار است فرایند مداوم باشد، بستر گرانول بهتر از پراکندن پودر در آب است چون به مراتب کربن فعال کمتری مصرف می شود
- EBCT معمولا حدود 15 دقیقه است ولی ممکن است کمتر یا بیشتر باشد
- سطح ویژه (میزان سطح موجود به ازای هر گرم کربن) بیانگر کیفیت کربن فعال است. به صورت عمومی هر چه سطح ویژه بیشتر، کربن فعال مرغوب تر ( معمولا ۵۰۰ الی ۱۵۰۰ $m^2/g$ )

# Activated carbon quality (Iodine number)

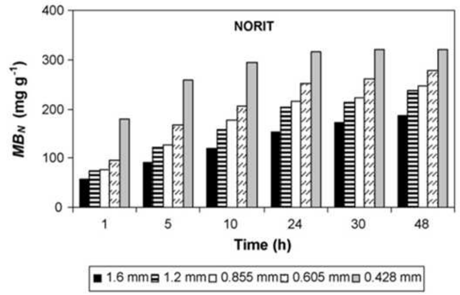
- The Iodine number is a widely used parameter for activated carbon quality for its simplicity and rapidness. It is defined as the mg of iodine adsorbed by each gram of the AC when the iodine residual is 0.02 mol/L.
- The Iodine number can be used to assess microporosity since the size of the iodine ion is small and can easily reach the micropores. The relationship between surface area and iodine number cannot be generalized as it varies with changes in carbon raw material, processing conditions, and pore volume distribution.



# Activated carbon quality (Methylene blue number)




- The Methylene blue number measures the amount of MB adsorbed onto the sorbent. Due to the size of MB, it is an indication of the mesopore structure of the AC.
- It is a good indicator for the adsorption of larger molecules like other dyes, or humic acids in landfill leachate.

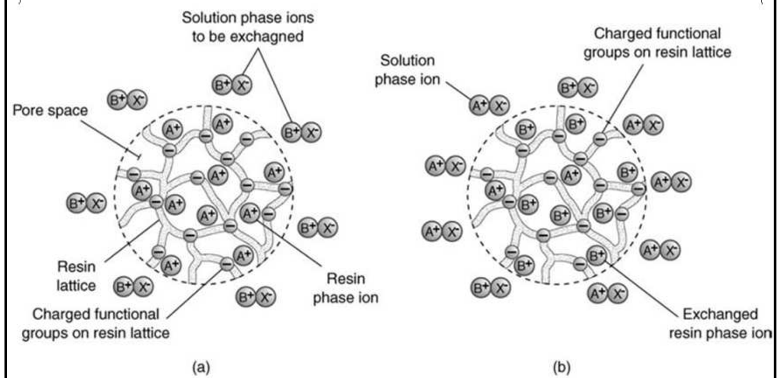



# Ion exchange

- In water reclamation applications, ion exchange involves the replacement of an ion in the aqueous phase for an ion in a solid phase. The solid phase ion exchange material is insoluble and can be of natural origin such as kaolinite and montmorillonite minerals, or a synthetic material such as a polymeric resin.
- The exchange materials have fixed charged functional groups located on their external and/or internal surface, and associated with these groups are ions of opposite charge called "counter ions"



# Ion exchange



# Ion exchange

- Ion exchange resins have an affinity or selectivity for certain counter ions in water, which affects the process performance. In general, a higher selectivity is exhibited for counter ions with the higher charge.
- Ion exchange has been used in water reclamation applications for the removal of nitrogen, heavy metals, and total dissolved solids. The most widespread use of the ion exchange process is in domestic water softening, where sodium ions from a cationic exchange resin are exchanged for the calcium and magnesium ions in the water to be treated, thus reducing the hardness.



# رزین ها

- گروه های عاملی به ستون فقرات رزین متصل گشته اند. یون های متصل به گروه های عاملی تبادل می شوند
- گروه های عاملی می توانند اسیدی باشند (بار منفی) و یا بازی باشند (بار مثبت). مثلا گروه عاملی اسیدی قوی مانند سولفونات $SO_3^-$ می تواند متصل به کاتیون ها باشد (رزین کاتیونی). به عنوان مثال:

$$CaCl_2 + 2\{\boxed{\equiv} - \mathbf{SO_3^- Na^+}\} \rightleftharpoons \{\boxed{\equiv} - \mathbf{SO_3}\}_2\mathbf{Ca}^{2+} + 2NaCl$$



# Important parameters for IX resin

- The exchange capacity of a resin is defined as the quantity of an exchangeable ion that can be taken up. The exchange capacity can be expressed as meq/mL or meq/kg or mg/g or mole/g or …
- The resin size is important with respect to the hydraulics and kinetics. In general, smaller particles lead to larger pressure drop, but the rate of exchange is inversely proportional to the square of the particle diameter
- The stability of a resin is also important for long-term performance. It should not degrade, break, etc.



# فشار

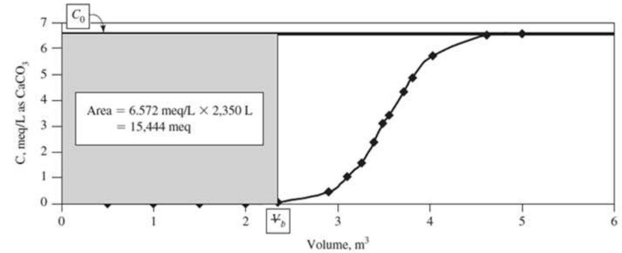
- هر چه سرعت بیشتر باشد، افت فشار بیشتر خواهد بود (دبی تقسیم بر سطح مقطع)

$$\mathrm{SLR} = \frac{Q}{A_c}$$

- افت فشار کمتر بهتر است چون رزین ها صدمه نمی بینند
- اکثر رزین ها نمی توانند بیش از ۱۵۰ کیلوپاسکال (گیج) را تحمل کنند. ولی چون در طول بهره برداری فشردگی بستر و افزایش فشار داریم، همیشه پایینتر طراحی می کنیم (کمتر از ۷۰ کیلوپاسکال گیج برای بستر تمیز)

## ظرفیت عملی تبادل یونی

- ظرفیت عملی همیشه کمتر از ظرفیت تئوریک رزین است
- معمولا برای خریداری رزین، آزمایش پایلوت انجام می شود
- نمودار breakthrough پس از آزمایشات به دست می آید




## Zeolites

- Zeolites are microporous, aluminosilicate (Al, Si) minerals used as commercial adsorbents and catalysts. Zeolites have a porous structure that can accommodate a wide variety of cations, such as $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution.
- Zeolites occur naturally but are also produced industrially on a large scale. More than 200 unique zeolite types have been produced, around 40 of which occur naturally.



## Zeolites

- The term **molecular sieve** refers to a particular property of these materials, i.e., the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the dimensions of the channels.
- Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential to supply zeolites is virtually unlimited.



## پیشتصفیه آب ورودی

- آب ورودی نباید کدورت بیش از حد (5 NTU) داشته باشد
- نباید اکسید کننده باشد ← کلر آزاد باید کم باشد که عمر رزین کاهش پیدا نکند. اگر کلر آزاد داریم، مقدار cross-link باید زیاد باشد
- رسوب بر روی رزین ها نامطلوب است. به عنوان مثال آهن و منگنز در ورودی مجموعا باید کمتر از 0.3mg/L باشند
- بعضی از ترکیبات ممکن است با گروه های عاملی واکنش های برگشت ناپذیر بدهند (پس باید مواظب بود)