Ion Exchange

Definition of Ion Exchange

Ion exchange is the process through which ions in solution are transferred to a solid matrix which, in turn releases ions of a different type but of the same polarity. In other words the ions in solutions are replaced by different ions originally present in the solid

Ion Exchange as a Sorption Process

- Since ion exchange occurs between a solution and the internal surface of a solid it can be viewed as a special type of sorption process
- There are many similarities between adsorption and ion exchange. The two processes are often analyzed using similar models
- Unlike adsorption ion exchange requires an interchange of materials, i.e., the ions (as opposed to a unidirectional transfer) since the *electroneutrality* of the solution must be maintained

Ion Exchange as a Physical Process

- During ion exchange the ions being exchanged are *reversibly* removed from the wastewater and transferred to the ion exchanger
- This means that ion exchange is a physical separation process in which the ions exchanged are not chemically altered
- Since the chemical characteristics of the ions exchanged are not modified the use of ion exchange in wastewater treatment is associated with the removal of hazardous ionic material(s) from the wastewater and its transfer to the ion exchanger

Ion Exchange as a Physical Process (continued)

- Since the ion exchanger only collects the hazardous material the spent exchanger must be treated at the end of a cycle
- Typically this involves the regeneration of the ion exchanger by contacting the spent exchanger with a concentrated solution of an ion (such as H^+ or OH^-) which can replace the ions adsorbed on the exchanger during the treatment process
- This results in the generation of a spent regenerating solution containing the waste ions in a concentrated form

Ion Exchange in Water Softening

- Water softening is not a wastewater process. However it is worth mentioning it because it constitutes the largest application of ion exchange processes
- Water softening consists of removing divalent ions, such as Ca^{++} or Mg^{++}, from water (these ions result in the so-called water hardness)
- Typically these ions are removed by precipitation at pH above 10 using the lime-soda process. This process utilizes lime to raise the pH to the desired value (thus adding Ca^{++} ions to the water)

Ion Exchange in Water Softening

- Mg^{++} is typically removed as $Mg(OH)_2$ while Ca^{++} is typically precipitated by adding soda ash (Na_2CO_3) as calcium carbonate
- Ion exchangers can be effectively used to remove the hardness from water without raising the pH. In this case Na^+ is exchanged for Ca^{++} or Mg^{++}. The exchanger is then regenerated with concentrated NaCl solutions
- Ion exchange, although more expensive than the lime-soda process, results in a lower concentration of residual hardness (i.e. below the 30-50 mg/L (as $CaCO_3$) achievable with the lime-soda process)

Ion Exchange in Water Deionization

- Ion exchangers are also used in complete water deionization processes
- In this case both cationic and anionic exchangers are used
- Regeneration of the exchangers is accomplished with strong acids or bases

Ion Exchangers in the Treatment of Inorganic and Organic Wastes

- In the vast majority of cases ion exchanger are used to treat wastewaters containing *inorganic wastes* (i.e., *inorganic ions*)
- The kinetics of sorption of organic species from non-polar solvents by ion exchangers is typically unfavorable
- In addition, ion exchangers are generally not very effective against large organic molecules, mainly because the size of the molecules which dramatically reduces the exchange rate

Ion Exchangers in the Treatment of Inorganic and Organic Wastes (continued)

- However, ion exchangers are effectively used in the treatment of specific organic compounds (such as phenol sorption or decolorization of kraft paper mill effluents). In this case the ion exchanger does not act as such but more as an conventional adsorbent

Motivation for the Use of Ion Exchange Processes in Wastewater Treatment

Many industrial wastewaters contain substances that:

- **are in ionic form**
- **are heavy metals in a soluble form**
- **can be economically recovered and reused**
- **if removed under the form of sludge would produce a hazardous material to be disposed of under RCRA**

Common Applications of Ion Exchange in Industrial Wastewater Treatment

- Removal of heavy metals from electroplating wastewaters and other industrial processes
- Polishing of wastewater before discharging
- Nitrogen control (removal of ammonium ion from wastewaters)
- Removal of salt buildup in close-loop utility water (e.g., removal of salts from cooling water blowdown)
- Purification of acids and bases to reuse them
- Removal of radioactive contaminants in the nuclear industry

Examples of Ion Exchange Processes in Industrial Wastewater Treatment

- **Recovery of chromic acid from plating rinsewaters**
- **Recovery of metals from acid copper-plating and nickel-plating rinsewaters**
- **Recovery of metals from mixed rinsewaters**
- **Removal of chromates from cooling water circuits**
- **Recovery, purification and re-use of spent acids from metal pickling and etching processes**
- **Removal of radioactive components from the wastewaters of nuclear power plants**

Advantages of Ion Exchange in Wastewater Treatment Processes

- Capability of handling and separating components from dilute wastes
- Possibility of concentrating pollutants
- Capability of handling hazardous wastes
- Possibility of recovery expensive materials from waste (e.g., precious metals)
- Possibility of regenerating ion exchanger
- Possibility of recycling components present in the waste and/or regenerating chemicals

Disadvantages of Ion Exchange in Wastewater Treatment Processes

- Limitation on the concentration in the effluent to be treated
- In general, lack of selectivity against specific target ions
- Susceptibility to fouling by organic substances present in the wastewater
- Generation of waste as a result of ion exchanger regeneration
- Down time for regeneration

Ion Exchange Materials

- Ion exchange materials are made of organic or inorganic matrices containing ionic functional groups
- Both natural ion exchange materials (zeolites) and synthetic ion exchange materials exist
- The vast majority of the ion exchangers used in industrial wastewater treatment is of synthetic origin
- The most common type of synthetic ion exchange materials are organic ***resins***

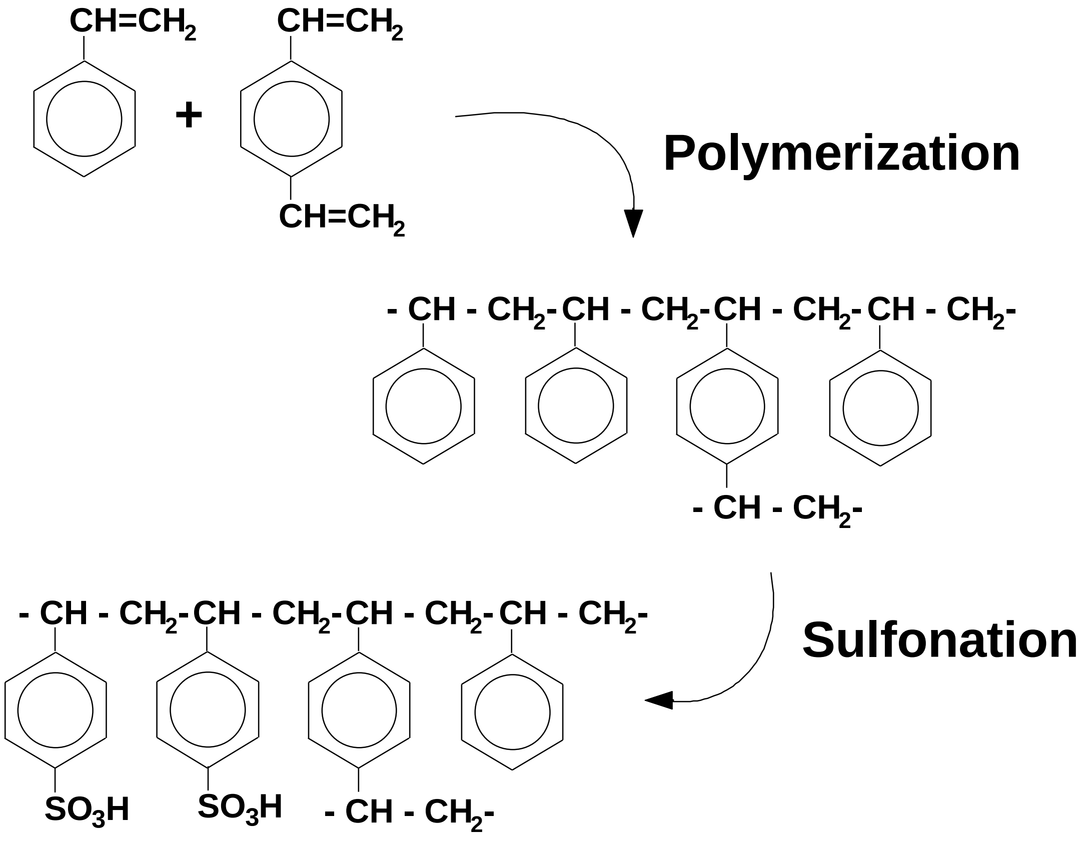
Ion Exchange Resins

- Ion exchange resins are organic compounds polymerized to form a porous tridimensional matrix
- A crosslinking agent (e.g., divinylbenzene) is added during the polymerization reaction to generate the tridimensional structure
- The resins, in the from of spherical particles, are chemically activated by reacting the polymer matrix with a compound capable of introducing the desired ion exchange functional group (e.g., with sulfuric acid to introduce sulfonic groups)

Degree of Crosslinking in Ion Exchange Resins

- **The amount of crosslinking agent added during the polymerization reaction determines the degree of crosslinking, i.e., the number of carbon-carbon bonds interconnecting (crosslinking) the polymeric chains**
- **A high degree of crosslinking imparts a more rigid structure to the resin but reduces the porosity of the matrix and the ability of larger ions to diffuse through it**

Preparation of Styrene-Divinylbenzene Cationic Exchangers



Strong vs. Weak Ion Exchangers

- **Strong ion exchangers have highly ionized functional group. As a result they may easily exchange their H^+ or OH^- groups at any pH**
- **Weak ion exchangers, like the corresponding acids or bases, are only partially ionized unless they are in a pH range above 7 (for weak acid cation exchangers) or below 7 (for weak basic anion exchangers)**

Functional Groups in Ion Exchange Resins

The functional groups most commonly found in ion exchange resins are:

- **Strongly acidic cationic exchanger:**
  sulfonic group (R-SO_3H)
- **Strongly basic anionic exchanger:**
  quaternary ammonium group (R-$R_3N^+OH^-$)
- **Weakly acidic cationic exchanger:**
  carboxyl group (R-COOH)
- **Weakly basic anionic exchanger:**
  amine group (R-NH_3OH)

Ion Exchange Reactions

The *reversible* reactions associated with ion exchange are:

- **Strongly acidic cationic exchanger:**

$$2RSO_3H + Ca^{++} \Leftrightarrow \left(RSO_3\right)_2 Ca + 2H^+$$

- **Strongly basic anionic exchanger:**

$$RR'_3NOH + SO_4^{-2} \Leftrightarrow \left(RR'_3N\right)_2 SO_4 + 2OH^-$$

- **Weakly acidic cationic exchanger:**

$$2RCOOH + Ca^{++} \Leftrightarrow \left(RCOO\right)_2 Ca + 2H^+$$

- **Weakly basic anionic exchanger:**

$$RNH_3OH + SO_4^{-2} \Leftrightarrow \left(RNH_3\right)_2 SO_4 + 2OH^-$$

Ion Exchange Reaction Equilibrium

For the general ion exchange *reversible* reaction:

$$a\,A^{+a} + b B_x \Leftrightarrow a\,A_x + b B^{+b}$$

with: $a\,a = b b$

subscript *x* = subscript identifying the ionic species adsorbed on the resin

the equilibrium relationship takes the form:

$$K_B = \frac{\left[A_X\right]^a \left[B^{+b}\right]^b}{\left[A^{+a}\right]^a \left[B_X\right]^b} = \frac{q_A^a\,C_B^b}{C_A^a\,q_B^b} = \frac{\left(q_A / C_A\right)^{\gamma}}{\left(q_B / C_B\right)^{\gamma}}$$

K

Ion Exchange Reaction Equilibrium (continued)

The selectivity coefficient K_B is <u>not</u> a true equilibrium constant (although often referred to as such) but depends on the experimental conditions.

Example:

$$Ca^{2+} + 2H_X^+ \Leftrightarrow Ca_X + 2H^+$$

$$K_B = \frac{\left(q_{Ca}/C_{Ca^{2+}}\right)}{\left(q_H/C_{H^+}\right)}$$

Separation Factor in Ion Exchange

Another "constant" often used to describe ion exchange equilibrium relationships is the separation factor, a_B, defined as:

$$a_B = \frac{\left(q_A / C_A \right)}{\left(q_B / C_B \right)}$$

For example:

$$Ca^{2+} + 2H_X^+ \Leftrightarrow Ca_X + 2H^+$$

$$a_B = \frac{\left(q_{Ca} / C_{Ca^{2+}} \right)}{\left(q_H / C_{H^+} \right)}$$

Ion Exchange Selectivity

- The selectivity coefficient K_B and the separation factor a_B are directly proportional to the preference of a given ion exchange resin toward different types of ions
- For the same concentration of different ions the relative preference of an ion exchanger depends primarily on two factors, i.e.:
  - ionic charge
  - ionic size

Ion Exchange Selectivity (continued)

- **Ions with higher valence are typically preferred by the ion exchange resin. For example a typical cationic resin has the following preference:**

  $$Th^{4+} > Al^{3+} > Ca^{2+} > Na^{+}$$

  Similarly, an anionic resin typically has the following preference:

  $$PO_4^{3-} > SO_4^{2-} > Cl^{-}$$

- **Exceptions are also possible as in the following case:**

  $$SO_4^{2-} > I^{-} > NO_3^{-} > CrO_4^{2-} > Br^{-}$$

Ion Exchange Selectivity (continued)

- **Among ions having the same charge, the ions having the smallest hydrated diameter are preferred by the resin (Remark: ions with larger unhydrated ionic diameter tend to have smaller hydrated diameter and are therefore preferred)**
- **The resin preference for one ion over another is also affected by the degree of crosslinking (and hence the pore size)**

Typical Order of Ion Exchange Preference by Cationic Ion Exchangers

- **Monovalent cations:**

$Ag^+ > Cu^+ > K^+ > NH_4^+ > Na^+ > H^+ > Li^+$

- **Divalent cations:**

$Pb^{2+} > Hg^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} >$
$> Zn^{2+} > Fe^{2+} > Mg^{2+} > Mn^{2+}$

- **Trivalent cations:**

$Fe^{3+} > Al^{3+}$

Typical Order of Ion Exchange Preference by Anionic Ion Exchangers

$CNS^- > ClO_4^- > I^- > NO_3^- > Br^- > CN^- > HSO_4^- > NO_2^- >$

$> Cl^- > HCO_3^- > CH_3COO^- > OH^- > F^-$

Ion Exchange Selectivity Coefficients at 25 °C

Equilibrium Isotherm to Describe Ion Exchange Equilibrium

- Instead of equilibrium models the ion exchange experimental equilibrium data of two ionic species are correlated using adsorption equations similar to the Langmuir or Freundlich equations
- If this approach is used then additional experimental data are collected in test column from which breakthrough curves can be obtained

Capacity of Ion Exchangers

- The capacity of an ion exchanger is the amount of ionic species that can be exchanged per unit mass of dry exchanger
- The exchange capacity is a function of the number of available exchange sites in the resin
- The exchange capacity is commonly expressed in milliequivalents of ionic species per gram of dry weight of ion exchange particles (meq/g)
- The capacity of most ion exchange resin is in the range 2 - 10 meq/g
- Operating factors such as pH may affect the capacity of the exchanger

Swelling of Ion Exchange Resins

- **When placed in water ion exchange resin particles tend to swell**
- **The degree of swelling is affected by the degree of crosslinking of the polymer. More crosslinked resin have a greater mechanical resistance than less crosslinked resin, and tend to swell less**

Swelling of Ion Exchange Resins (continued)

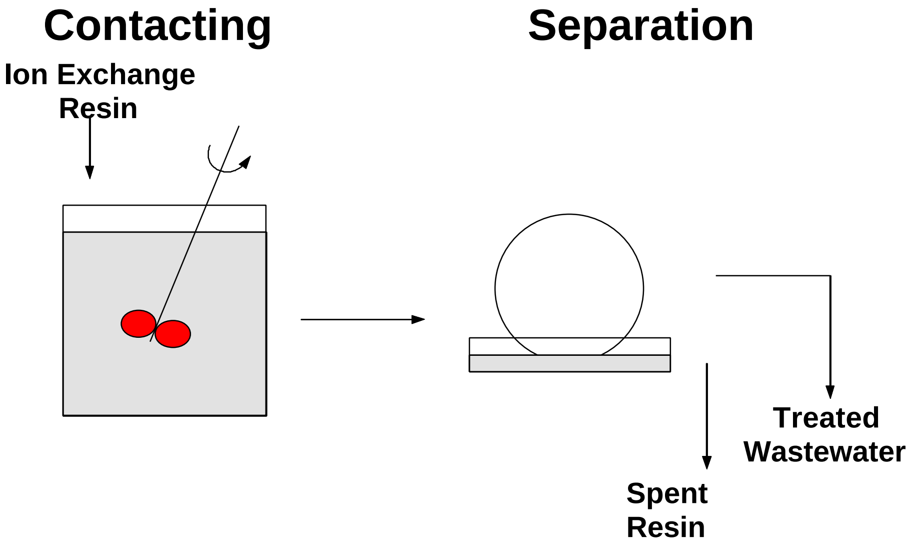
- Swelling is also affected by the ions being taken up by the resin and their hydrated diameter. More hydrated ions tend to make the resin swell more than less hydrated ions
- The degree of swelling can be quite significant (e.g., 50% during regeneration). Therefore, the ion exchange columns should be designed accounting for the swelling of the bed

Types of Ion Exchange Operations

- **Batch Operation**
- **Moving-Bed Operation**
- **Fixed-Bed (Column) Operation**

Ion Exchange Batch Operation

The wastewater is placed in an agitated tank and added with the ion exchange resins. After equilibrium has been reached the resin is filtered and the water is discharged. The resin in not typically regenerated



Design of Ion Exchange Batch Processes

A mass balance for an ionic pollutant in an differential interval, *dt*, during a batch operation is:

$$V\,dC = -K\,A_p\left(C - C^*\right)dt$$

where: *V* = volume of wastewater (m³)

***K* = mass transfer coefficient between ion exchange particles and wastewater (m/s)**

A_p = cumulative surface area of ion exchange particles (m²)

***C* = ionic pollutant concentration (g/L)**

***C** = concentration of ionic pollutant in equilibrium with concentration q in the particle at time *t* (g/L)**

Design of Ion Exchange Batch Processes

The previous equation can be integrated to give:

$$t = -\frac{1}{K a_p} \int_{C_o}^{C} \frac{dC'}{C' - C'^*}$$

where: *a* = surface area of particles/liquid volume

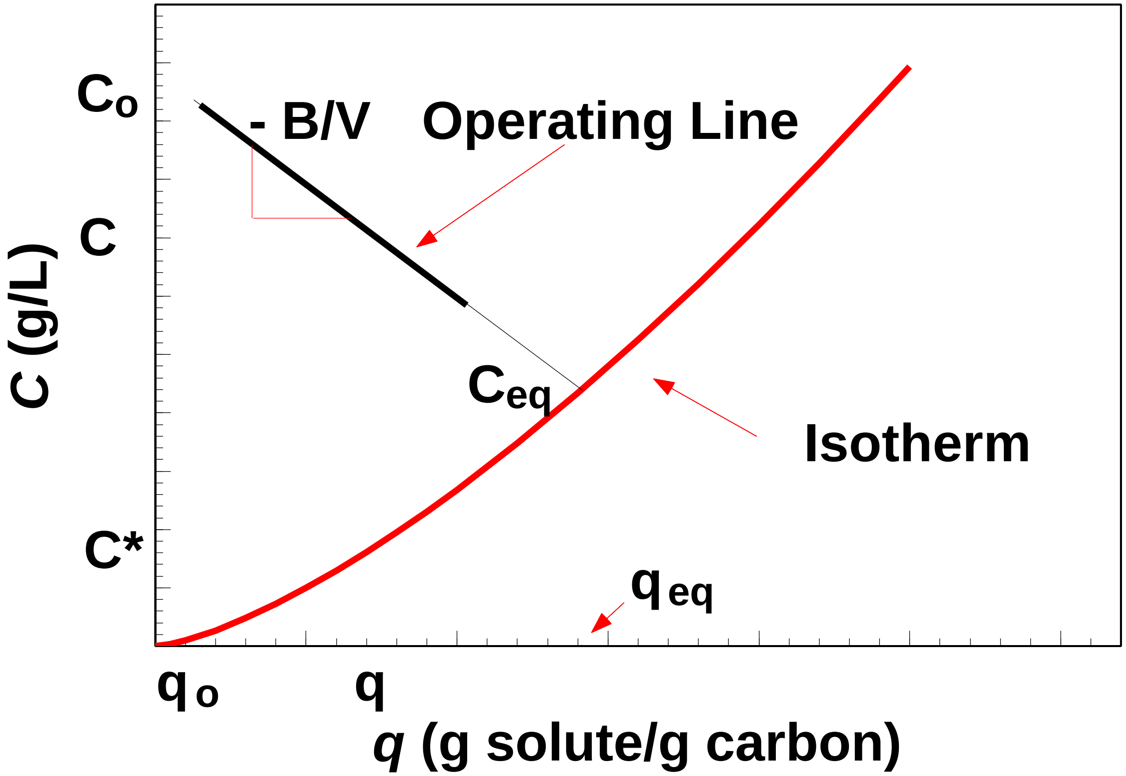
This equation can be integrated if the equilibrium isotherm is known and by knowing that the mass balance at a generic time, *t*, is given by:

$$V\left(C_o - C\right) = B\left(q - q_o\right)$$

where: subscript "o" indicates initial concentrations

Design of Ion Exchange Batch Processes

The previous integral can be evaluated graphically from the following graph:



Approximate Design of Ion Exchange Batch Processes

During the initial stages of the ion exchange transfer process it is:

$$C >> C^*$$

Then:

$$t \cong -\frac{1}{K a_p} \int_{C_o}^{C} \frac{dC'}{C'} = \frac{1}{K a_p} \ln \frac{C_o}{C}$$

This equation can be used to approximately estimate the time required for the pollutant concentration in the wastewater to drop to a desired level.

Moving-Bed Ion Exchange Operation

The resin and the wastewater are moving countercurrently in the column. The process is continuous. This means that not only is the wastewater continuously fed and removed from the column but also that fresh resin is added and spent resin is removed. The spent resin is then regenerated and fed back to the column

Fixed-Bed Ion Exchange Columns

- **"Cocurrent" Column**
- **"Countercurrent" Column**
- **Mixed Bed Column**

Remark: in any kind of fixed-bed operation with a single phase passing through a column (e.g., a wastewater over a bed of activated carbon or ion exchange resins) the terms *cocurrent* and *countercurrent* lose their meaning. However, in ion exchange operations these terms are used to indicate the direction of the regenerating solution with respect to that of the wastewater

Cocurrent Fixed-Bed Ion Exchange Column

- The term "cocurrent" indicates that the direction of the flow of the regenerating solution (at the end of a cycle) is the same as that of the incoming wastewater (during normal operation)
- Cocurrent operation, although not the most efficient, is the most common because of its simple design and operation
- Regeneration is conducted with 1 - 5 N acid or base solutions
- Typical column height: 0.6 - 1.5 m
- Wastewater flow rate: 8 - 40 bed volumes/hr

Countercurrent Fixed-Bed Ion Exchange Column

- In these columns the regenerating solution enters the column in a direction opposite to that of the wastewater. This improves the efficiency of the regeneration process resulting in smaller amounts of spent regenerating solution utilized. This approach also allows the more concentrated regenerating solution to contact the "cleaner" part of the resin first
- Special care must be pay to preventing fluidization of the resin during regeneration

Design of Fixed-Bed Ion Exchange Processes

- **Fixed-bed ion exchange columns have many similarities in common with fixed-bed adsorbers**
- **For example in fixed-bed ion exchange columns an "exchange zone" similar to the adsorption zone is formed and travels through the column until the breakpoint is reached**

Design of Fixed-Bed Ion Exchange Processes (continued)

- As a result the design of such processes can be carried out using an approach similar to that described to design adsorption fixed-bed columns
- More complex models also exist to account for the fact that ion exchange is also associated with charge transport and electroneutrality

Simplified Method for Estimation of Fixed-Bed Ion Exchange Performance

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

$$q_B B = \zeta q_{So} B = Q t_B \left(C_o - \frac{C_B}{2} \right)$$

where: q_{So} = saturation capacity of the ion exchanger for a specific ion

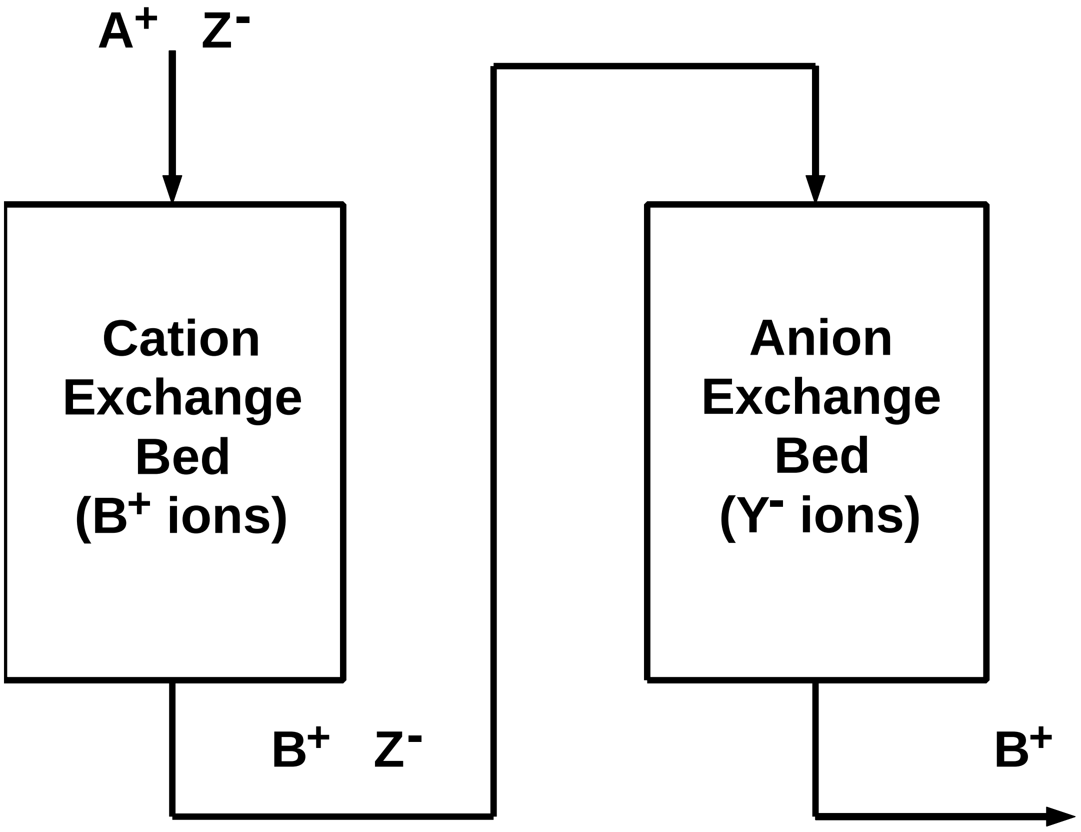
ζ = amount of pollutant adsorbed in the bed/maximum amount of pollutant that could be adsorbed in the bed (at full capacity)

Simplified Method for Estimation of Fixed-Bed Ion Exchange Performance

The time required to reach breakthrough is:

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

Two-Stage Ion Exchange Operation



A^+ Z^-

Cation Exchange Bed (B^+ ions)

B^+ Z^-

Anion Exchange Bed (Y^- ions)

B^+ Y^-

Ion Exchange System for Chromate Removal and Water Reuse

After Eckenfelder, *Industrial Water Pollution Control*, 1989, p. 297

Regeneration of Fixed-Bed Ion Exchangers

- **Regeneration of ion exchangers in fixed-bed columns is typically conducted in place by passing a regenerating solution (typically a strong acid or a strong base depending on the type of ion exchanger) through the column**
- **Since the ion exchange reaction is reversible the more concentrated H^+, although less preferred by the resin than other ions already adsorbed by the resin, are able to replace those ions thus regenerating the ion exchange bed**

Regeneration of Ion Exchangers

- For example, the reversible reactions associated with ion exchange in the presence of a strongly acidic cationic exchanger:

  $$2RSO_3H + Ca^{++} \Leftrightarrow \left(RSO_3\right)_2Ca + 2H^{+}$$

  can be reverted to the left (with consequent release of Ca^{++} ions) if a strong acid is passed through the bed
- Other concentrated solutions other than acids or bases can be used as regenerating solutions (e.g., NaCl). In such a case the regenerated resin will be loaded with the resulting ion (e.g., Na^+ instead of H^+)

Mixed Bed Ion Exchange Column

- **In this type of column two types of resin particles (one cationic and the other anionic) are mixed and placed in the column**
- **As the wastewater passes through the column nearly complete deionization occurs**
- **Although the effluent from this type of column is very pure regeneration is inefficient**
- **Regeneration can be carried out only after backwash takes place, during which the resin particles are classified**
- **Air is then used to re-mix the resin particles before putting the column back in service**

Mixed-Bed Ion Exchange Operation

After Weber, *Physicochemical Processes for Wastewater Control*, 1972, p. 293

Characteristics of Ion Exchange Columns for Wastewater Treatment

Ion exchanger particle diameter	0.4 - 0.8 mm
Bed height	0.6 - 2.5 m (2 - 8 ft)
Height-to-diameter ratio	2 to 1
Bed expansion	25 - 50%
Hydraulic loading	1.4 - 6.8 L/m^2 s (2 - 10 gpm/ft^2)

After Wentz, *Hazardous Waste Management*, 1989, p. 158 and
Metcalf and Eddy, *Wastewater Engineering*, 1991, p. 757

Additional Information and Examples on Ion Exchange

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

- **Sundstrom, D. W. and Klei, H. E., 1979, *Wastewater Treatment*, Prentice Hall, Englewood Cliffs, NJ, pp. 356 - 367.**
- **Wentz, C. W., 1989, Hazardous Waste Management, McGraw-Hill, New York, pp. 156 - 161.**
- **Corbitt, R. A. 1990, The Standard Handbook of Environmental Engineering, McGraw-Hill, New York, pp. 6.202 - 6.208.**
- **Treybal, R. E., 1968, *Mass Transfer Operation*, McGraw-Hill, New York, pp. 490 - 568.**

Additional Information and Examples on Ion Exchange

- **Metcalf & Eddy, 1991, Wastewater Engineering: Treatment, Disposal, and Reuse, McGraw-Hill, New York, pp. 740 - 741; 756 - 757.**
- **Weber, W. J., Jr., 1972, *Physicochemical Process for Water Quality Control*, Wiley-Interscience, John Wiley & Sons, New York, pp. 260 - 305.**
- **Freeman, H. M. (ed.), 1989, *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill, New York, pp. 6.59 - 6.75.**
- **Eckenfelder, W. W., Jr., 1989, *Industrial Water Pollution Control*, McGraw-Hill, New York, pp. 291 - 299.**