ION EXCHANGE

- Definition

Ion exchange is basically a reversible chemical process wherein an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle.

Removal of undesirable anions and cations from solution through the use of ion exchange resin

Applications

- Water softening
- Removal of non-metal inorganic
- Removal or recovery of metal

Ion Exchange

Chemical Reaction

• reversible chemical reaction

• insoluble solid (resin) and a solution (wastewater)

• ions are interchanged

Used only on dilute solutions

- Cationic Resin
- exchange H^+ for other positively charged ions
- Replaces: nickel, copper, chromes (Cr III),
- cadmium, lead
- Weak Acid Resin
- Requires less acid to regenerate
- Strong Acid Resin
- Achieves lower cation concentration

- Anionic Resin
- exchange OH- for other negatively charged ions
- Replaces: chromates (Cr VI), sulfate, cyanide, carbonate

- Weak Base Resin
- Requires less base regenerate
- Strong Base Resin
- Achieves lower anion concentration

- Anionic Resin Column
- Cationic Resin Column
- Series of Anionic and Cationic Resin

- Columns
- Mixture of Anionic and Cationic Resin in one

Column

- Metal-Specific Resin Column

Factors Affecting Resin Choice

- Contamination ions
- pH

Resin Fouling

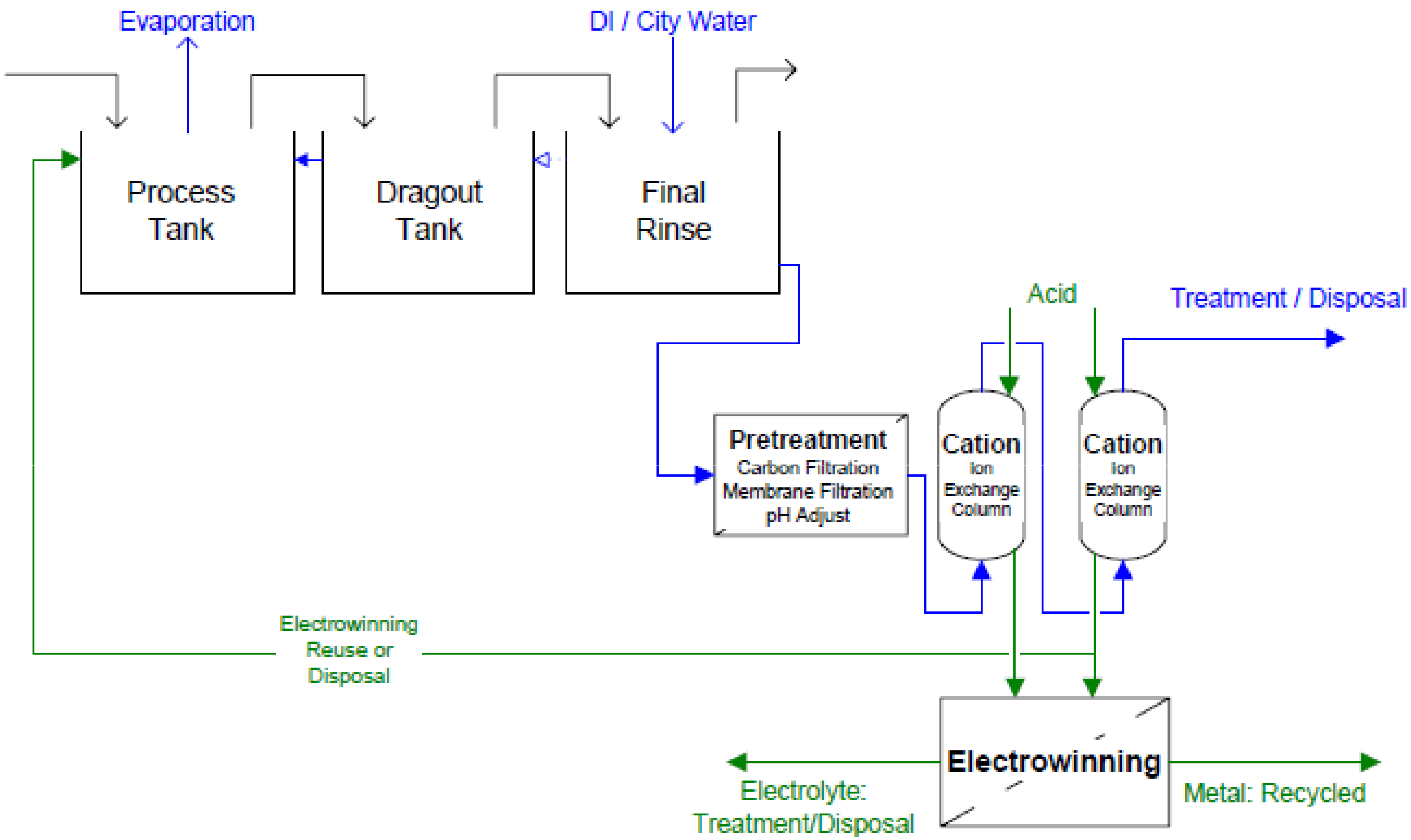
- Oil and grease
- Total suspended solids > 10 ppm
- Oxidant

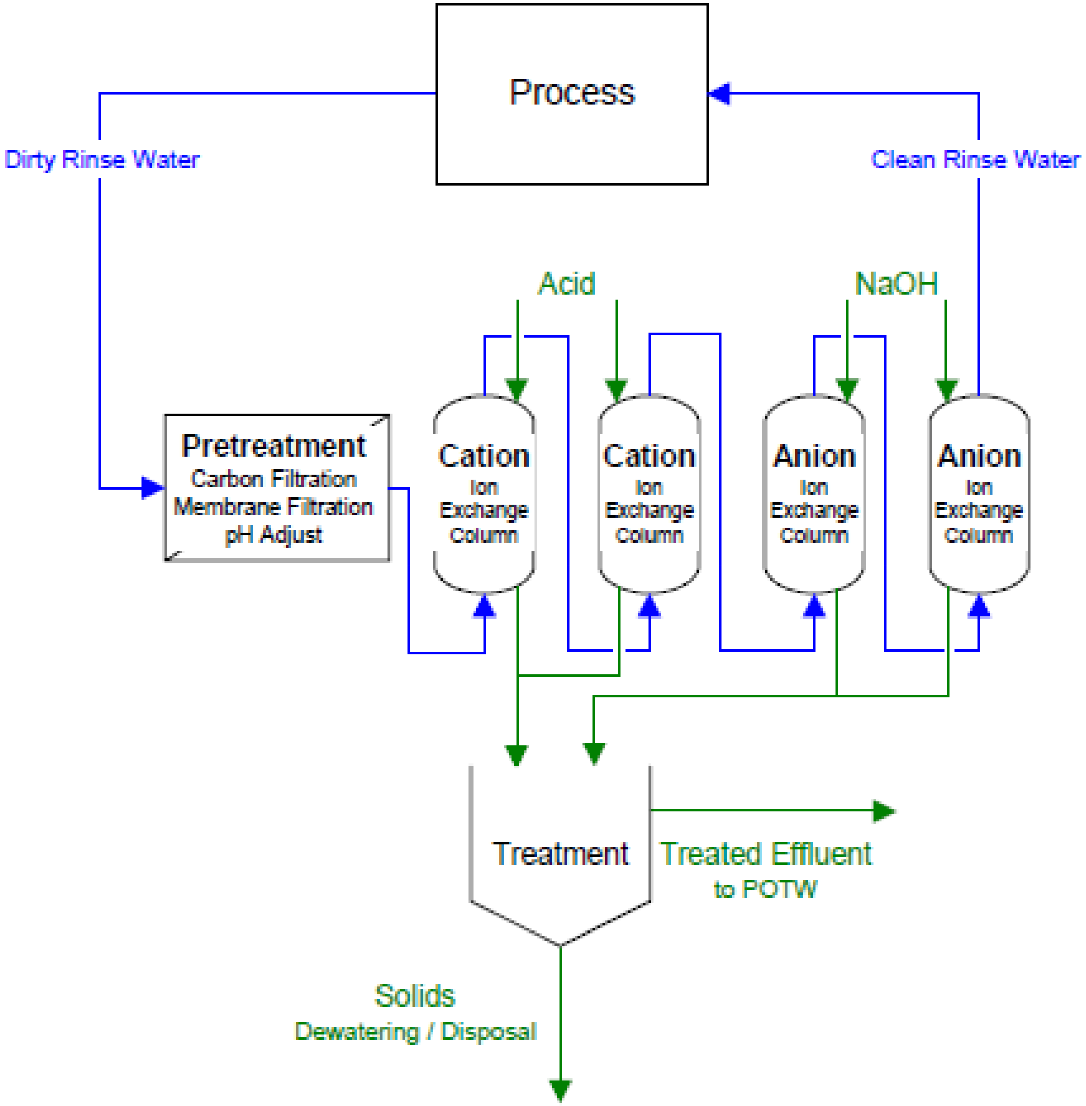
Pretreatment for Rinse Water

Chemical Recovery from Rinse Water

Remove Contaminants from Plating Bath

Wastewater Treatment


Evaporation
DI / City Water
Process Tank
Dragout Tank
Final Rinse
Acid
Treatment / Disposal
Pretreatment
Carbon Filtration
Membrane Filtration
pH Adjust
Cation Ion Exchange Column
Cation Ion Exchange Column
Electrowinning Reuse or Disposal
Electrowinning
Electrolyte: Treatment/Disposal
Metal: Recycled



Process
Dirty Rinse Water
Clean Rinse Water
Acid
NaOH
Pretreatment
Carbon Filtration
Membrane Filtration
pH Adjust
Cation
Ion
Exchange
Column
Cation
Ion
Exchange
Column
Anion
Ion
Exchange
Column
Anion
Ion
Exchange
Column
Treatment
Treated Effluent
to POTW
Solids
Dewatering / Disposal

ION EXCHANGE

❖ Similar in many ways to adsorption treatment, but chemical mechanism is ion exchange rather than adsorption.

❖ An ion exchanger is a material to which certain ions are sorbed in exchange for ions already bound to exchanger.

❖ For example– water can be softened by ion exchanger that adsorbs Ca and Mg, releasing Na in exchange.

❖Zeolite is natural mineral that softens water by ion exchange.

Reaction looks like

$$Ca^{+2} + 2Na.Ex \rightleftharpoons Ca.Ex_2 + 2Na^+$$

$$Mg^{+2} + 2Na.Ex \rightleftharpoons Mg.Ex_2 + 2Na^+$$

Ex = exchanger solid

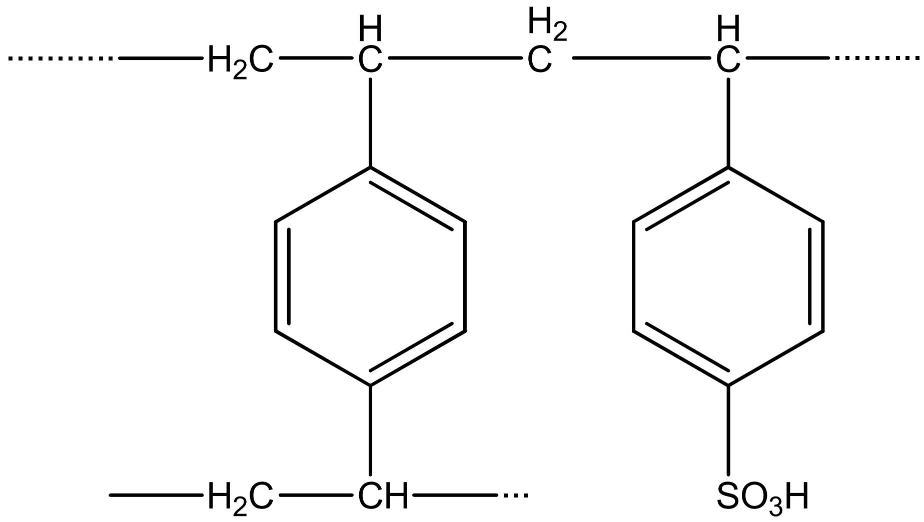
Exchanger is regenerated using strong brine

$$Na^+ + Ca.Ex_2 \xrightleftharpoons{\text{Strong brine}} 2Na.Ex + Ca^{+2}$$

$$2Na^+ + Mg.Ex_2 \xrightleftharpoons{\text{Strong brine}} 2Na.Ex + Mg^{+2}$$

Most exchangers are now synthetic resins

e.g.



Sulphonic groups --SO_3H is ion exchanger.

H^+ swaps with cation.

Preference series for which ions exchange

$Ba^{+2} > Pb^{+2} > Sr^{+2} > Ca^{+2} > Ni^{+2} > Cd^{+2} > Cu^{+2} > Co^{+2} > Zn^{+2} >$
$Mg^{+2} > Ag^{+2} > Cs^{+} > K^{+} > NH_4^{+} > Na^{+} > H^{+}$

For strong acid resins (e.g. sulphonates with SO_3H group)
More preferred ions are swapped for less preferred –e.g. Ca^{+2} for H^+

For anion exchangers (use carboxylic group –COOH)
$SO_4^{2-} > I^- > NO_3^- > CrO_4^- > Br^- > Cl^- > OH^-$

(Preference varies with the resin)

❖Design

- ❖ Design procedure and treatment systems are very similar to those for activated carbon

- ❖ Bench scale column tests are used to develop curves of breakthrough (C vs V).

- ❖ Resin is generally placed in pressure tanks similar for GAC

- ❖ Overflows rates ($\approx$ 6-8 gpm/ft^2)

❖**Iron and Maganese removal**

❖ Iron(II) and Magnese (II) exists in acidic and reducing environments (e.g. wetlands and in aquifer below wetlands).

❖Iron(II) and Magnese (II) are soluble and remain in water following conventional treatment

❖but precipitate at the point of use, causing stains on plumbing fixtures and in laundry.

❖Also support growth of iron bacteria(iron slime) in well screens, distribution systems.

Fe and Mn can be addressed in variety of ways

1. In situ treatment- injection wells around water supply wells to precipitate Fe and Mn in the ground.

2. Sequestration – phosphate chemicals added to water to bind with and 'sequester' Fe and Mn preventing later precipitate.

3. Ion exchange treatment with Greensand (glauconite) – natural ion exchanger with Fe and Mn.

Removal reaction

$$Z\text{-}MnO_2 + \begin{matrix} Fe^{+2} \\ Mn^{+2} \end{matrix} \longrightarrow Z\text{-}Mn_2O_3 + \begin{matrix} Fe^{3+} \\ Mn^{3+} \\ Mn^{2+} \end{matrix}$$

Where $Z\text{-}MnO_2$ = Mn coated glauconite

Regeneration with potassium permanganate

$$Zn\text{-}Mn_2O_3 + KMnO_4 \longrightarrow Z\text{-}MnO_2$$

4. Oxidation

Goal is to oxidize Mn^{2+}, Fe^{2+} to get precipitates.

Aeration (works for Fe, not for Mn)

$$2Fe^{2+} + 4HCO_3^- + \frac{1}{2} O_2 + H_2O \rightarrow 2\,Fe(OH)_3 + 4CO_2$$

Precipitated iron is then settled and filtered (most removal by filtration)

Chemical oxidation

Addition of strong oxidizer- chlorine or $KMnO_4$

Precipitated iron settled and filtered.

Reaction with permanganate

$3Fe^{3+}$ + $6HCO^{3-}$ + $KMnO_4$ + $2H_2O$ → $3Fe(OH)_3$ + MnO_2 + $KHCO_3$ + $5CO_2$

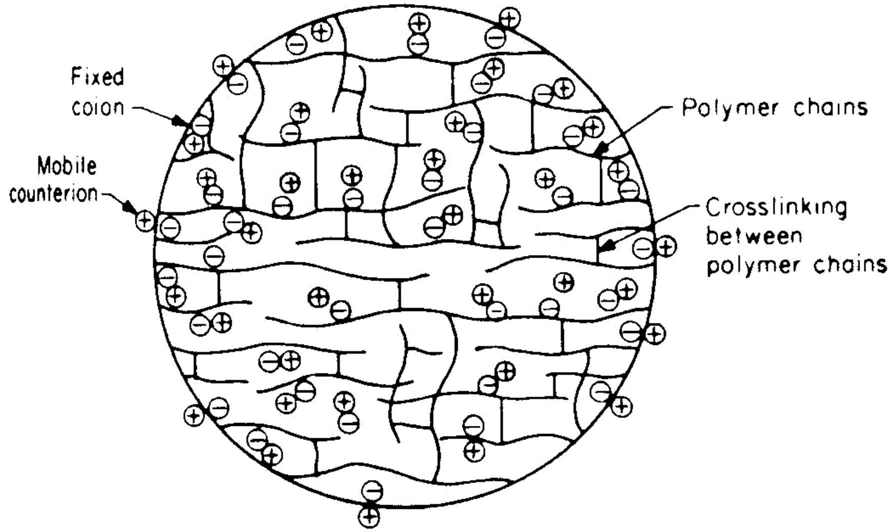
$3Mn^{2+}$ + $6HCO^{3-}$ + $2KMnO_4$ → $5MnO_2$ + $2KHCO_3$ + $2H_2O$ + $4CO_2$

5. Lime soda ash softening

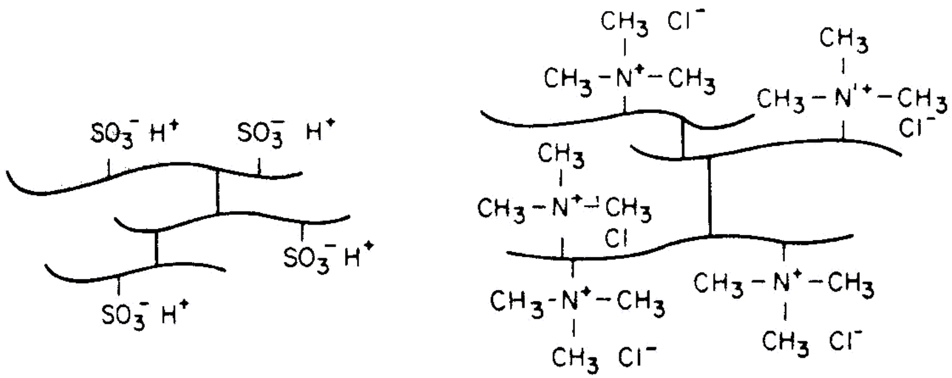
Fe and Mn removed during softening if pH is raised above 9.8

ION EXCHANGE (Medium - resin)

- Consists of an organic or inorganic network structure with attached functional group
- Synthetic resin made by the polymerisation of organic compounds into a porous three dimensional structure
- Exchange capacity is determined by the number of functional groups per unit mass of resin



(a)

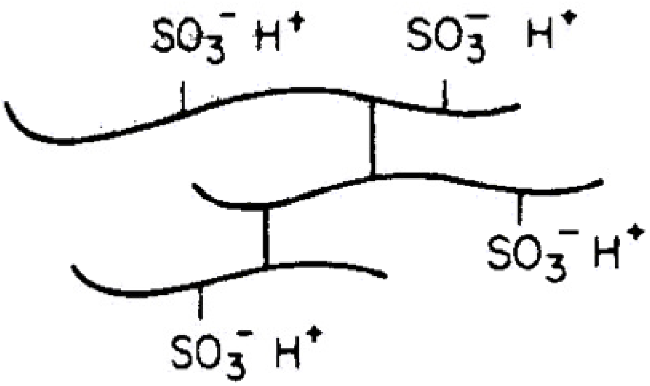


(b)

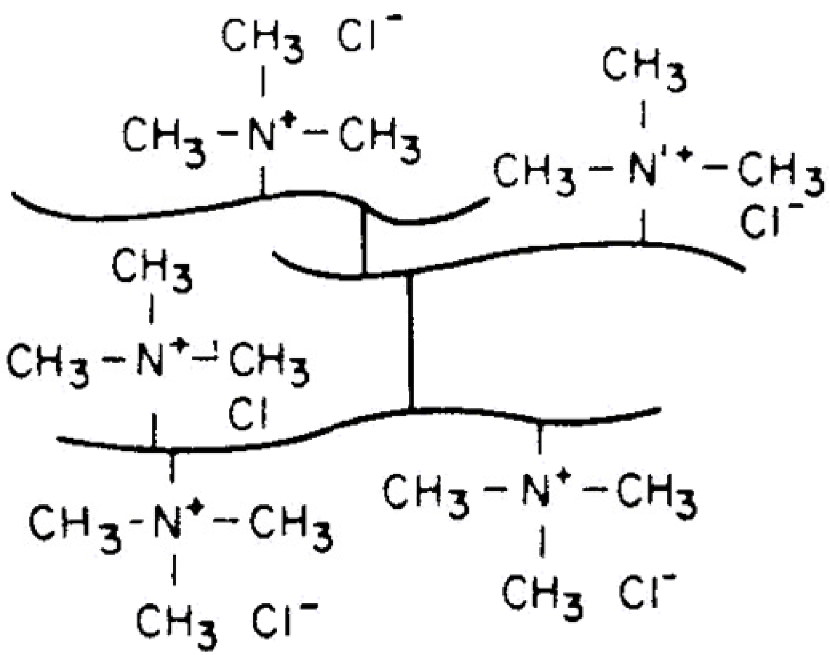
ION EXCHANGE
(Type of Resin)

a. Cationic resin - exchange positive ions
b. Anionic resin – exchange negative ions

(a)



(b)



ION EXCHANGE
(Exchange Reactions)

- Cation exchange on the <u>sodium</u> cycle:

$$Na_2 \cdot R + Ca^{2+} \Leftrightarrow Ca \cdot R + 2Na^{+}$$

where R represents the exchange resin. When all exchange sites are substantially replaced with calcium, resin is regenerated by passing a concentrated solution of sodium ions (5-10%) through the bed:

$$2Na^{+} + Ca \cdot R \Leftrightarrow Na_2 \cdot R + Ca^{2+}$$

ION EXCHANGE
(Exchange Reactions)

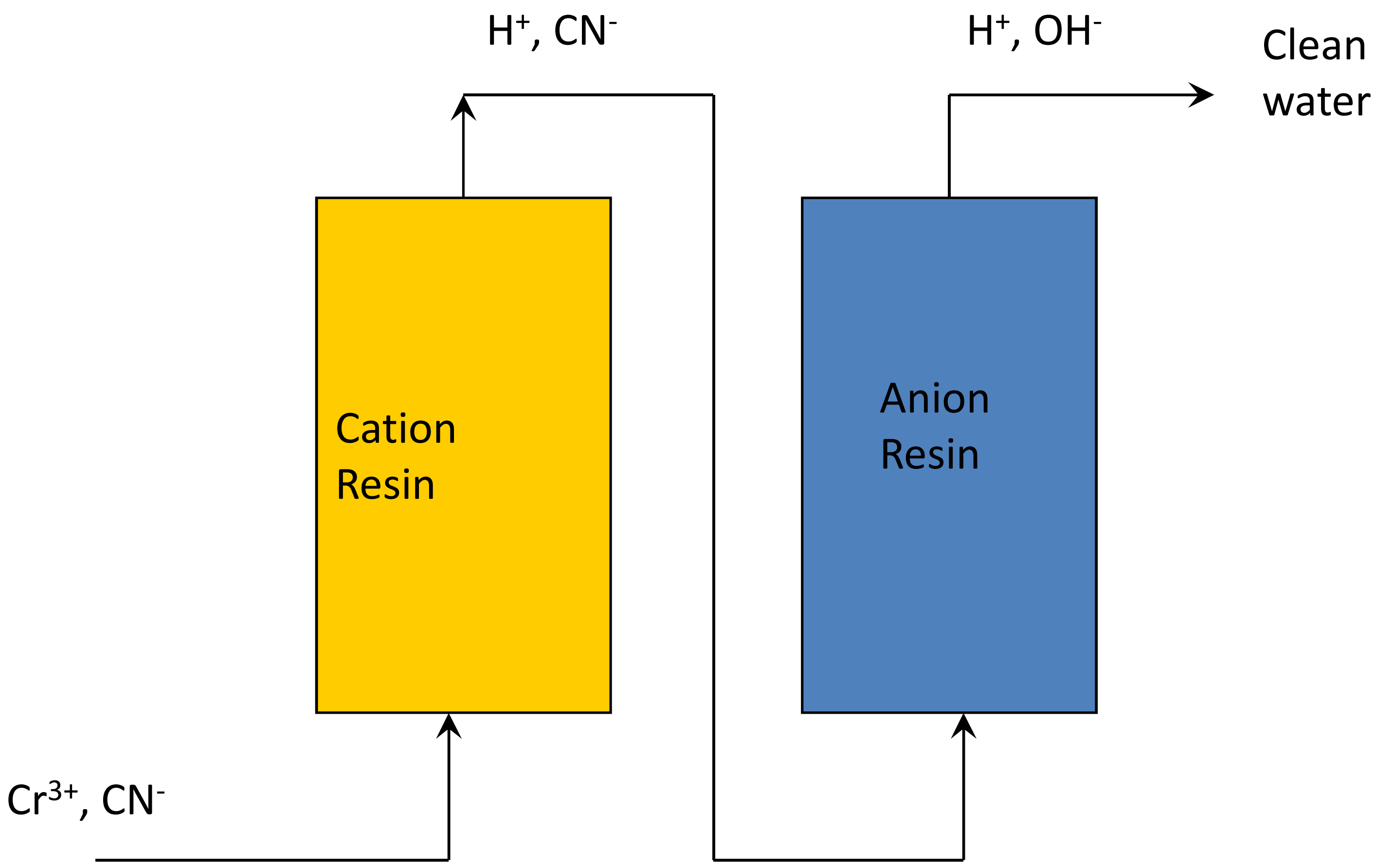
- Anion exchange replaces anions with hydroxyl ions:

$$SO_4^{2-} + R \cdot (OH)_2 \Leftrightarrow R \cdot SO_4 + 2OH^-$$

where R represents the exchange resin. When all exchange sites are substantially replaced with sulphate, resin is regenerated by passing a concentrated solution of hydroxide ions (5-10%) through the bed:

$$R \cdot SO_4 + 2OH^- \Leftrightarrow SO_4^{2-} + R \cdot (OH)_2$$

ION EXCHANGE
(Basic Principles)



ION EXCHANGE
(Selectivity)

- Cations:

  $Ra^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+} > Ag^{+}$
  $> Cs^{+} > K^{+} > NH_4^{+} > Na^{+} > Li^{+}$

- Anions:

  $HCRO_4^{-} > CrO_4^{2-} > ClO_4^{-} > SeO_4^{2-} > SO_4^{2-} > NO_3^{-} > Br^{-} > HPO_4^{-} >$
  $HA_sO_4^{-} > SeO_3^{2-} > CO_3^{2-} > CN^{-} > NO_2^{-} > Cl^{-} > H_2PO_4^{-}, H_2AsO_4^{-},$
  $HCO_3^{-} > OH^{-} > CH_3COO^{-} > F^{-}$

Note: The least preferred has the shortest retention time, and appears first in the effluent and vice versa for the most preferred.