GREEN ENGINEERING

“INNOVATIVE ION EXCHANGE TECHNOLOGY FOR TREATMENT OF AQUEOUS EFFLUENT STREAMS & DEVELOPING GREENER PROCESSES THROUGH RECOVERY & REUSE OF VALUABLE PRODUCTS.”

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GREEN ENGINEERING PRINCIPLE

- Prevent waste rather than treat/clean up waste
- Separation and Purification Operations designed to minimize energy & material use
- Recycle

- Innovative Exploitation of Ion Exchange Technology in line with the above Principles
  - for developing new Greener Processes;
  - also making Current Processes Greener;
ION EXCHANGE TECHNOLOGY : BASICS

- Reversible Interchange of Ions between Solid & a Liquid through diffusion Process, in which no structural change occurs in solid (Ion Exchanger)
- Separation Process in which mobile Ions from an Electrolytic solution are exchanged for Ions that are electrostatically bound to the functional group contained within a solid matrix (Ion Exchanger)
- Removes positive or negative Ions from solution and releases equivalent amount of other ions of same charge into solution
- In solid matrix when Functional Group are negatively charged , exchange will involve Cations (Cation Exchanger) & Functional Group are positively charged, exchange will involve Anions (Anion Exchanger)
- Inorganic materials like Zeolites, Phosphates, Alumina & Organic materials Cellulose, Proteins etc. can act as Ion Exchanger, but in practice Synthetic organic cross-linked Polymers having functional groups are used as Ion Exchangers.
ION EXCHANGE RESIN CHEMISTRY

- Styrene-Divinyl Benzene Co-Polymer:

CROSSLINKING TO MAKE ION EXCHANGE RESINS
ION EXCHANGE RESIN: CHEMISTRY

- Styrene-Divinyl Benzene Co-Polymer:

Styrene + Divinyl benzene $\rightarrow$ Polymer + Catalyst

Polymer $\rightarrow$ Sulfonating acid

Polymer $\rightarrow$ Catalyst

Polymer $\rightarrow$ Cation exchange Resin

Polymer $\rightarrow$ Anion exchange Resin

$\text{PSO}_3^- + \text{H}^+ \rightarrow \text{Cation exchange Resin}$

$\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^- \rightarrow \text{Anion exchange Resin}$
ION EXCHANGE RESIN STRUCTURE

Polymer chains

Cross-links

Fixed resin functional groups

Exchangeable Counterions
ION EXCHANGE RESIN: TYPES

- **Cation Exchange Resins:**
  - A) **Strong Acid Exchange Resins (SAC)** e.g., Styrene-DVB Co-polymers having -SO3H groups or its Na+ ion form;
  - B) **Weak Acid Exchange Resins (WAC)** e.g., Crosslinked Polyacrylic acid having –COOH groups

- **Anion Exchange Resins:**
  - A) **Strong Base Exchange Reins (SBA)** e.g., Styrene-DVB Co-polymers having – NR3 + cations with Cl- or OH- Anions;
  - B) **Weak Base Exchange Resins (WBA)** e.g., Styrene-DVB Co-polymer having –NR2 groups

- Based on synthetic methods, porosity of particles are controlled to obtain **Gel** type and **Macroporous** type which are required for different application.
ION EXCHANGE RESIN: TYPES

• Other Types:
  • **Adsorbing Ion Exchange Resins**, e.g., Styrene-Divinyl Benzene Co-polymers having varying Divinylbenzene content; **Used for organic & weak Electrolytes**
  • **Chelating Ion Exchange Resins**, e.g., Styrene-Divinyl Benzene Co-polymer having different functional groups like Aminophosphonic acid, Iminodiacetic acid, Thiol, Thio-Uronium functional groups for Chelation; **Used for selective extraction of specific metals**
  • **Liquid Cation Exchangers**: Bis-(diethylhexyl) Phosphoric acid (HDEHP), 2-diethyl hexyl diethyl hexyl phosphonic acid (HEHEHP) in Hydrocarbon; **Used for extraction of Rare earths**
  • **Liquid Anion Exchangers**, e.g., Trioctylammonium Chloride, Trioctylmethylammonium Chloride in Hydrocarbon; **Used for extraction of various Anions**
A = Cation Exchange Resin
B = Anion Exchange Resin
C = Non Ionic Adsorption Resin
ION EXCHANGE PROCESS : KEY ISSUES

• ION EXCHANGE EQUILIBRIUM & SELECTIVITY:
  • - The Ion Exchange Isotherm
  • -The Separation Factor
  • -The Selectivity Co-efficient
  • -The Thermodynamic Equilibrium Constant
  • -The Distribution Co-efficient
  • Selectivity Co-efficient are not constant & vary with Experimental conditions viz., Conc. of solution, Temp., presence of other ions.

• Rules of Thumb for Exchanging Ions: i) increasing charge, ii) increasing atomic no. ; e.g., for cations:
  • $Li^+ < H^+ < Na^+ < K^+ < Cs^+ < Mg^{2+} < Co^{2+} < Ca^{2+} < Sr^+ < Ce^{3+} < La^{3+} < Th^{4+}$ ; &

  for Anions: $F^- < CH_3COO^- < Cl^- < Br^- < CrO_4^{2-} < NO_3^- < I^- < C_2O_4^{2-} < SO_4^{2-}$ ;
ION EXCHANGE PROCESS: KEY ISSUES

- **ION EXCHANGE SEPARATION PROCESS & SORPTION: THREE TYPES**
  - **Physical Sorption**: No exchange of Ions, adsorption –desorption process through inter-molecular attractive forces. Temp. has pronounced effect
  - **Chemical Sorption**: Separation through Chemisorption of solutes in matrix, difficult to desorb by temp. effect
  - **Electrostatic Sorption (Ion Exchange)**: Coulombic attractive forces between Ions and charged Functional Groups
  - Many factors affect the Sorption Process viz., Temp., size of solute, degree of cross-linking of the Exchanger, presence of other ions, dissociation of electrolytes etc.

- **Ion Exchange Capacity**: No. of Functional Group on Resin, denoted by meq/gm of dry resin in H\(^+\) or Cl\(^-\) form or meq/ml of wet resin supplied;

- **Ion Exchange capacity** varies for different type of Resin & is most important factor for an Ion Exchange Column system
ION EXCHANGE PROCESS: KEY ISSUES

• The operating or breakthrough Capacity of an Ion Exchange system is the volume of the solution that can be treated and depends on: Nature of functional group, Degree of cross-linking, Conc. of the solution, Ionic valence, Ionic size, Temp., Presence of other ions;

• Kinetics & Dynamics:
• The Ion Exchange Reaction occurring between Resin & the Solution involves following five distinct steps:
  a) Diffusion of the ions through the bulk solution to reach Ion Exchange Particles;
  b) Diffusion of the ions through the hydrated film surrounding the particle;
  c) Diffusion of the Ion through the film-particle interface;
  d) Diffusion of the Ion through the particle;
  e) The actual chemical reaction involving exchange of ions
• Steps (a), (c) & (e) are fast; Steps (b) & (d) controls the kinetics
ION EXCHANGE SYSTEM OPERATION

- Four Modes of Operation:
  - i) Batch, ii) Fixed Bed, iii) Fluidized Bed, iv) Continuous
- Most commonly used Continuous System (Column) operation involving four basic steps: 1. Service (Loading), 2. Backwash, 3. Regeneration, 4. Rinse.

- Column Design Basis:
  - Column dimension (L/D ratio) & Resin volume are decided based on volume of solution to be treated per day, Pressure drop across column & volume expansion at various steps (normally 50% Resin is filled)
  - Service: Defines volume of solution to be treated per cycle & Rate of flow, based on Operating Capacity of Resin (BV/Hr.)
  - Backwash: Washed with water mostly in the reverse direction to remove residual hold up solution, break-up of resin clumps, remove fine suspended particles, eliminate gas pockets, avoid compacting and brings uniformity in resin bed
ION EXCHANGE SYSTEM OPERATION

- **Regeneration**: Replaces Ions exchanged during Service & returns resin to its critical exchange capacity.

- **Regeneration Efficiency**: The ratio of the total equivalents of Ions removed from a resin to the total equivalents of Ions present in the volume of regenerant used.

- Strong Acid & Strong Base Resins are good in Service & work in broad pH range, but difficult to regenerate. *(Poor Regeneration efficiency)*;

- Weak Acid & Base Resins are used in narrow pH range, but easy to regenerate *(Good Regeneration efficiency)*;

- Type of Resin, Service (Breakthrough Capacity) & Regeneration are exploited innovatively to develop Greener Processes *(Fishing out of valuable molecules in Effluent, recovering them & suitably applying chemical modification to for Recycle)*
ION EXCHANGE PROCESS DEVELOPMENT

Typical Laboratory Scale Evaluation:

- Column used: 1” Dia & ~ 1 m length
- Resin Height: ~ 80 cm
- Volume: 400 ml
- Typical Adsorption isotherm determined to estimate the x/m values.
- Conduct the actual ion exchange experiments by passing the streams using a peristaltic pump at flow rates (normally 3-5 BV/Hr.) corresponding to a flux of 5 m³/m²
- Determine the Breakthrough Capacity (exhaustion curve) for the system.
- Validate the results.
- Calculate the scale up factors for Pilot plant trials.
ION EXCHANGE PROCESS DEVELOPMENT

Pilot Plant Scale Evaluation:

- Column used: 4” Dia & ~ 1 m length
- Resin Height: ~ 50 cm
- Volume: ~ 4000 ml
- Conduct trials & validate the results.
- Minimum of 5 trials for reproducibility.
- Validate the results & generate relevant Design Operational Basis (DOB) data for plant implementation.
ION EXCHANGE TECHNOLOGY: SCALE-UP ISSUES

- **Step 1**: Determine the Volume of Solution to be treated per cycle & amount of Ions to be removed
- **Step 2**: Establish the resin capacity & regeneration level
- **Step 3**: Determine the Volume of resin needed
- **Step 4**: Determine the Column diameter, Pressure drop & Backwash requirement
  - Cross-sectional Area = Resin Reqd./ Bed Height
  - Column Diameter = \( \sqrt{\text{Cross-sectional Area} \times 4 \pi} \);
- **Step 5**: Determine Regenerant requirement & Flow Rate
  - Generally 1-2 meter Resin bed height & 100% free board Volume is taken for Column height design & Flow rate of 4-5 times of cross-sectional area is used for efficient exchange.
  - More no. of Columns are also used based on need & Conc. of Regenerant, its volume & Temp. are varied to get effective regeneration.
Resin column

Top Distributor Plate having 3 mm dia holes & venting arrangements

RESIN

SPARGER
Bottom Perforated plate, support for Resin & Filter
IMPLEMENTATION: ANION EXCHANGER

- Problem: Removal of Chloride Ions (Cl\(^-\) ) from Aq. Q\(^+\) OH\(^-\) Process Stream

Issues: - Recycle stream in Process : key for Process economics & Greenness
- Stream unstable on heating, increase in Carbonate formation on exposure, corrosive, Cl\(^-\) accumulation undesirable for the process,
- Difficult to dispose & costly

Solution:

- Efforts by Chemical methods like fractional crystallization, extraction with various agents like Solvents & others are unviable & generate huge waste.
- Study using SBA resin in OH\(^-\) form explored and detail Lab & Pilot scale Column trials provided all the data like Breakthrough Capacity, Process conditions like Temp. & flow rate for Service & Regeneration methods.
- Successfully implemented in Plant scale ( 50 M3 /day) with controlled Cl\(^-\) level (< 200 ppm) in Process stream & made process economical & Greener. Regeneration efficiency albeit poor, but most economical.
IMPLEMENTATION: ANION EXCHANGER

- **Problem**: Removal of Costly Metal Complexes from Process Stream & Recovery and Reuse.
- **Issues**: - Leaching of Metal Complexes in Process is inherent
  - Contamination in Product not desirable,
  - Loss of Costly metal complex affects economics
- **Solution**: - Efforts to reduce leaching in process did not work due to Process limitations & Extraction by Chemical methods not feasible.
  - Extensive lab trials with various solid adsorbents including Ion Exchangers done & found Anion Exchange Resin (SBA) very effective in capturing as the complex is found to be anionic.
  - Regeneration of Resin is difficult and practically very inefficient to recover metal complex. Incineration of resin and recovery of metal is found most economical.
  - Lab & Pilot scale trials done to determine Breakthrough Capacity and as the metal complexes are in ppm level, adoption of this approach is viable.
  - Plant scale implementation done & from Resin incineration, costly metal is recovered & recycled to make process economically viable.
IMPLEMENTATION: CATION EXCHANGER

- **Problem:** Removal of PTC (Q⁺ OH⁻) from large Organic Process stream
- **Issues:**
  - Undesirable in down-stream steps due to impurity formation
  - Washing generates large Aq. Effluent stream
  - Recovery & Recycle will make process more economical
- **Solution:**
  - Selective capture of Q⁺ OH⁻ in SAC column by passing organic stream
  & Backwashing to remove organics by liquid feed input & then water
  - Regeneration with Acid to recover PTC for recycle as well as regeneration of SAC column for reuse.
  - Lab & Pilot scale study done to establish all process condition for Plant implementation
  - Resulting in ease of plant operation, Better Product Quality, Substantial pollution reduction and recovery of PTC
IMPLEMENTATION: ION EXCHANGE ADSORBER

- **Problem**: Recovery of ArSO$_3$H from Aq. Effluent & Recycle
- **Issues**: - High Effluent load to ETP and non-biodegradability
  - Loss of valuable raw material & higher treatment cost

**Solution:**
- Efforts to remove ArSO$_3$H from Aq. washings by various chemical methods economically did not work out
- Trials with Anion Exchange Resins although found good in loading, but Regeneration efficiency is very poor & not feasible
- Trials with Adsorbing Type non-ionic Ion Exchange Resin gave good result both in Loading & Regeneration with alkali. Lab & Pilot study gave reproducible result & generated scale-up data for Plant.

- 90% COD reduction of Aq. effluent stream with ~99% recovery of ArSO$_3$H which in turn recycled in Process by reacting with one of the reactant using suitable chemical method.
IMPLEMENTATION: ION EXCHANGE ADSORBER

Problem: Recovery of ArCOOH from Aq. Effluent & Recycle

Issues: - High Effluent load to ETP and non-biodegradability
- Loss of valuable raw material & higher treatment cost

Solution:
- Efforts to remove ArCOOH from Aq. washings (effluent) by various chemical methods economically did not work out
- Trials with Anion Exchange Resins although found good in loading, but Regeneration efficiency is very poor & not feasible
- Trials with Adsorbing Type non-ionic Ion Exchange Resin gave good result both in Loading & Regeneration with alkali. Lab & Pilot study gave reproducible result & generated scale-up data for Plant.

- 90% COD reduction of Aq. effluent stream with ~95% recovery of ArCOOH which in turn recycled in Process using suitable chemical purification.
SUMMARY: PATHWAY TO GREENING

- Critical Analysis of Process Streams & Aq. Effluent streams, Process could be made Greener by Innovative adoption of Ion Exchange Technology by “Fishing Out” valuable species from large volumes of effluent solution.

- Recovery of these valuable species (raw materials, catalyst, intermediates & Products) through effective Regeneration techniques in minimum volume & Recycle these species (as such or through chemical modification), Atom economy can be improved in an indirect way, without making change in the basic process.

- This strategy can be adopted in many existing processes where major change of process in both chemistry and hardware are difficult & hence Sustainable Processes can be developed in terms of Economics & Greening of the Process.
INSPIRATION

• WE DO NOT INHERIT THE EARTH FROM OUR ANCESTORS, WE BORROW IT FROM OUR CHILDREN----- David Brower
SUCCESS IS A JOURNEY, NOT A DESTINATION. THE DOING IS MORE OFTEN IMPORTANT THAN THE OUTCOME- Arther Ashe

THANKS