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Wastewater treatment by ion exchange method: a review of past and recent researches

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ABSTRACT

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. Ion exchange can be a process of purification, separation and decontamination of aqueous or ion containing solutions. Ion exchange resins are used in wastewater treatment process plants to interchange one ion with another to fulfill the purpose of demineralization. In this assignment, we look at the working principle, equipment design, advantages and disadvantages, and industrial applications of ion exchange as a water pollution remediation technique.

KEYWORDS

Ion exchange;
Electrolyte;
Resin;
Water treatment.

INTRODUCTION

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. Ion exchange can be a process of purification, separation and decontamination of aqueous or ion containing solutions. They are usually ion exchange resins, zeolites, clay or soil humus. They are primarily either cation exchangers that exchange positively charged ions or anion exchangers that exchange negatively charged ions. Along with absorption and adsorption, ion exchange is a form of sorption.

Ion exchange systems generally contain ion exchange resins which are operated on a cyclic basis. Water is passed through the basis till it is saturated, in which condition, the water coming out of the resin contains more than desired concentration of the ions that have to be removed. The resin is then regenerated by backwashing the resin to remove the accumulated solids, flushing removed ions from the resin with a concentrated solution of replacement resin. Hence the production of backwash limits the use of ion exchange in wastewater treatment.

In this assignment, we look at the working principle, equipment design, advantages and disadvantages, and industrial applications of ion exchange as a water pollution remediation technique.

PRINCIPLE

Ion exchange resins are used in wastewater treatment process plants to interchange one ion with another to fulfill the purpose of demineralization. There are 2 types of ion exchange resins, one is the system of cation resins and the other one is the anion ex-

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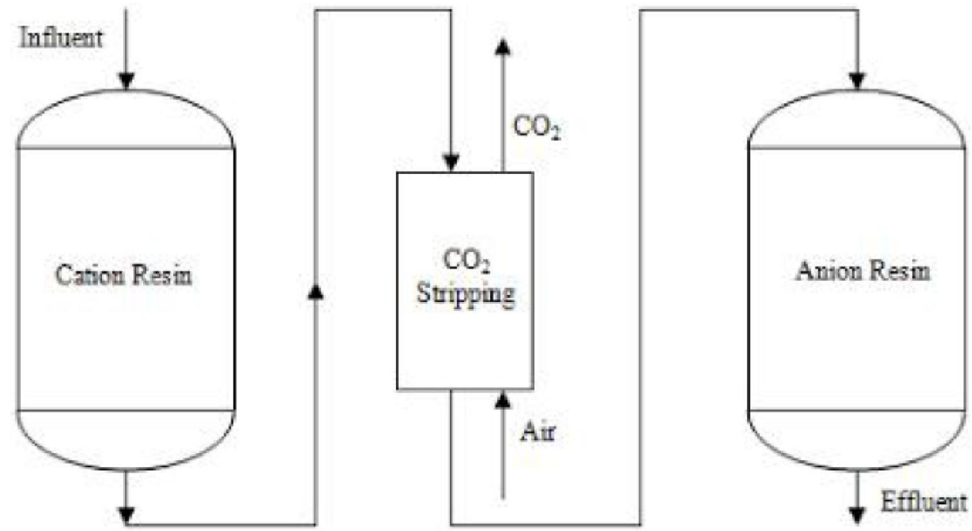

Figure 1 : An ion exchanger

change resins. Its materials can be also broken down to different groups and systems but it depends on whether it is weak acid anion, or a strong base cation or it can also be a weak base anion. The type of exchangers is not that important as resins are very sensitive of the phenomena of fouling which is caused by active presence of the organic matter in water which is not treated. Therefore, it is important that a separate section should be used to remove any type of suspended solids, if present. It should be done before the influent undertakes any treatment process. Also, soluble organics should also be removed if possible so as to put fewer loads on the ion exchange unit.

The working of the whole process can be explained by a simple example. In a demineralizer, water of the influent passing through cation exchange resin will lose all cations. These metallic cations become acids and the ion loss is replaced by same corresponding number of Hydrogen ions. These generated acids are then removed via a regenerated anion exchange resin which is alkaline. But this time, the anions are replaced by corresponding amount of hydroxides in wastewater. The bed capacity is limited to a certain fixed amount, so the resin becomes exhausted and thus undergoes the regeneration process. Anion resin is regenerated via sodium hydroxide whereas cation exchange resin is regenerated using either sulphuric or hydrochloric acid.

Distinct ion exchange bed, other than clustered together conferring to its functional groups can also be separated into various types depending on its solubility. Obviously for it to be operational, the constituents must be insoluble in normal circumstances and for that to occur, usually high molecular weight composite has to be chosen. Bead size is also another measure that decides the type of resin suitable for general use. Essentially a certain granular size is wanted so that the molecules that form the entire structure does not clasp on together too compressed and there should be a certain null and void volume to avoid massive fluid head loss. The physical characteristics on how the beads are organized will also disturb the ion exchange bed physical robustness whether it is good enough to endure expansion and contraction due to change in temperature without danger of bursting or failing taking place. One more thing to take note is that conditional to the procedures used for backwashing and particularly in cases whereby there is an unrestrained high flow rate caused by mismanagement; this can lead to blow off of resins coming out from the vessel and causing in capacity loss of the beds. Consequently, typical attrition losses can be predictable to be within 5 to 20% dependent on which type of ion exchange resin present in the systems.

Ion exchange softening, similarly known as Sodium Zeolite Softening is a characteristic example of how the ion exchange process works to decontaminate the water by eliminating the hardness level instigated by existence of calcium and magnesium. This is generally used in steam boilers and industrial water treatment presentations. When the bed gets totally saturated with Ca and Mg ions, it is renewed and regenerated mainly by increasing the total of sodium ions. This is done by first doing backwashing to minimalize compactness of the bed and to discharge surrounded air pockets. Afterwards, it will be monitored by the real regeneration process by means of brine solution. When this is accomplished, rinsing will be voted for to eliminate whatever extra brine left in the exchange bed. In current designs, all these processes are done using automated programs which can sense the level of saturation and tell the operators to act as a result. Generally, depending on the influent characteristics, this will define the frequency desired to carry out the full regeneration cycle.

ADVANTAGES AND DISADVANTAGES

The advantage of ion exchange as a water remediation technique is that it is very cost effective. Very little amount of energy is required and regeneration of resins is very economical. If resins are maintained efficiently, they last for many years before they have to be replaced. However, there is a long list of limitations attached to this particular technique, which makes it one of the lesser used technique.

Calcium sulphate fouling

"Sulphuric acid is one of the cheapest cation resin regenerant and is widely used. Some water supplies contain a high proportion of calcium which on reaction with sulphuric acid forms calcium sulphate. This fouls the resin and blocks drain pipes with a buildup of scale. Under such circumstances, hydrochloric acid is used as a substitute".

Iron fouling

Bores yielding anaerobic water from underground supplies contains iron in Fe2+ state in abundance. Small amounts are readily removed by sodium cycle softeners but care must be taken to prevent contact with air prior to treatment. Oxidation of Fe2+ to Fe3+ occurs and consequent precipitation of ferric hydroxide which clogs again, resin beds and prevents ion exchange. Iron fouling is the commonest cause of softener failure.

Adsorption of organic matter

Presence of organic matter in water supplies is a very common problem. Untreated water from lakes and rivers usually contains dissolved organic material derived from decaying vegetation which imparts a yellow or brown colour to it. These substances can become irreversibly adsorbed within the anion beads, reducing their exchange capacity and leading to a reduction in treated water quality. The aforementioned organic matter is removed, prior to demineralisation, by flocculation with alum or ferric salts followed by filtration which removes the metal hydroxide floc and the co precipitated organic compounds. This treatment also removes any fine silt which represents another source of resin fouling. Both organic and iron fouled units can be chemically cleaned on site but complete removal of impurities is rare and resin performance usually suffers after fouling.

Organic contamination from the resin

The resins themselves can be a source of nonionized organic contamination. New commercial grade resin often contains organics remaining after manufacture, unlike very old resins, which shed organic fragments as the polymer structure opens up very slowly. Although such contamination can be ignored for many uses, it is necessary that they are removed, by passing the demineralised water through an ultra filtration membrane.

Bacterial contamination

Resin beds do not act as filters for the removal of bacteria or other micro-organisms. Persistent accumulations of organic matter, if not flushed, serve as a growing bed for bacteria, since they are a source for nutrients. Hence, when sterile water is required it can be obtained by treating the demineralised water by non-chemical means such as heat, ultraviolet irradiation or very fine filtration. Resins beds can be decontaminated with disinfectants such as formaldehyde, but heat or oxidizing disinfectants such as chlorine, damage the resins, hence must not be used.

Chlorine contamination

As stated above, chlorine damages resins. This means that even town supply water is an unsuitable demineraliser feed because of the trace of chlorine it contains. It is customary to treat such feeds by passing them through activated carbon which removes chlorine very efficiently.

APPLICATIONS

Softening

A strong acidic cation exchange resin is used in sodium form. Water hardening occurs due to the presence of alkaline earth metals such as calcium and magnesium. These ions prevent soap from forming micelles. Ion exchange method is used to soften water by exchanging these elements with sodium ions.

Demineralization

When all the minerals from water must be removed to produce extremely pure H_2O, ion exchange method can be used. The water must first be passed through cation resins in hydrogen form, where all the cations in the water will be removed and then it must pass through anion resins in hydroxyl group where all the anions will be removed with the ones from the resins. Thus at the end of the process we expect these new ions, H^+ and OH^-, to combine to form water molecule. The treated water contains only slight amount of sodium and silica. This technique is used mostly in purifying drinking water and for household use.

In sugar industry

Color removal from cane sugar syrups after evaporation- the crystallized sugar that we use in our day to day life is processed to increase the crystalline yield by removing the organic compound that also impart color to the sugar. The color removal process uses strongly basic anion exchange macro porous resins, regenerated with NaCl solution. The macro porous nature allows the molecules with high molecular mass to be removed.

In beverages

a. Used in the treatment of water used to make beer or soft drinks.
b. Removal of metals
c. Removal of bad taste and smell
d. Imparting or removing color with non ionic adsorbent.
e. Gelatin demineralization- produced from the collagen produced in pig skin and bones, gelatin must be dematerialized to provide high purity.

Chemical industry

a. Removal or recovery of metals: recovery of gold from industrial jewelries is one of the most known applications of ion exchange method.
b. Production of chlorine and caustic soda: in the production of caustic soda and chlorine, absence of divalent metals is crucial. Ion exchange is one of the ways in which it is achieved which reduced the concentration of calcium to a very low value.
c. It is also used in the removal of sulphuric acid and organic acids from streams during phenol production.

As a catalyst

In petrochemical industries, where mineral acid was used earlier as a catalyst, nowadays a strongly acidic cation exchange resin in the H+ form is used. Examples of the reactions that use this method are:

a. Alkylation
b. Condensation
c. Etherification
d. Dehydration
e. Hydrogenation

In pharmaceutical industries

a. Extraction and purification of antibiotics: ion exchange resins are used for the purification of drugs after extracting them from the fermentation broths. Examples: streptomycin, gentamycin etc.
b. Slow release formulation: the resins are sometimes used as drug carriers. They help carry the active ingredient via adsorption into the body where it is slowly released.
c. Taste masking: resins are used to mask the taste and smell of drugs.

DESIGN

The aim of ion exchange is the reduction of Total Dissolved Solids (TDS) in water to an acceptable value. Water contains several ions which are responsible for its hardness (Ca^{2+} and Mg^{2+}) and alkanity (HCO_3^-, Cl^-, SO_4^{2-}, NO_3^- etc). These ions can be separated through ion exchange by either cation or anion resins, depending on their polarity. Ion exchange processes can be divided into various categories:

1. Softening
2. Dealkalization
3. Demineralization

A typical ion exchange unit is shown in the figure:

Ion exchange resins are kept in a specially built tank forming a bed, which is usually 30-65 inches deep. In some cases, specially support materials such a gravel or anthracite are used. In the process, water enters through the top of the exchangers, spreads uniformly over the surface of the resin, ion exchange takes place and the treated water is collected from the bottom.

Several new ion exchange processes are used now because of their higher operating efficiencies and low leakage rates. These include cross flow and co-current flow regeneration of exchange resins.

There are mainly two types of ion exchange resins:

Cation exchange resins

Strong acid cation resins have H^+ ions as the exchanger which exchange ions with the cation present as TDS in untreated water. For regeneration, a dilute acid solution is passed through the ex-

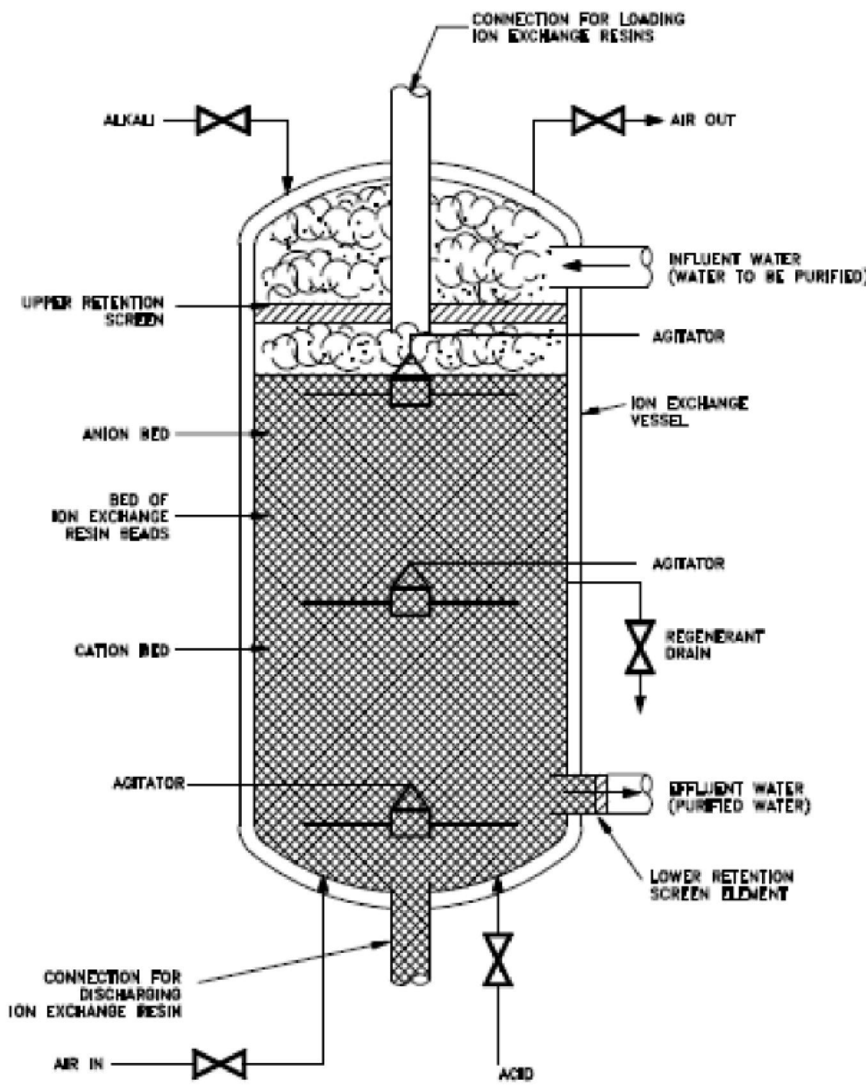

Figure 2 : A typical ion exchange (Source: knowledge publications.com)

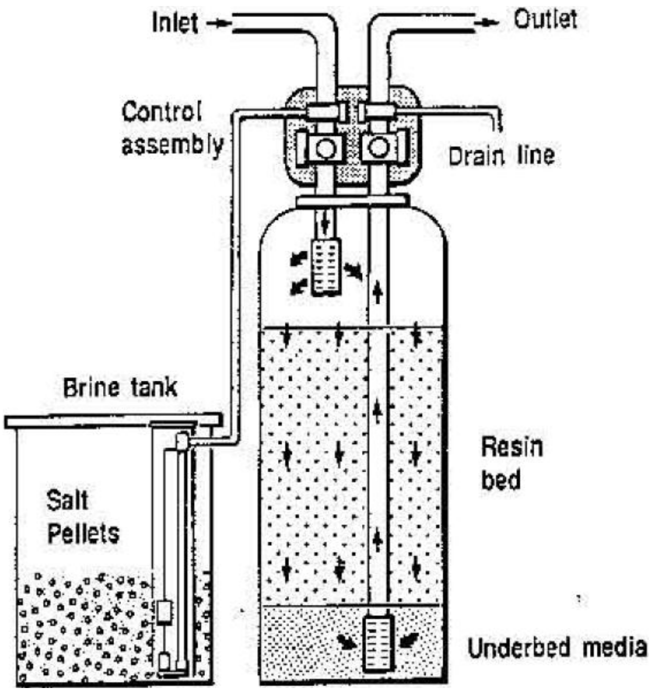

Figure 3: Softening by ion exchange (Source: www.aquatechnology.net)

hausted bed which leads to cations exchanging with the H^+ ions present in the acid.

Anion exchange resins

Strong base anion resins have OH^- ions as the exchanger which exchange ions with the anions present as TDS in untreated water. For regeneration, a solution of dilute NaOH is passed through the exhausted resins which is exchange back the anions with OH^- ions present in the base.

Softening

While designing ion exchangers for softening process, resins are selected such that they have rapid kinetics and a structured exchange matrix that facilitates efficient cleaning even in adverse conditions with the same level of performance across the operating temperatures. There are various factors to be kept in mind while designing softening resin exchangers

If the flow rate of water is high, resin columns with more depth are required for effective exchange. Pressure loss should be minimized over the column area. In order to avoid channeling, the service flow should be kept more than 2 gpm/ft^2.

The temperature of water affects the pressure drop in the column. Cold water will increase the pressure drop. Also, it reduces the rate of ion exchange and there by a greater depth of the resin column is required for adequate exchange. At the same time, for warm water a faster backwash is required in order to provide sufficient bed expansion.

The more the hardness of water, more depth of the resin columns will require ensuring sufficient ion exchange. This is because hard water will have more number of complicating ions. Also, cleaning resins might require cleaning agents in this case which can damage the resins.

Softening resins (Na^+, K^+) have different affinities for cations present in water. Hence, the ions in water will not only replace the ions in the resins, but also other ions which have less affinity towards the resins. Organic compounds and bacteria can foul ion exchange sites, thereby reducing the capacity of ion exchange, as well as creating sites for harmful bacteria.

As the conductivity of water increases, more amount of TDS will be present in it, which means that more numbers of ions will be exchanged from the resins, and hence the bed capacity will be used up faster and there is a possibility of hardness leakage.

Dealkalization and demineralization

Alkanity in water is present in the form of carbonates, bicarbonates, carbon dioxide and hydroxides. Ion exchange process is usually a batch process. The demineralization process of ion exchange involves the following:

1. Resin bed exhaustion
2. Resin bed backwashing
3. Resin regeneration
4. Resin rinsing

While selecting the resins the following things should be kept in mind:

For strong acid cation exchanger, Na^+ is the best choice as it will be the first one to escape from the resin.

For strong base anion exchanger, SiO_2/HCO_3^- is the best choice as it loosely held by the resin cations and will be the easiest to escape.

Reactions that take place at resin exhaustion are:

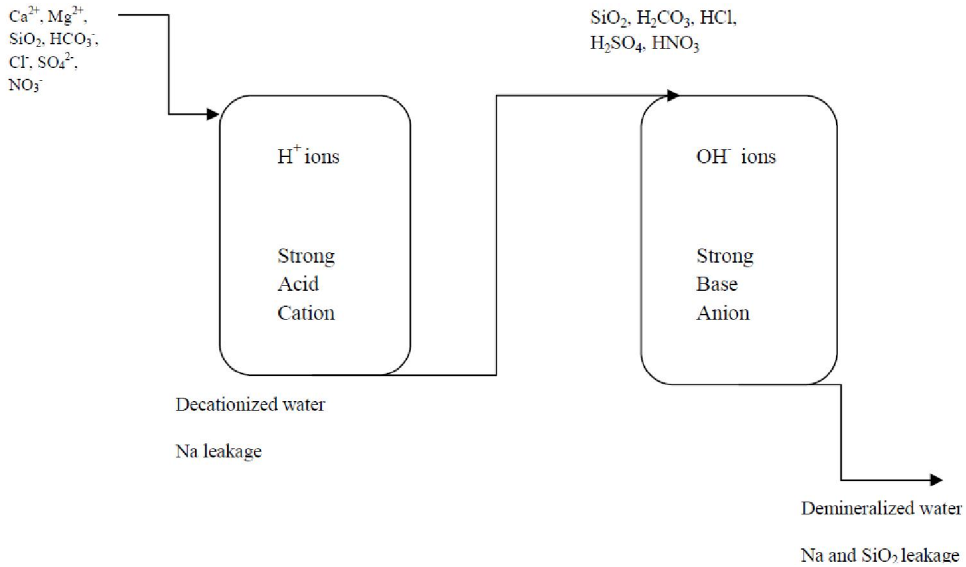

Figure 4 : Demineralization of water (Source: www.soci.org)

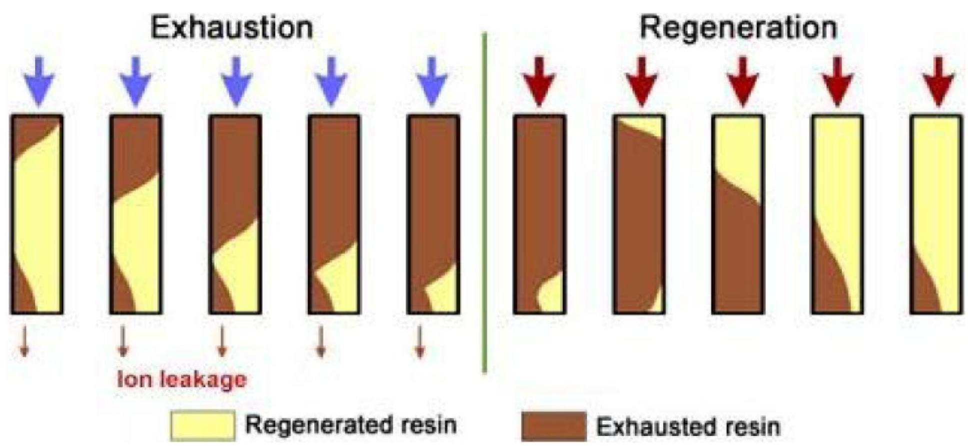

Figure 5 : Co-current flow regeneration (Source: dardel.info)

Cation exchange

$$R^-H^+ + M^+A^- \leftrightarrow R^-M^+ + H^+A^-$$

where, R^-H^+: regenerated resin; M^+A^-: TDS; R^-M^+: Exhausted resin

Anion exchange

$$R^+OH^- + H^+A^- \leftrightarrow R^+A^- + H^+OH^-$$

where, R^+OH^- : regenerated resin; H^+A^- : TDS; R^+A^- : Exhausted resin

While regenerating resins, two types of methods are used:

Co-current flow: In this the regenerating agent is made to flow in the same direction as the feed was flowing. It is less efficient as compared to the other method.

Countercurrent flow: In this type of regeneration, the regenerating agent is passed through the exhausted resin bed in a direction opposite to that of the feed. It is more efficient as it reduces the leakages and also decreases the operating costs at the same increasing its effectiveness.

The breakthrough curve of an ion exchanger shows the ion concentration in the effluent on the y axis versus the effluent throughput volume on the x axis. The area above the breakthrough curve denotes the quantity of ions exchanged by the resin given by:

$$\int (Co - C)dV$$

At breakthrough volume, the area above the breakthrough curve is equal to the amount of ions removed by the resin. At complete exhaustion, the area above the breakthrough curve is equal to maximum amount of ions removed by the resin. Hence in this way we can determine the amount of ions ex-

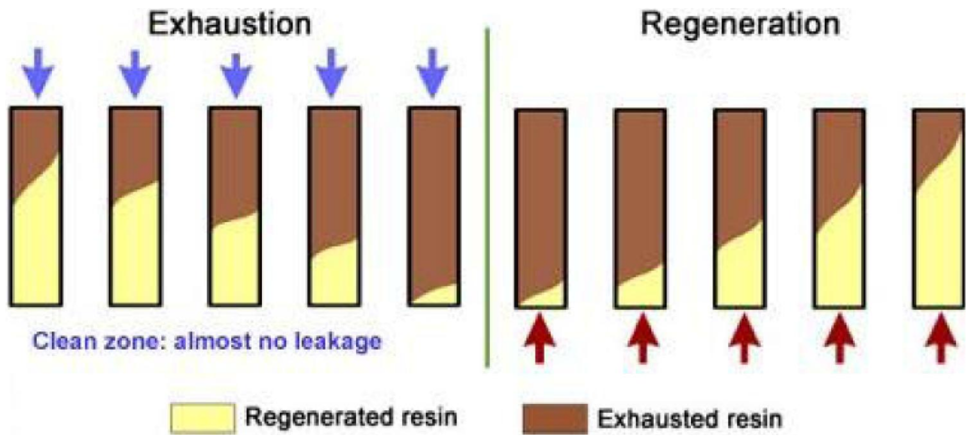

Figure 6 : Countercurrent flow regeneration (Source: dardel.info)

changed and design an ion exchanger likewise keeping in mind all the above criteria.

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