

Principles of Ion Exchange in Wastewater Treatment

In treating many types of wastewater, ion exchange is required. This article examines the principles of ion exchange and gives an overview of different types of resins.

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Whenever an ion is removed out of an aqueous solution and is replaced by another ionic species, this is what we generally refer to as "ion exchange". There are synthetic materials available that have been specially designed to enable ion exchange operations at high performance levels. Among many other applications, these so called "ion exchangers" can be used in processes of environmental protection such as purification, decontamination, recycling or even for the design of new environment-friendly production processes.

Synthetic and industrially produced ion exchange resins consist of small, porous beads that are insoluble in water and organic solvents. The most widely used base-materials are polystyrene and polyacrylate. The diameter of the beads is in a range of 0.3 to 1.3 mm. The beads contain around 50% of water, which is dispersed in the gel-structured compartments of the material.

Since water is dispersed homogeneously through the bead, water

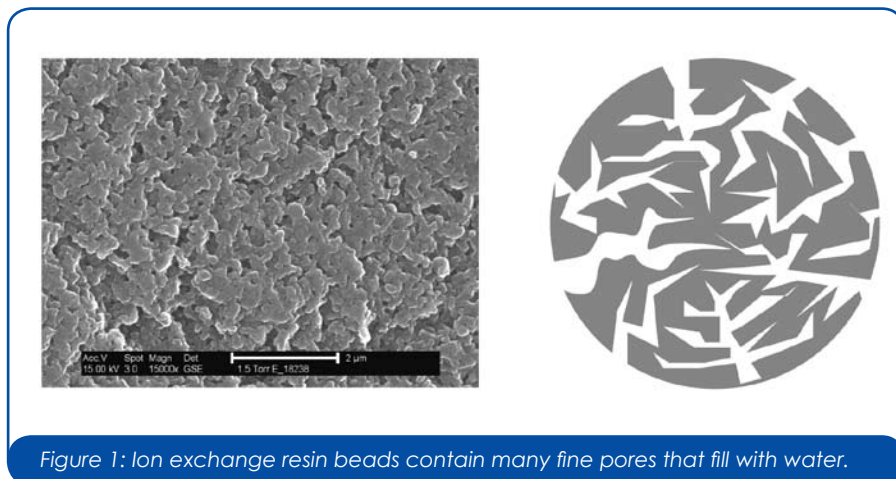


Figure 1: Ion exchange resin beads contain many fine pores that fill with water.

soluble materials can move freely, in and out.

To each of the monomer units of the polymer, so called "functional groups" are attached. These functional groups can interact with water soluble species, especially with ions. Ions are either positively (cations) or negatively (anions) charged.

Since the functional groups are also charged, the interaction be-

tween ions and functional groups is exhibited via electrostatic forces. Positively charged functional groups (e.g. a quarternary amine) interact with anions and negatively charged functional group (e.g. a sulfonic-, phosphonic- or carboxylic acid group) will interact with cations.

The binding force between the functional group and the attached ion is relatively loose. The exchange can be reversed by another ion passing across the functional group. Then another exchange reaction can take place and so on and so forth. One exchange reaction can follow another.

The Principle of Selectivity

There is a huge variety of existing ions. Let us especially have a look at the different types of cations. We distinguish different types of alkali-cations (sodium, potassium), of earth- and rare-earth-alkali-cations (magnesium, calcium,



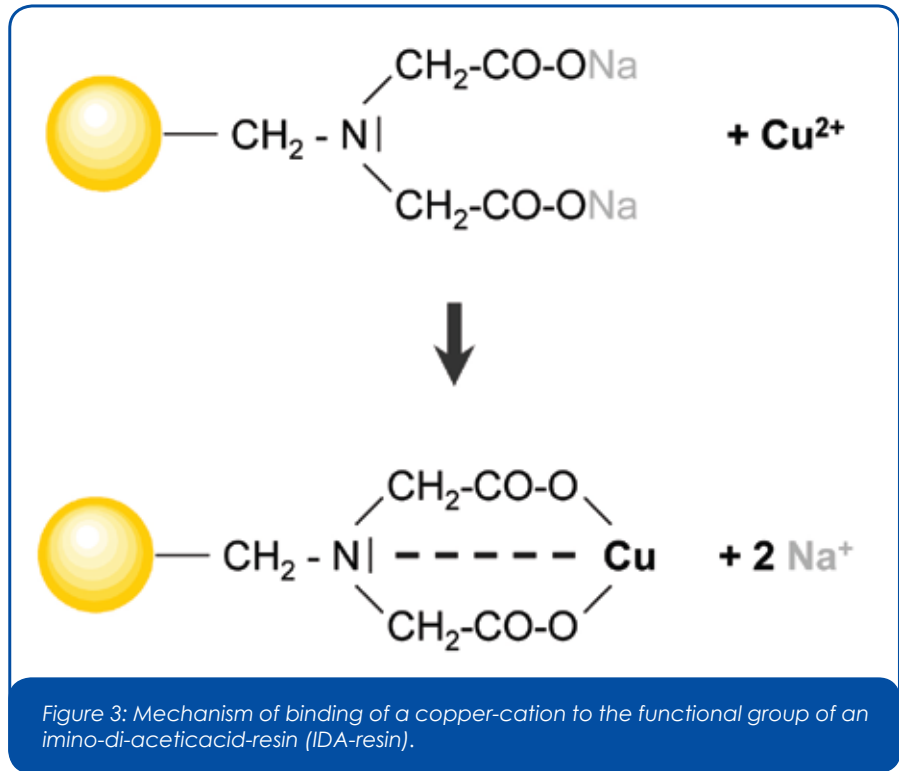
Figure 2: a fixed and a mobile ion are changing places in a so-called ion exchange reaction. This simple reaction scheme is the base for more than 500 applications involved in the purification of water and other fluid media.

strontium, barium, lanthanum, iridium), heavy metal ions (lead, cobalt, nickel, mercury), light metal cations (aluminium, beryllium, titanium), semi-metal-cations (germanium, gallium, indium), noble metal cations (gold, silver, platinum, palladium).

By investigating the adsorption of different kinds of cations on ion exchange materials, it is found that different ions do interact differently with the functional groups of ion exchangers. Some are strongly bound, some are less strongly bound.

This results in the fact, that a weakly bound ion can preferably be displaced by a stronger binding ion. This effect is called the principle of "selectivity". A more selective ion binds more strongly than a less selective ion.

The effect of selectivity can be used to remove distinct ions from water and to replace them with



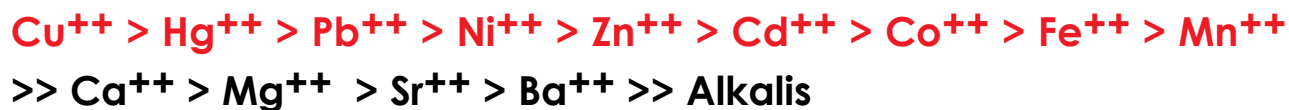


Figure 4: Selectivity series of an imino-di-acetic acid (IDA)-resin. Only a selection of ions (mainly divalent ones) is given. Heavy metal ions are preferably bound.

others. Applications are found not only in industry, but also in household, where the use of ion exchangers for water softening is well known. In water softening applications the hardness causing calcium-cations are bound and exchange the weaker binding sodium or hydrogen cations.

Especially for wastewater applications so called "chelating resins" have been developed, which have a high selectivity for toxic heavy metal ions. These materials selectively adsorb the toxic components from the waste stream and leave the less toxic components, such as earth alkali and alkali metals untouched.

The high affinity of chelating resins towards heavy metal ions is accomplished via the formation of a so-called "complex - bonding". In this special type of bonding the functional group and the ion do not only interact via electrostatic forces. Additionally there is a so-called "coordinative bonding" which supports and strengthens the

interaction, making it tighter than a usual binding. In Figure 3 there is an example of this type. The exchange of sodium ions by a copper ion is shown. The copper is bound via two electrostatic types of bonds and by the interaction of the sole electron pair of the nitrogen atom of the functional group.

The selectivity of ion exchange resins is expressed via the so-called selectivity series. Figure 4 shows the selectivity series for an IDA resin. As can be seen, the heavy metal ions bind more strongly than the alkali earth ions and these bind more strongly than alkali metals.

The Principle of Equilibrium and Mass Action

Selective ions displace less selective ions as mentioned previously. The exchange continues as long as there are enough selective ions available for the resin to exchange and/or until the functional groups are saturated with the selective ions.

In some cases this means that

all of the functional groups have lost the less selective ion and have taken up a selective ion. It can also mean that the exchanger reaches a certain level of loading with a certain ratio of functional groups that remain un-exchanged and still carry the less selective ions. This effect is called the effect of equilibrium or in other words the effect of mass action.

This effect comes from the fact that the less selective binding ions still affect the degree of exchange. Due to the weaker interaction force however, its effect is not as great. Even though the attraction forces are weak, the effective force increases with the concentration of the less selective ions. For example, if the attraction force is 100 times weaker but the concentration is 100 times higher; the less selective ions can equal the higher selective species in the final reaction. This is called the impact of mass action. As a result, to understand the exchange rate in a certain exchange situation, both the binding force and the concentration levels must be considered.

Thus dealing with ion exchange applications in wastewater treatment requires a full knowledge of water composition to judge competing effects. Once known, a better understanding of the efficiency of the process can be realised. If the ratio of concentrations of less selective to highly selective ions is low, high operating capacities resins can be expected. If the ratio of concentrations is high, lower operating capacities will be realised. Therefore the efficiency of a wastewater treatment process always depends on the water composition which is individual - as already mentioned.

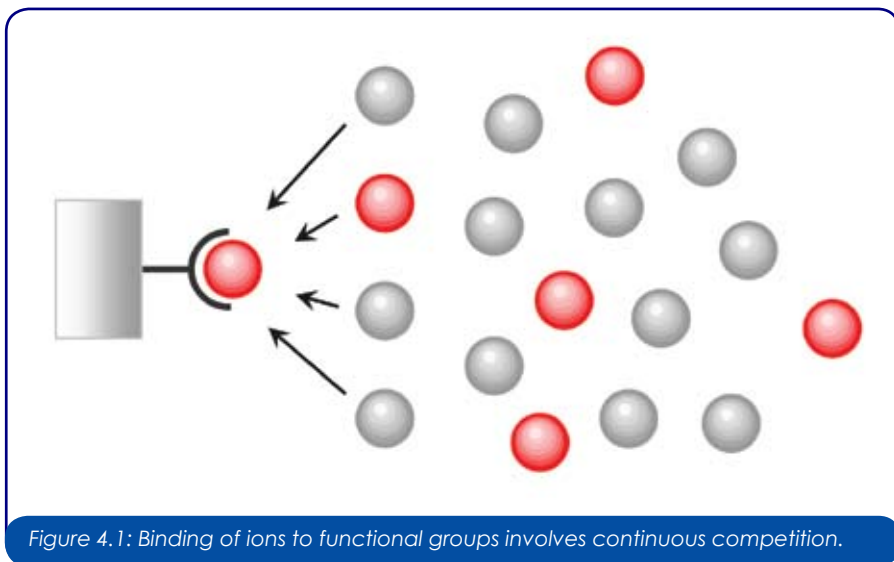


Figure 4.1: Binding of ions to functional groups involves continuous competition.

Regeneration of Ion Exchangers

The principle of displacement of selectively binding ions by less selective binding ion is the basis for each regeneration procedure. Most ion exchangers can be regenerated by acids (excess of H⁺-ions), salt-brines (excess of sodium or chloride ions) or by alkali (excess of OH⁻ ions). During regeneration the adsorbed ions are removed and replaced by the ions named above.

The spent regenerant solution contains the formerly adsorbed pollutants in a concentrated form. In some cases the solutions must be treated for disposal. In other cases the solutions can be re-used in the production process where the wastewater was generated.

For effective regeneration, the stronger an ion binds on the ion exchanger, the more regenerant solution must typically be applied. Thus a resin with high selectivity may have advantages regarding the efficiency of removal from the wastewater, but the regeneration efficiency must also be taken into account to judge the overall value of the process.

Adsorber Resins

Next to ion exchange resins stands a close group of products, the so called adsorber resins. From the outside they look similar: little beads of a porous material. The striking difference is the lack of functional groups.

Even though adsorber resins are not functionalised, they have the potential to remove ingredients from water. Typically organic materials with low solubility in water can be adsorbed. These so called hydrophobic substances tend to get close to lipophilic surfaces. Adsorber resins provide a huge surface of these lipophilic surfaces inside their pores, resulting in a high capacity for hydrophobic molecules.

Adsorber resins adsorb through mechanisms similar to activated carbon. They can be regarded as a kind of "fully synthetic" activated carbon.

The appropriate way to regenerate these materials strongly

depends on their physical properties. Those are characterised by their vapour pressure (volatility) or solubility in organic solvents, bases, or acids.

Volatile substances can be removed by steam-stripping, whereas non-volatile substances can be removed by liquid stripping media, in which they are soluble.

In contrast to activated carbon, the adsorber resins can be regenerated more than 1000 cycles without thermal reactivation. These materials do not bleed minerals and possess a much higher mechanical stability than activated carbon. They do not form dust or fines by abrasion that plug the filter bed and pollute the regenerant or the treated water with suspended solids.

Equipment Considerations

Ion exchangers are typically applied in pressure vessels. They are equipped with appropriate internal plumbing that has two purposes: first it prevents the ion exchange

resin from being washed out of the vessel and secondly it provides the appropriate distribution of liquid flow through the ion exchange bed.

In the simplest case, the internal system is a screen, mounted above a porous backing plate. More commonly, slit nozzles (strainers), mounted in star- or so called fishbone piping, or fixed in equal distances directly onto the base- or cover plate are found.

The slit width in these strainers is 0,2 to 0,3 mm, which is fine enough to effectively restrain the ion exchange or adsorber resin beads. At the same time pressure drop is low.

Usually the pressure vessel is filled to only half of its volume. The empty space above the ion exchanger bed is called "freeboard". The freeboard has several functions: First of all it allows the ion exchanger bed to "breathe". This is necessary because the exchangers often shrink or swell during operations of exhaustion, regeneration

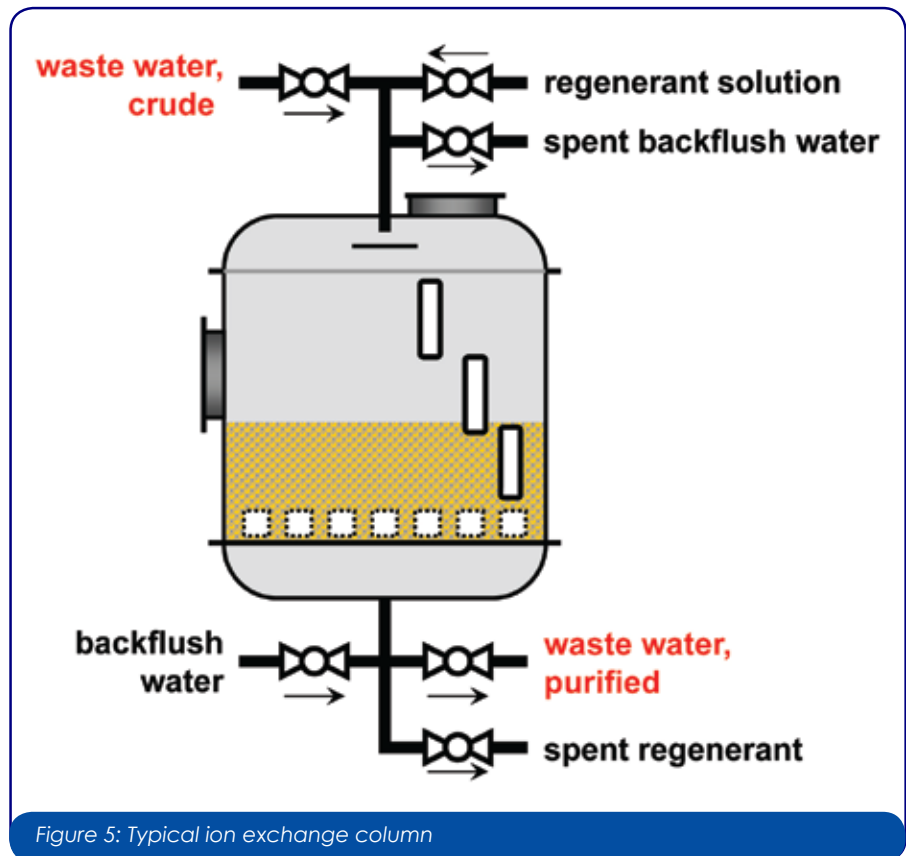


Figure 5: Typical ion exchange column

Case Study: Evaluation of Different Waste Water Treatment Methods in a Particular Case

Frame Conditions		Flow rate: 100 m ³ /h , c Cu 100 mg/L, c NaCl: 10 g/L, rest concentration c Cu: 0,5 mg/L
Reverse Osmosis	Disadvantages	<ul style="list-style-type: none"> • high specific energy consumption • no selectivity, salt is accumulating in retentate • concentration factor in maximum f = 30, otherwise over saturation of NaCl • electro winning of Cu not possible due to chloride in concentrate
Nanofiltration	Disadvantages	<ul style="list-style-type: none"> • low selectivity, salt partially accumulates in retentate • no sufficient rejection of Cu; limits difficult to reach
Evaporation	Disadvantages	<ul style="list-style-type: none"> • same disadvantages as with reverse osmosis • at flow rate of 100 m³/h extremely large invest costs
Precipitation	Disadvantages	<ul style="list-style-type: none"> • to provide 0.5 h of residence time agitated vessels of 50 m³ volume need to be installed. Also precipitation tanks of the same size and a filter press • to reach rest concentrations of less than 0.5 ppm toxic and expensive sulfidic precipitants have to be used (additionally flocculants and polyelectrolytes) • electro winning from precipitate not possible • a precipitation with lime and/or caustic alone will not allow to reach rest concentrations below 0.5 ppm
Selective Ion Exchange	Advantages	<ul style="list-style-type: none"> • small footprint and low installation costs • rest concentrations of < 0,5 ppm are secured • concentration factor of f > 200 possible • with sulfuric acid as regenerant solution copper can be directly recovered by electro winning. At the same time the regenerant acid is recovered • in case no electro winning is provided the spent regenerant has to be treated by precipitation but in much smaller vessels than in the case of precipitation as a stand alone treatment step

Box 1

and conditioning. The specific volume of the resin can change by up to 70% of its original volume.

Secondly the freeboard is used for backwashing the ion exchanger bed. Thereby the backwashing water is flowing through the resin bed in upflow mode and fluidises the bed. Depending on the linear velocity the bed expands by a certain ratio and the beads leave their fixed positions and roam around. Backwashing loosens the bed, breaks up clumps, and destroys larger channels that have been established. At the same time entrapped suspended particles or broken beads are removed. When backwashing is finished the bed lays down in a homogenised package that permits uniform flow in following operating steps.

If an empty pressure vessel is to be filled with ion exchange

beads these can easily be filled in by hydraulic transportation. In the same way a pressure vessel can be emptied by washing out the beads. In the planning of an ion exchange plant for this procedure dedicated pipelines have to be considered.

It is very useful to provide sight glasses in the walls of the pressure vessels to permit observing the condition of the filter bed during operation. Especially the larger filters should be equipped with windows. The windows should be arranged in a manner that the bottom window tracks the bulk of the filter bed, the medium window tracks the surface, and the top window tracks the freeboard.

The most practicable way to connect the pressure vessel to the piping is to only have one connection at the top and one connection

at the bottom with different connections realised by T-connectors.

Figure 5 shows an ion exchange column with its basic constituents.

In technical installations ion exchange columns are rarely stand-alone units. Usually they are installed as twins in series (Lead/Lag - concept) or triplets (Merry go round-concept). Having more than one filter unit permits continuous operation with one filter on-line and the other one in the regeneration cycle. It is sometimes useful to have two filters in series whereby the lag-one serves as a polisher or a police filter for the first one.

Fields of Applications for Ion Exchangers

The application of ion exchangers is particularly advantageous if the pollutant has to be removed from

Example of Plant Design

Flow rate	q = 100 m ³ /h
Copper concentration in crude waste water	c Cu 100 mg/L
Target rest concentration in waste water	c Cu: 0,5 mg/L
Further waste water ingredients	c NaCl: 10 g/L
Resin type	Lewatit® Monoplus TP 207
Bed volume per filter	5 m ³
Resin volume in total	10 m ³
Number of filter units	2 (for lead lag-operating mode)
Specific velocity	20 BV/h
Cycle time	15 hours
Filtered volume per cycle	300 BV equalling 1500 m ³
Operating capacity of resin	30 g/L
Efficiency	under the given frame conditions the operating capacity is 48% of the total capacity
Regenerant	H ₂ SO ₄
Concentration of regenerant	10%
Volume of regenerant per cycle	2 BV = 10 m ³
Concentration of copper in spent regenerant	15 g/L (in case of connected electro winning step even higher concentrations can be accomplished)
Rinse water demand per cycle	2 BV = 10 m ³ (rinse water can be used to prepare regenerant solution)

Box 2

wastewater binds with especially high selectivity. Then the filters' capacity is mainly used up to adsorb the pollutant only and is not consumed by other, non-critical components.

Simultaneously a second advantage is realised, particularly if the pollutant is already in a low concentration. The results are long cycle times and high concentration factors in comparing the concentration of the pollutant in the spent regenerant and in the original wastewater. Concentration factors higher than 10 already are advantageous but in some practical cases concentration factors of 1000 and higher can be achieved. As a rule of thumb the concentration of a pollutant in wastewater should not extend 300 ppm to allow efficient operation.

A third advantage is realised when wastewater streams are

relatively large and alternate treatment methods simply exceed the size of the regular equipment. As an example, site space does not permit the installation of evaporation ponds or precipitation tanks. In this case an ion exchange filter unit can be used to change a large wastewater stream into a small concentrated spent regenerant stream that is more convenient to be treated further in smaller conventional processes.

In Box 1 the advantages and disadvantages of competing wastewater treatment methods are discussed in a case study. Similar trains of thought are passing through the head of a wastewater engineer while he is planning a wastewater treatment concept.

In this case the advantages clearly lay on the side of the ion exchange technology when it is combined with post-treatment of

the spent regenerant by precipitation or electro winning. The same advantages can also be found in other cases, particularly, when the spent regenerant solution is reused in the related production process. This case is often found in applications at metal finishing, in the winning and refining of metals, in the production of organic materials as well as in the production of batteries. **AW**

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