

Ion Exchangers for Environmental Protection

In the March issue, we examined the principles of ion exchange and gave an overview of different types of resins. Here we will look at the different ways in which ion exchangers can be used to clean wastewater.

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Ion exchangers can be used in five different ways to keep wastewater clean.

The first method is by direct filtration of the wastewater. Without any pre-treatment but pH-adjustment, the water is directly filtered over the ion exchange resin. After filtration, it is directly discharged into the environment.

In the second method the ion exchanger is used as a polishing or "police" filter. Here the ion exchanger is placed downstream of another wastewater treatment unit that removes the major amount of pollutants. The ion exchanger removes the normal residual leakage of pollutants coming from the heavy load primary treatment unit, or the entire load should an operational failure occur. Regardless, the ion exchanger is there to ensure that the concentration levels of pollutants are

safely below the emission limits.

Police filters are compulsory when the wastewater is treated continuously and/or the heavy load treatment step alone can not reach the emission limits.

Both the direct filtration – as well as the polishing concept are categorised as "end of the pipe" wastewater treatment or as "additive environmental protection".

The third method simply refers to water recycling. It is mainly applied to dilute process streams that can reasonably be desalinated and converted into demineralised water. Within this approach the main idea is to reduce the amount of discharged wastewater while preserving fresh water resources.

The fourth method is back-integrated into the production process. It entails recycling of process streams. If these

streams are merely disposed after exhaustion, they create heavy loads to the waste treatment plant. Examples are the mineral acids used to pickle metals and electrolyte solutions applied for surface plating. During use, these process streams get enriched with impurities due to corrosion of metal surfaces or to the generation of side products. If the concentration of impurities exceeds a certain critical level, these process solutions become exhausted and must be renewed or disposed.

The generated wastewaters will not only be charged with the impurities, they will also be heavily loaded with the active component used in the process stream.

Ion exchangers often can be used to selectively filter the impurities from the process bath while keeping the active ingredient in solution. In this manner, the

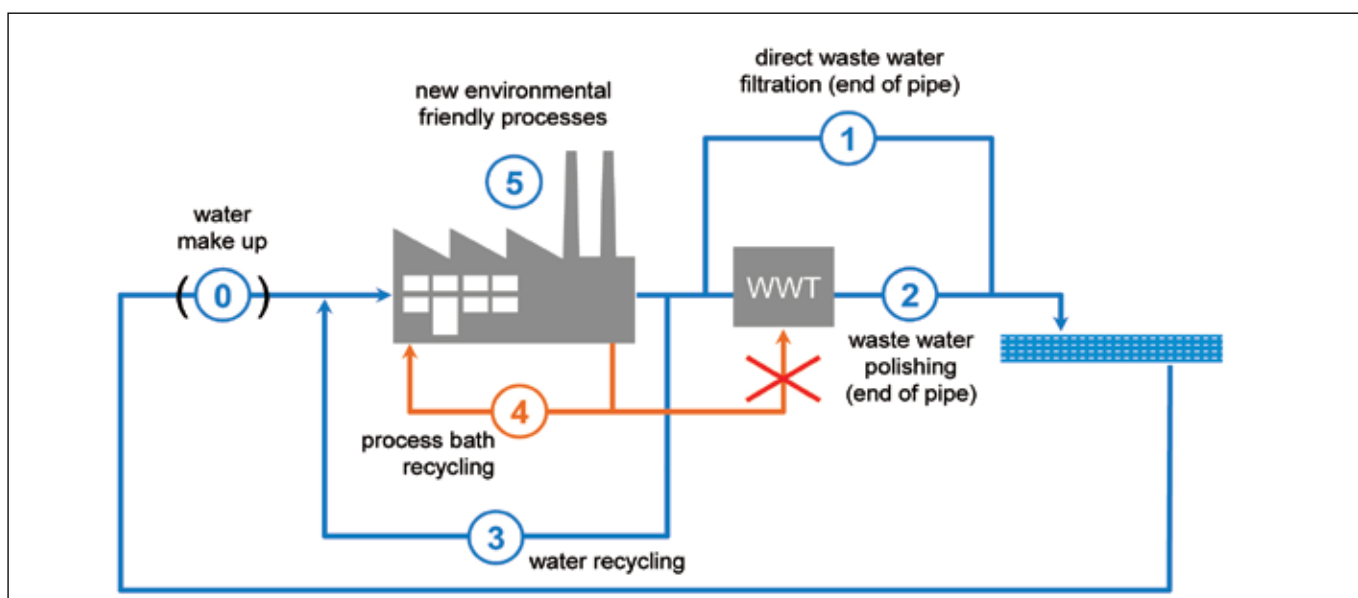


Figure 1: Different concepts to keep wastewater clean with ion exchangers

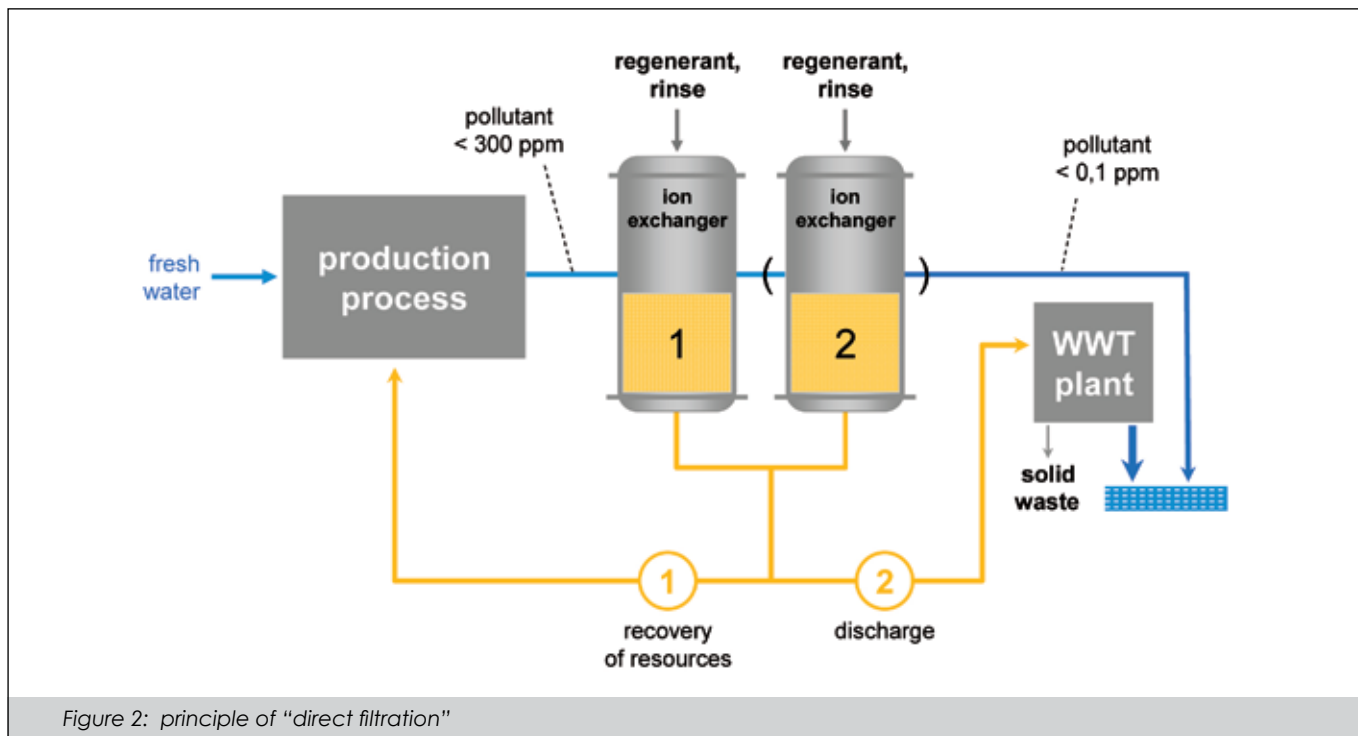


Figure 2: principle of "direct filtration"

generation of heavy load wastewater is reduced and valuable chemicals are saved. There also are advantages in the product quality. Permanent cleaning of the process both reduces disturbing effects of the pollutants and helps to keep quality under control.

The fifth method is complete process integration. For existing processes it requires an extensive rearrangement – a so called re-engineering – of the entire production process. Often it is employed to replace hazardous chemicals with less hazardous chemicals and/or to drastically reduce the consumption of water and save energy-resources.

Unlike end-of-pipe strategies, the fifth concept makes use of ion exchangers not simply to improve environmental protection measures. It can advance new sophisticated approaches that are completely process integrated.

Now we will take a closer look at the first three methods of cleaning wastewater.

DIRECT FILTRATION

The principle of direct filtration is illustrated in Figure 2. It is applicable to water that is slightly contaminated from a production process. It may contain one or more pollutants. To allow economic operation the

concentration level of pollutants in sum should not exceed 300 ppm.

The hazardous component is removed by means of a selective ion exchanger. If more than one hazardous species is present, two cases can be distinguished. First, in an ideal case, all pollutants can be adsorbed on the same ion exchanger. If, for example, all the contaminants are heavy metal cations, they can be adsorbed by means of an IDA-resin (Lewatit® TP207).

In a second, more challenging case, species with different chemistries, e.g. a mixture of cationic and anionic pollutants require treatment. In this case, for each group of ions, separate adsorbents must be provided for the different classes of contaminants. Here, a selective cation exchanger must be combined with a selective anion exchanger in series. Anionic heavy metal containing ions are metal-cyanide-complexes or oxo anions of chromium, molybdenum, tungsten, vanadium, arsenate, and antimonate.

Under optimal operating conditions ion exchangers can reduce the concentration of pollutants to less than 0.1 ppm. There are special cases known, where residual concentrations of less than 0.01 ppm can be achieved.

After exhausting the ion exchange filters require regeneration. The next very important question is what to do with the spent regenerant solution.

The most favourable way is to reuse the spent regenerant in the production process. (Figure 2, pathway (1)). To allow this kind of solution, the regeneration method has to be adapted to the production process through the proper selection of the regenerant chemistry and concentration.

If reusing is not possible, the spent regenerant solution must be treated. (Figure 2, pathway (2)). In many cases this is a precipitation reaction, where the pollutant is chemically converted into a water-insoluble solid that can be incinerated, disposed of in a landfill, or used as a raw material in metal-winning.

The concept of direct filtration with treatment of the spent regenerant only makes sense in case the process delivers a significant reduction of the waste stream. This typically means that the spent regenerant stream is about ten times smaller than the original waste stream.

Overall there are two aims for the concept of "direct filtration". One is compliance with wastewater regula-

tions; the second is to recover valuable material.

THE POLISHING-FILTER-CONCEPT

The concept of polishing or “police-filters” is illustrated in Figure 3 and uses the example of heavy metals as described previously.

Grossly contaminated water (as a rule the pollutant concentration is greater than 1 g/L) first is treated in a heavy-load-treatment step. In this case, precipitation of the metal ions through the dosage of milk of lime and/or caustic is employed. The metal ions are converted into sparingly soluble hydroxides and can be removed by filtration.

Usually a precipitation process removes 99% of the pollutant from the wastewater. With a starting concentration of 1000 ppm, a 99% removal rate means that a residual concentration of 10 mg/L is present, which is normally too high for direct discharge.

To ensure that the wastewater is in compliance with regulations for emission into the environment, the water is conveniently treated with an ion exchange unit to take care of the final purification of the water.

In this step, the ion exchange filter further reduces the pollutant concen-

tration with an efficacy of 99%. In sum the combination of heavy load and fine purification treatment steps yield a degree of removal of 99.99% with residual concentrations typically less than 0.1 ppm.

The spent regenerant solution usually is passed back into the heavy load treatment step. In the case depicted in Figure 3 this is the precipitation tank. As a result, there is only one secondary waste discharge. In Figure 3 this is the filter press. No other method to treat and dispose of the spent regenerant is required. The heavy metal containing sludge is discharged to a landfill. If it contains exclusively one kind of heavy metal (mono-sludge) it can often be used in smelters as a raw material.

The concept of combining a heavy load purification unit with a polishing step is not confined to heavy metal removal. The same concept can be applied to the removal of toxic anions such as chromate, borate, arsenate, etc. It is also applicable to the removal of organic impurities. For example, phenol can first be removed by steam stripping with polishing by adsorber resins. The adsorber resin is regenerated with steam and the condensate is passed back into the steam stripper.

The polishing filter type ion-exchange applications usually employ selective ion exchange reactions. The main reason for this is that these types of wastewaters contain large amounts of neutral salts that are added in the heavy load treatment step. For example, in precipitation circuits, large amounts of lime and caustic are added to adjust the pH. As a result, high concentrations of calcium and sodium are generated. Because both of these cations compete with heavy metals in ion exchange reactions, selective ion exchangers are most effective.

An example of filtration curves (break through curves) of different heavy metals found in one type of wastewater is presented in Figure 4. The effluent concentration of the metal ions is plotted against the filtered volume. Due to the pre-treatment by precipitation, the water has an extraordinarily high content of calcium (10 g/L as CaCl₂).

Despite the high calcium concentration, the heavy metal ions are efficiently removed. In the first phase of the filtration the residual concentrations are below 0.1 ppm. This is usually in compliance with environmental legislation.

After a certain point, the residual concentrations of metals suddenly

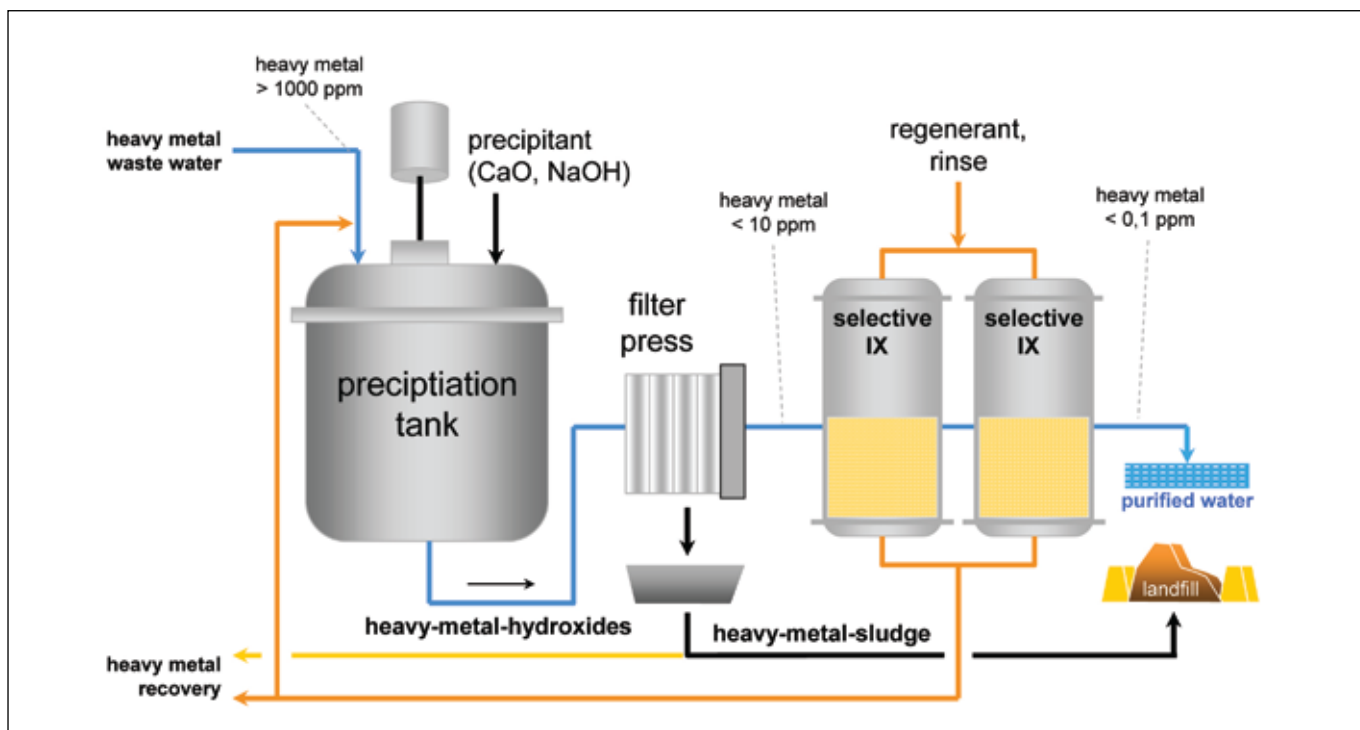
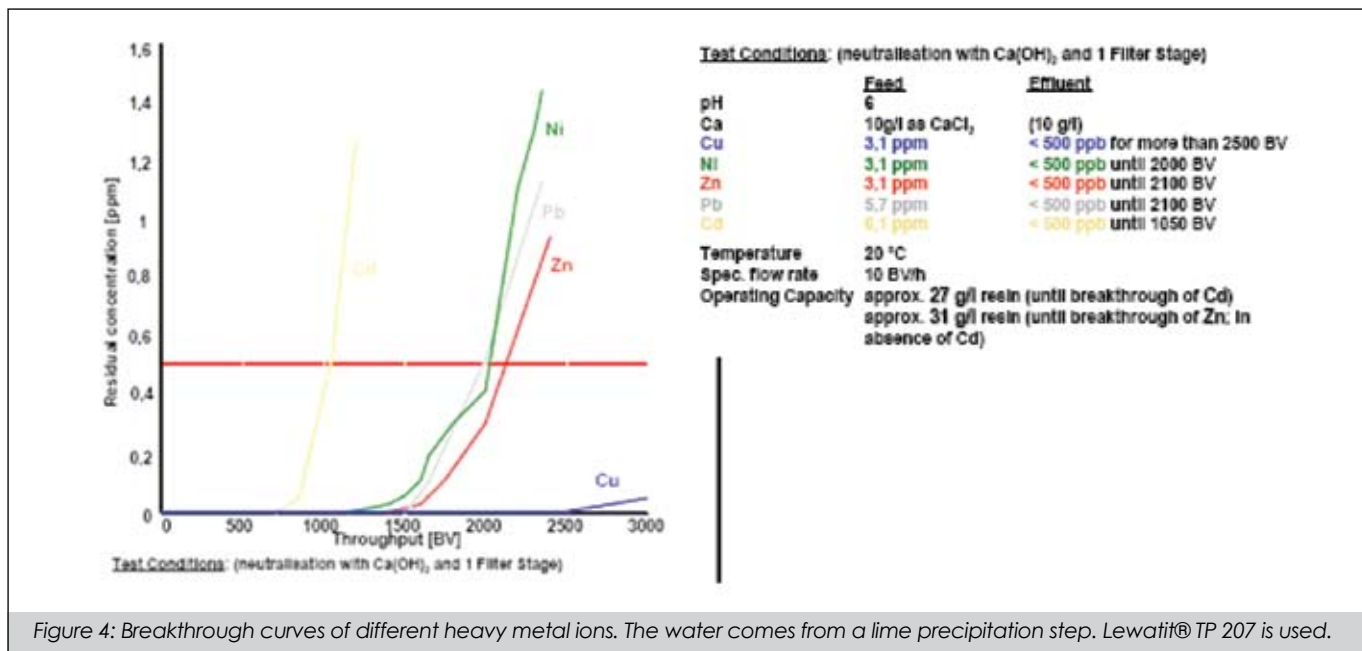


Figure 3: principle of a “polishing-filter”



increase. Note that the ions do not break through all at the same time. In this example cadmium breaks through first and copper is the last. The breakthrough of metals more or less follows the order of selectivity.

Cadmium has the lowest selectivity of all the metal ions, resulting in the early break through of cadmium.

Returning to the polishing concept, it is important to mention that pH adjustment may be required after the heavy load treatment step. For example, after precipitation, the pH may be too high to efficiently use an ion exchange resin. This is because at high pH heavy metals may be in an inappropriate form that does not interact with the functional groups. This may be negatively charged hydroxyl-complexes (e.g. zinc, lead, cadmium and aluminium) or it may be that at high pH metals are present as hydroxide-particles in colloidal form. Since both forms cannot be adsorbed by cation exchangers, the pH must be reduced to a value between pH = 5 and pH = 7. This will re-dissolve colloids and/or transform metals back into the cationic form.

Another critical performance issue is the presence of complexing agents such as EDTA, NTA, and cyanide in the wastewater stream. These complexing agents should be destroyed (i.e. oxidation) upstream of the ion exchanger.

In addition, sulphide precipitation (sulphides, thioles, thiazoles, thiocarbamates) should be avoided in combination with ion exchanger polishers. Not only are these chemicals toxic in excess, they also produce an ugly smell when the ion exchanger is regenerated with acid.

In addition, hydroxide precipitation in combination with ion exchange resins typically meets the required effluent concentrations. As a result, the use of sulfide precipitation agents in this concept is simply a waste of money, notwithstanding their toxic properties and miserable odour. The use of sulfide agents makes sense only within the concept of precipitation as the stand alone treatment step. Here hydroxide precipitation alone is not sufficient to reach heavy metal concentrations in the ppb range.

Finally it is important to mention that regular back flushing is necessary, especially for ion exchangers used to polish effluents from filter presses. This is because filter presses always release suspended solids, particular at the beginning of the new filtration cycle. The solids are captured inside the ion exchange bed. Furthermore, there are post-precipitation and crystallisation effects that produce solids inside the resin bed.

If these particles are not thoroughly removed they may disturb the process and also reduce the life of the resin.

WATER RECYCLING CONCEPT

In some processes, mainly in the rinsing of manufactured products, only slightly contaminated water with low salt content is produced. The resulting salt content may even be lower than that of the raw water. In such cases water recycling through an ion exchange process is useful. The produced demineralised water can be reused in the production process.

The process scheme is shown in Figure 5. The plant consists of a cation and an anion exchanger. Cations are exchanged by protons (H⁺) and anions are exchanged by hydroxyl ions (OH⁻). Protons and hydroxyl ions react to form water. Downstream of the ion exchange unit, salt concentrations are remarkably low and the conductivity can easily be less than 5 µS/cm. Should even lower conductivity be required, a mixed bed (>18 MΩ *cm) can be added. Ultrapure water quality can be prepared by means of the mixed bed product.

If the rinse water also contains ionic detergents (wetting agents), the use of a scavenger filter is necessary. In these cases activated carbon or an adsorber resin is used.

Without the scavenger, cationic detergents will irreversibly foul cation resins. Likewise, anionic detergents block strongly basic ion exchangers. Therefore, these substances must be

removed ahead of the ion exchange filters.

The normal products used in water recycling units are macroporous strongly acidic resin (e.g. Lewatit® SP112) in combination with a weakly basic resin (Lewatit® MP64). If the rinse water contains high concentrations of weakly acidic anions such as CN^- , H_2BO_3^- , HSiO_3^- or HCO_3^- , a third ion exchange filter should be considered. This filter contains a strongly basic resin like Lewatit® K 6362. A weakly basic resin can not capture these specific ions alone.

If a strongly basic resin is employed, the weakly basic filter should never be over-run. Otherwise there is the danger of irreversible binding of special ions such as metal-cyanide-complexes, chromate and other components. They cannot be removed from the strongly basic sites. Complexing agents based on carboxylic acids, amine or phosphonic acid, can also be irreversibly adsorbed by ion exchangers.

If the water contains suspended solids, droplets of oil or emulsified oil, these substances should be removed before contacting the ion exchanger. An appropriate pre-treatment by emul-

sion break down, phase separation or filtration should be provided.

Strong oxidants, such as free chlorine or peroxides should not come in contact with the ion exchangers. These agents harm the ion exchangers by oxidising the functional groups as well as the polymer backbone of the beads.

Another frequently occurring problem in water recycling units is growth of bacteria and algae. Algae growth in tanks can be reduced by the use of wall material that is impervious to light. Other measures include the use of disinfection by UV-lamps in tanks. Bacteria growth can be reduced by non oxidising disinfecting agents.

Once an ion exchanger is contaminated by bacteria, a treatment with caustic followed by a thorough backwash delivers good results. In cases of strong bacterial contamination a short time treatment with more aggressive disinfecting agents can be applied.

CONCLUSION

The previous examples demonstrate that ion exchangers can be used in different ways to keep wastewaters free from hazardous compounds. Ion exchang-

ers are powerful tools on the top shelf of the wastewater engineer's toolbox. They can be used alone or in combination with other treatment methods.

Water treatment concepts involving ion exchangers can be designed in different ways, like the easy to install additive "end-of pipe" process. Process-integrated measures that directly operate on process streams in the heart of the process can be employed too.

In the preceding examples, ion exchangers deliver economic solutions to problems because the principle of selectivity can be put into action. Selectivity is economical because the consumption of chemicals and energy targets the treatment of one trace component, and keeps other non-hazardous components untouched.

Given this selectivity advantage, it is very important that different types of ion exchangers and adsorber resins are available. Multiple types allow the engineer to select the most suitable resin for a given application. **AW**

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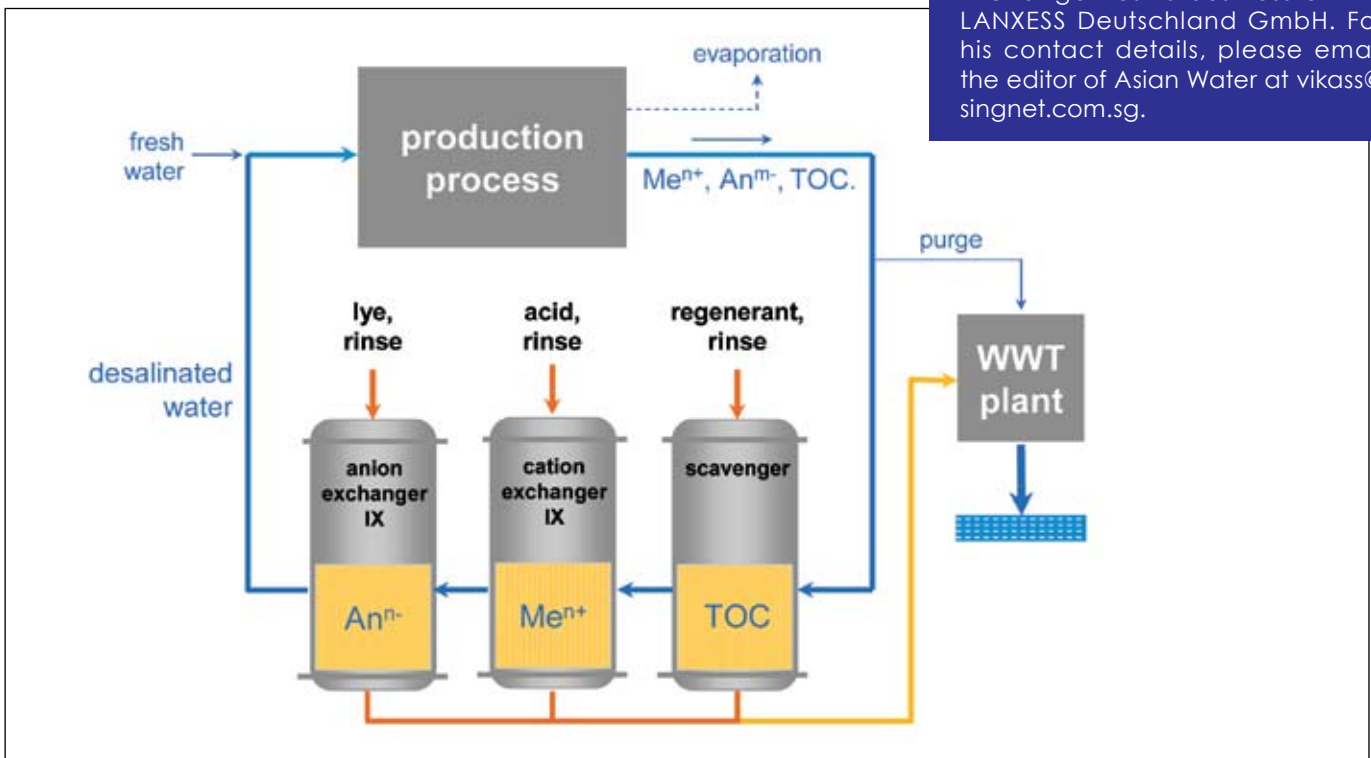


Figure 5: the operating scheme of a water recycling unit