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Keeping Waste Water Clean with Lewatit® Ion Exchangers

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The World of Waste Water

In this world, there are as many types of waste waters as there are industrially produced goods and manufacturing processes. Waste waters are a natural consequence of human activity. Where people live and work, waste waters will always be found. Waste water from industrial production can contain an unspeakable variety of different inorganic and organic chemicals, in all combinations and concentration levels. The whole spectra of synthetic and natural chemicals can be found in these streams. Waste waters vary in composition in step with their related production processes. The concentration levels of these ingredients, however, are not always so clearly defined. They vary in ranges according to the fluctuations in the production processes and are normally characterized by average, minimum or by peak values.

There are waste waters that occur only in small quantities per day. These can easily be collected and disposed of over time. In contrast, there are remarkably huge waste water streams of several thousand cubic-meters per hour. They can only be handled with continuously operating large scale plants, often the same size as the production units. Waste water streams are often combined in networks and can influence one another. In between they are stored, treated, mixed, further treated, etc. Usually they are running through several pipelines, tanks and treatment units before they are finally discharged into the environment. Getting a clear picture of waste water is not an easy job. One has to go through a thorough analysis to clarify its nature. Thereby a chemical analysis is just the first step of a much more work intensive project.

The Toolbox of a Waste Water Technician

As a consequence of their unique character, every measure to keep waste waters clean is individual and has to be adjusted to the specific environment of the distinct waste water. There rarely are solutions off-the-shelf. Efficient solutions can only be

Mechanic Treatment
• screening • sedimentation • flotation • filtration • microfiltration
• ultrafiltration • nanofiltration • reverse osmosis

Physical Treatment
• adsorption by solid adsorbers • extraction with liquid extractants
• flocculation / coagulation

Chemical Treatment
• precipitation
• wet oxidation
– fenton
– ozonolysis
– oxygen
• autoclave-hydrolysis • reduction • ion-exchange • chemisorption
• incineration

Thermal Treatment
• evaporation • distillation • steam-stripping

Biological Treatment
• aerobic biological degradation • inaerobic biological degradation
• degradation by immobilized & specialized • microorganisms

Figure 1: The toolbox of a waste water technician. There is a variety of unit operations available. Each has to be used and combined in the most efficient possible way to achieve a technically, economically and ecologically useful solution.

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obtained by specialists with a solid knowledge of all the relevant chemical, physical, biological and economical backgrounds. To find these solutions, waste water specialists require a well-equipped tool-box, containing different unit-operations, based on a variety of operating principles. Typically, each one of these unit-operations is so complex, that dealing with one alone is already a specialty in itself. Having a full overview of them all is nearly impossible, but there are a few waste water technicians that come very close.

Individual waste waters can theoretically be cleaned by different methods. Looking at a specific case, it is often possible to name several methods at first glance. For instance, in the case of a water stream polluted with the toxic organic compound phenol, the following methods can be applied to remove it from the water:

- Adsorption with activated carbon
- Steam stripping or distillation
- Wet oxidation
- Reverse osmosis
- Extraction with organic liquid/liquid extractants
- Adsorption with ion exchangers
- Biologic degradation

The challenge now is to choose the most effective, inexpensive, and most ecologically relevant method under the given frame conditions. This task almost always involves laboratory testing, and often pilot testing. Only by means of laboratory testing can the interested parties be sure that the planned treatment process will work at the end of the day. At the same time it is possible to generate useful data for the design of a full-scale unit.

To Find Optimum Waste Water Treatment Concept

Questions to be answered within a Waste Water Treatment Project: During the development-phase for a suitable waste water treatment concept, the following questions have to be answered:

- Where does the water come from and how is it generated? Is it a mixture of different waste waters? Does the composition change with time? Is there a buffer tank in between that helps to equalize fluctuations?
- Where is the waste water sent to after the treatment? Is there a buffer tank where it is further diluted? Is there a chance to adjust the pH before it is discharged?
- What is the ideal form of a secondary waste stream resulting from the waste water treatment? How should the secondary waste stream look like so that it can be re-used in the production process or sent to a downstream waste treatment process?
- Who will operate the waste water treatment unit? Which level of education is required? Who maintains the process control equipment? Is it better to have manual process control or full automation?
- What kinds of energies (electric power, steam, water, and chemicals) are available and which of these would be advantageous to use?
- What are the relevant local regulations? Which ingredients of the waste water are especially critical and which one can be neglected?
- Which unit operation is especially efficient to treat the waste water and can eventually remove more than one of the critical ingredients at the same time?

Figure 2: It does not take much to test ion exchange resins in laboratory scale. A pump and a glasscolumn are most important. The rest is standard equipment.

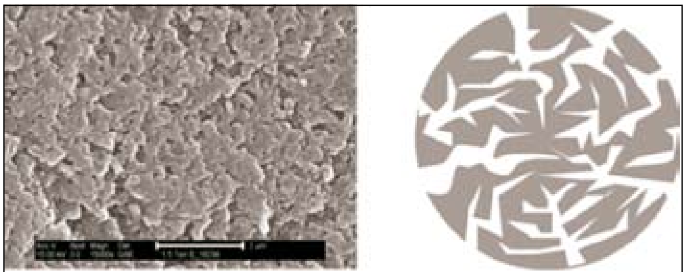

Figure 3: Ion exchange resin beads contain many fine pores that fill with water. The water content of some types is up to 70%.

- How can different unit operations be combined and which order has the most advantages. How do the different steps mutually influence each others? How have the steps to be tuned to allow the best fit and also the highest level of usage.
- What are the most effective operating supply items (types of ion-exchangers, types of activated carbon, and other adsorbers), consumer item qualities (steam, process water, agents), separating medias (e.g. types of membranes and filter cloth) ?
- What are the most effective operating conditions (dosing rates, residence times, contact times, flow velocities)?
- Are there any negative effects that can disturb the regular operation (e.g. plugging of nozzles, and other sensitive parts by fouling or crystallisation processes, intoxication of activated bio-mass, irreversible adsorption)
- Are there any toxic products resulting from side reactions (chlorinated hydrocarbons, metabolites of bacterial degradation)?
- What is the basic design (sizing) of the relevant units (sizing of filter-beds, membrane surface, volume of agitated tanks)?
- What are the appropriate materials of construction?
- What are the available foot-print and the height of the building? Is a separate building necessary?

With all the assorted questions, it is clear that many different aspects must be considered, and much information collected, before a suitable concept can be developed. The task requires the care of one or more specialists. Different parties must cooperate: the "producer" of the waste water, the original equipment manufacturer (OEM), the future operator of the waste water treatment plant, the equipment provider, local authorities, etc. Combining the information and coming to a viable solution is often like working on a puzzle or playing a game of chess. In many waste water projects, the application of ion exchange is warranted. In these cases there are suitable specialists available at LANXESS. We are eager to help find solutions by supplying relevant data from our files, and in some cases generating the required data through testing in our laboratories.

Principle of Ion Exchange and Overview over Different Types of Resins Constitution & Operating Principles

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 gelstructured compartments of the material. Since water is dispersed homogenously through the bead, 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 ether positively (cations) or negatively (anions) charged. Since the functional groups are also charged, the interaction between 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 on. One exchange reaction can follow another.

Existing Ions

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 alkalications (sodium, potassium), of earth- and rareearth-alkali-cations (magnesium, calcium, strontium, barium, lanthanium, iridium), heavy metal ions (lead, cobalt, nickel, mercury), light metal cations (aluminium, beryllium, titanium), semi-metalcations (germanium, gallium, indium), noble metal cations (gold, silver, platinum, palladium).

Dealing with ion exchange applications in waste water treatment requires full knowledge about water composition to judge competing effects. Once known, a better understanding of the efficiency of the process can be realized. 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 realized. Therefore the efficiency of a waste water treatment process always depends on the water composition which is individual — as already mentioned above.

Regeneration of Ion Exchangers

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

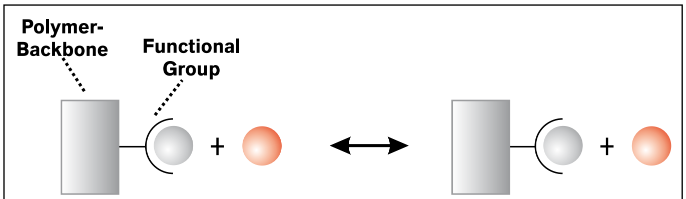

Figure 4: A fixed and a mobile ion are changing places in a so-called ion exchange reaction. This simple reaction scheme is the base for more than 500 applications involved in the purification of water and other fluid media.

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 waste water 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 waste water, but the regeneration efficiency must also to be taken into account to judge the over all 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 functionalized, 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 characterized 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.

Special Advantages and Fields of Applications for Ion Exchangers

The application of ion exchangers is particular advantageous if the pollutant that has to be removed from waste water 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 realized, 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 waste water. Concentration factors of > 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 waste water should not extend 300 ppm to allow efficient operation. A third advantage is realized when waste water 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 waste water stream into a small concentrated spent regenerant stream that is more convenient to be treated further in smaller conventional processes.

What Else has to be Considered

In planning and operating ion exchange units the following items must be avoided to maintain effective performance:

- Contamination of the ion exchange beads with droplets of oil, grease or slime that plugs the pores of the polymer beads.
- Feeding of molecular or ionic species that irreversibly bind to the functional groups.
- Feeding the filter with suspended solid containing liquids that will plug the bed in short time (TSS > 2 ppm).
- Strong variations of pH and salt content of the feed solution.
- Feeding with fluids of critical temperatures.
- Back flushing and taking back into service before the filter is completely exhausted without another filter in lag position.
- Permanently feeding strong oxidizing chemicals (e.g. Cl2 > 0.1 ppm).
- Permanently operating the unit at high pressure drops (> 1.5 bar).
- Using a density of strainers in base plates of less than 80 entry points per square meter.
- Providing not enough free-board in the use of resins, that undergo intensive (>30%) changes in volume throughout the cycles.
- Regeneration with concentrated nitric acid without special safety precautions (danger of explosion).
- Use of sulfuric acid as a regenerant solution in case the resin is highly loaded with calcium (danger of gypsum precipitation).
- To cut down regular backwashing.
- Plug pipelines for the release of backwashing water with slit nozzles or screens.
- Use bed depth less than 0.8 meters.
- Carry out neutralization reactions on resin with highly concentrated solutions (e.g. feed H+ into a resin that is in the OH- or free base form or vice versa).
- Transportation of resin suspensions with centrifugal pumps.
- Feed a column without distribution systems.
- Feed with linear velocities of less than 5 m/h.

Conclusion

Ion exchangers can be used in different ways to keep waste waters clean

High-performance Lewatit Ion Exchange Resins

form hazardous compounds. Ion exchangers are powerful tools on the top shelf of the waste water 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. 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 an engineer to select most suitable resin for a given application. Here, it is important to mention that the development of special adsorbers is not finished.

About the Author

Dr Stefan Neumann is working as Technical Manager on Ion Exchange Applications at LANXESS Deutschland GmbH since 2005. He has studied chemistry at the University of Cologne, Germany. He has earlier worked for University of Leipzig (HTWK), Germany, and Bayer Technology Services. He is currently head of Ion-Exchange - application laboratory for planning, coordination and evaluation of tests related to above mentioned working fields. He also works on marketing strategies to promote ion exchange products, technologies and applications. With over 100 products, LANXESS offers a range of ion exchange resins that can be used as a modular system to create individually tailored solutions.

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