Treating industrial wastewater

(Dis)Solving the high boiling problem

Sulzer equipment can cost effectively remove pollutants from large wastewater flows. Depending on the boiling points of the pollutants to be removed in relation to that of water, Sulzer recommends either a wastewater stripper or a liquid-liquid extraction unit.

A large number of pollutants in industrial wastewater are organic chemicals that are dissolved in water. These are only biodegradable in the rarest cases. Therefore, this wastewater cannot be cleaned in a municipal sewage treatment plant together with domestic wastewater. The substances often interfere with the microorganism metabolism or are even toxic. Such pollutants must therefore be removed before the wastewater is discharged, as, for example, in the case of pollution with organic solvents.

Depending on the source of the wastewater, the typical concentrations of the solvents lie in the range of 1–20% by weight. Such concentrations of pollutants are too low and the calorific value of the wastewater flow is too low for thermal treatment, which is basically incineration. The requirement for a secondary fuel would be very high—leading to high costs and additional environmental pollution.

Wastewater stripper

Stripping represents a well-proven and effective method of treating wastewater contaminated with solvents. In this process, wastewater is fed into the top of a rectification column and steam is passed through the column from the

Part of an extraction column on a truck. During the contact of the two liquids in the extraction column, the phenol is transferred from the water to the extract. The latter has a higher affinity for phenol than water.

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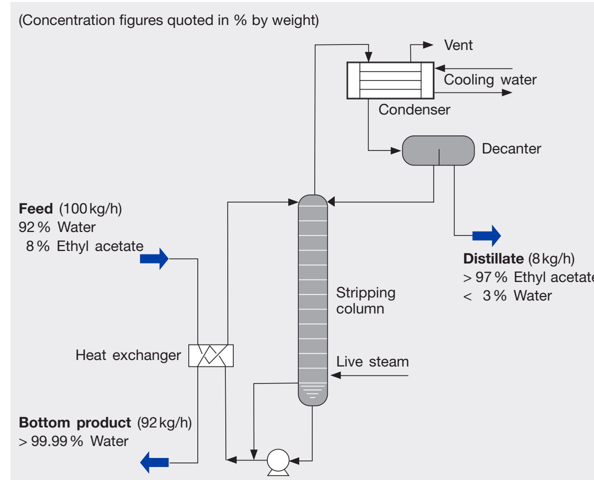


1 Wastewater stripper with optional decanter, including a wastewater example.

bottom in the opposite direction. This steam can be directly fed from an external steam network, but can also be generated in an evaporator. Figure 1 shows a diagram of this process.

Simple wastewater stripping is suitable for use for all solvents with a lower boiling point than water and for those that form a low boiling azeotrope with water. The solvent, which will be condensed as a concentrate at the head of the column, accumulates in the vapor phase. The maximum achievable solvent concentration is determined by the thermodynamic equilibrium and by economic considerations. Wastewater that is practically free from solvents can be removed from the bottom of the column. After it has been used for the preheating of the polluted wastewater flow, it can either be fed into the sewer system or be recycled in the process. The concentrate obtained at the head of the column can either be treated further, with the solvent being recycled, or can now be incinerated more cost efficiently.

If the solvent forms a heterogeneous azeotrope with water, and shows a miscibility gap, the decanter presented as an option in Figure 1 will be required. The water phase from the decanter is fed back into the stripping column, as it has a composition similar to the feed and is saturated with the solvent. The organic phase can be correspondingly treated further or be disposed of as a concentrate.

The costs of this process are mainly determined by the thermodynamics of the water-solvent mix. Depending on the vapor-liquid equilibrium, a different water concentration will result at the head of the column, and will therefore also lead to a different energy requirement for a sufficiently concentrated, solvent-rich flow. Typical solvents that can be removed through direct stripping without a decanter are alcohols and ketones. A decanter is required for esters, ethers, short-chain hydrocarbons, and other substances that do not mix with water. This process is also well suited for wastewater that is simultaneously polluted with several components.

Problem: high boiling substances

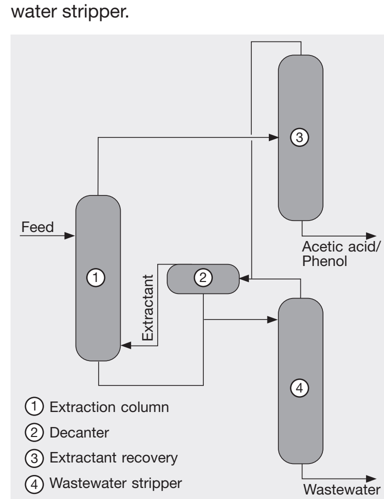
If wastewater is polluted with a chemical that has a boiling point above 100 °C at atmospheric pressure, the wastewater stripping process above is of limited use. If the substance forms an azeotrope with water that has a lower boiling point than pure water and that has a sufficiently high enrichment, then wastewater stripping can be performed with a decanter as described earlier. The solvent can thereby be effectively enriched in the distillate of a stripping column and can be removed well, despite the high boiling point.

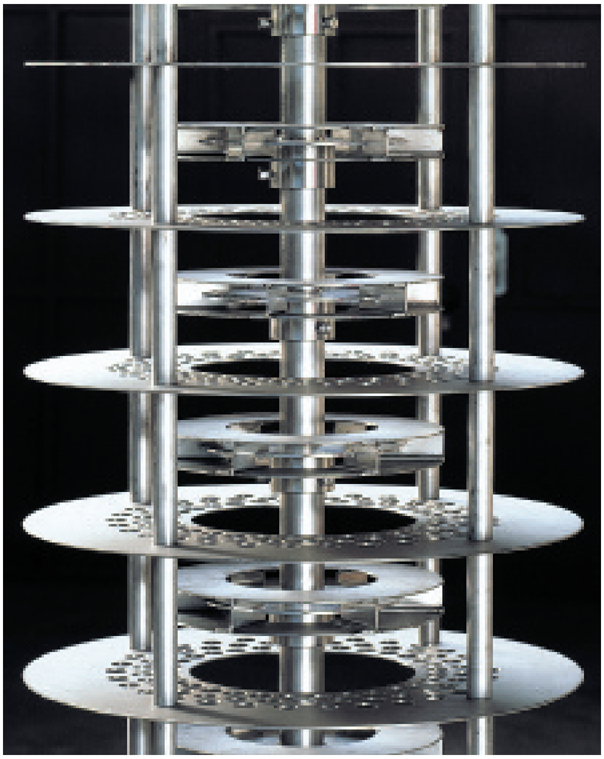
If the thermodynamic equilibrium is less favorable, however, direct stripping cannot be used. Phenol, for example, has a boiling point of 182 °C. Although it forms an azeotrope with water, the boiling point of this azeotrope is only 99 °C with a phenol content of 9% by weight. This almost corresponds with the solubility of phenol in water at 25 °C[1]. No concentration will take place in wastewater saturated with phenol. Because the boiling point of the azeotrope is very close to that of water, the stripping column will also need to have a very high separation performance.

This would require a high number of stages and a high reflux ratio. The corresponding column would therefore be high and would consume a great amount of energy. Considering the high water content in the azeotrope, direct stripping is therefore not practical.

Separation is also difficult in the case of water polluted with acetic acid. Acetic acid has no azeotrope with water and has a higher boiling point than water, so that all the water would be removed as a low boiling substance out of the distillate in direct "stripping." This process would not be stripping in the true sense, but would be wastewater evaporation and would thereby be extremely energy intensive. Treatment would also be possible using extractive or entrainer distillation, but both are complicated and also require a lot of energy.

2 Flow diagram of a liquid-liquid extraction unit, including solvent treatment and a wastewater stripper.





3 Internals of the Kühni-type ECR column.

Solution: Extraction

In such cases, liquid-liquid extraction offers an elegant solution to the separation problem. This process is based on the different solubility of a substance—the so-called transfer component—in two liquids that cannot be mixed with each other or that can only be partially mixed. If these two liquids are brought into contact with each other, a two-phase liquid-liquid dispersion results, and the transfer component divides itself according to the thermodynamic equilibrium between the two liquids.

The liquid that has a higher affinity for the transfer component—and that takes these up—is generally described as the extraction agent, while the liquid phase enriched with the transfer component is described as the extract. The donor phase with depleted transfer component is called the raffinate. Liquid-liquid extraction is mostly carried out at ambient temperature and pressure, so that no additional energy is required for heating or cooling.

In many cases, ketones, esters, or ethers are used as extraction agents for phenol and acetic acid. During the contact between the two liquids in the extraction column, a material transport of the phenol takes place from the water to the extraction agent, as the latter has a higher affinity for the phenol than water. The water will thereby become depleted of phenol and the extraction agent enriched. At the same time, however, the water will become saturated with the extraction agent that is being used, so that the water itself cannot be directly discharged after the extraction.

The extraction stage alone cannot purify the water, but the component with a high boiling point can be removed without an evaporation step. The water thereby takes up another material—the extraction agent. This agent has a lower boiling point than water and/or forms a low boiling azeotrope, and therefore it can be simply removed with the stripping process described earlier. In some cases, a solvent that is already present in trace quantities in the feed is used for the extraction. In this way, no additional materials are brought into the process.

The transfer component—in this case, phenol or acetic acid—must be removed from the loaded extraction agent in order to make the agent reusable for extraction. This is normally carried out in a rectification unit. Figure 2 shows the basic flow diagram of the complete process.

Comparison

Biodegradable solvents can also be removed by means of biological wastewater treatment in a sewage treatment plant. They are, however, mostly recycled for cost reasons. A comparison of the two processes described above, on the basis of the two flow diagrams, indicates that the removal of a high boiling component from wastewater using extraction is much more complicated than single-stage stripping. Key factors in an efficient process are the right choice of the extraction agent and the operating conditions of all the connected columns that have been adapted to the separation task.

The extraction agent must have certain properties: it must not be miscible with water—or at least be only slightly miscible—it must have a high affinity for the transfer component, and it should be as environmentally friendly

4 Pilot liquid-liquid extraction column with 60 mm diameter.

and cost-effective as possible. The thermodynamic equilibrium of the extraction agent, water, and transfer component are key determining factors for the energy demand of the complete system, because most of the energy is used for solvent recovery in the rectification column after the extraction column.

As a last step, the most suitable type of apparatus must be chosen for each process step. Depending on the origin of the wastewater, the pollutant concentration, volumetric flow rate, and required purity can be very different. The optimal column type for the extraction step must be selected according to these variables. On the one hand, the decisive factor for the selection is the thermodynamic liquid-liquid equilibrium, which, together with the solvent ratio, determines the necessary number of separation stages.

On the other hand, the concentration of the transfer component in the feed is of great importance. The physical properties of the liquid phases strongly depend on the concentration of the transfer component. This applies to density, viscosity, and, in particular, to interfacial tension, which have a great impact on the hydrodynamic conditions in the column. In addition, the flow rates of the raffinate and extract phase over the height of the column also change due to the mass transfer in the extraction

5 Loading of a modular system from Sulzer Chemtech for recovery of solvents and purification.

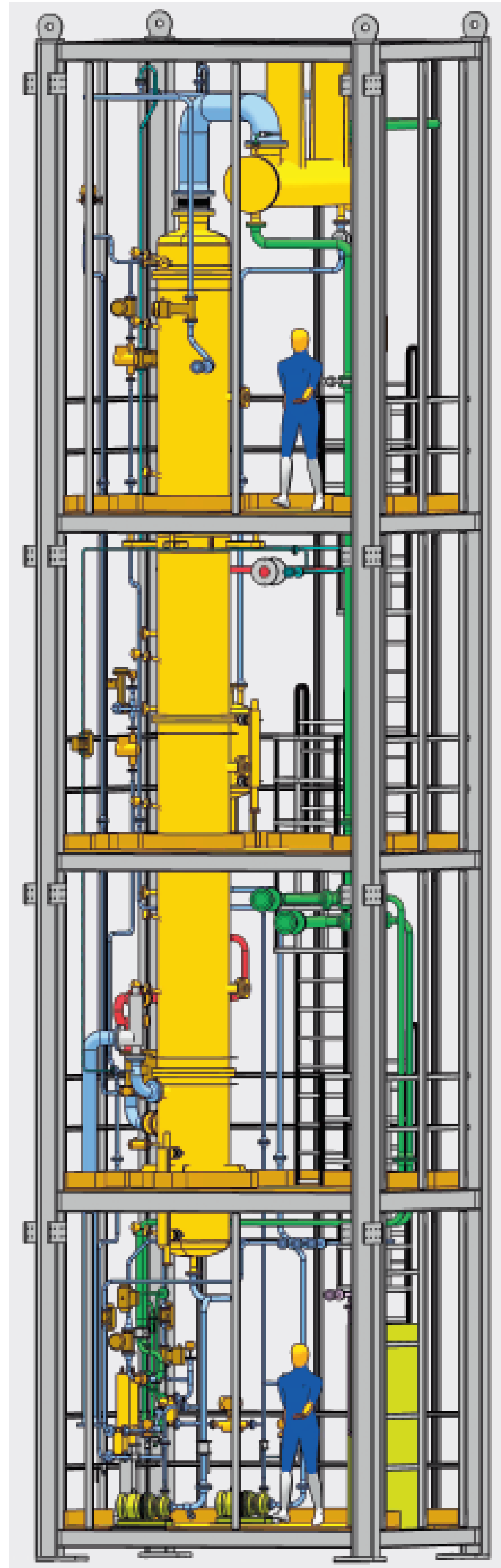
column. These changes are often so significant that the internals of the extraction column have to be adapted to these. This is the case when wastewater is polluted with 10% or more acetic acid by weight, for example.

The agitated Kühni column type ECR has proven to be very suitable for applications that require high separation performance and great flexibility. Figure 3 shows internals of this type of column, in which the geometry can be changed in each compartment. In this way, it is possible to compensate for any changes in physical property data and mass flow rates that arise typically in the case of large mass transfer. ECR extraction columns have already been successfully used for wastewater with up to 12% phenol by weight and 35% acetic acid by weight. Columns have been built with more than 30 theoretical stages.

Columns with structured Sulzer extraction packing type ECP are used for very large wastewater flows with throughputs of several 100 m^3/h. This type of column is characterized by a high hydrodynamic capacity but does not allow separation performances as high as ECR columns do. Together with liquid distributors specifically adapted to the packings, very efficient processes can be realized with these columns, in which large material flows can be treated that require only moderate separation performance.

Distillation trays are used in the stripper column for the post-treatment of wastewater, as there is often a large liquid load in these columns and a two-phase liquid in the upper part. The treatment of the extraction agent is often carried out in a rectification column with Sulzer distillation packing designed for high separation performance.

In comparison to biological treatment of municipal wastewater, industrial wastewater treatment often requires the use of different thermal separation processes. The optimal selection of the extraction agent, the type of equipment that will be adapted to the task, and the operational parameters require broad knowledge and experience in all areas of thermal separation technology. This is vital in order to be able to combine the individual unit operations to achieve an efficient process. The necessary data for the design and operation of the system is obtained through a comparison with reference installations and, in particular, for the extraction step, through pilot trials in the Sulzer Test Center[2]. Figure 4 shows a section of a pilot liquid-liquid extraction column in operation. Based on many years of experience, it is thereby possible to find a turnkey solution to remove many high boiling pollutants from a wastewater flow, as shown in Figures 5 and 6.


6 3D layout of a wastewater stripper in a Sulzer Chemtech modular construction.

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