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## Release

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## Industrial Water Treatment: Eco Protection Only Part of the Story

**Demand for water in China continues to rise but the country's resources are limited, making state-of-the-art water treatment technologies all the more important. The options range from membrane and biological techniques to the vision of treatment plants which generate electricity.**

Water is used for many purposes in industry, including cleaning, cooling and heating, as steam, feedstock or solvent or as part of a product. UNESCO estimates that between 5% and 20% of fresh water extracted worldwide is used in industrial processing. In China, the proportion of industrial water usage in overall demand was 23% in 2007 and that figure is expected to rise to 33% by 2030 when it will reach 265 billion m<sup>3</sup>. Demand will exceed available fresh water supplies by a considerable margin.

As it takes a new approach to the problem, the process industry is already building recovery and desalination plants to treat waste water. In the future, water recycling technologies will play an increasing important role in China. The goal is to re-use 20% of waste water by 2015. That equates to 3.7 billion m<sup>3</sup> per annum according to Innovation Center Denmark.

This makes the Chinese water treatment market attractive for technology suppliers. In 2011 alone, the country imported \$11 billion worth of equipment for the water industry, a 23% rise year-on-year.

A number of physical, chemical and biological techniques are available for treating a wide range of process and waste water streams. However, virtually every project is unique as the specific parameters (composition, temperature, pH, etc.) can vary considerably. The methods or combinations of technologies have to be tailored and depend on the desired result. Is purification the only objective or is there a need to recover constituents? What constituent is targeted and what quality level is required?

### **Membrane technology - a growth market**

Membrane technology is one of the most widely used techniques. The energy requirements are relatively modest, and it has a proven track record in high-volume scenarios. Highly specific, functionalized membranes are needed for the relatively small volumes of process water. Ceramic membranes are one option. Good mechanical, chemical and thermal stability make them suitable for aggressive media, and they are compatible with highly effective chemical cleaning agents and hot

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steam sterilization. They can be deployed in the production process to treat partial flows only and the loops can often be closed to prevent heat loss. Examples includes micro filtration membranes for treatment of contaminated oil-water emulsions, ultra filtration membranes for treatment of high-concentration alkali baths and nano filtration membranes for decolorization of chemically aggressive, hot textile effluent from textile finishing.

Membranes are however usually only the first step in the water treatment process. Between 30% and 50% of the original volume flow is left over as concentrate which has to be disposed of at considerable expense. This causes significant problems at municipal water plants where there is an unhindered flow of degradation-resistant substances into the receiving watercourses. Additional purification stages are necessary to permanently remove contaminants.

### **Recovering high-value substances by precipitation and flocculation**

Precipitation and flocculation can be deployed to remove contaminants prior to downstream purification stages and to treat concentrate and recover high-value substances such as metals and phosphate. Other substances can be removed by co-precipitation depending on the requirements which the precipitate is expected to meet. In a well-managed process, these techniques can easily be combined with other stages and also yield products of significant economic value.

Selective sorption and membrane techniques provide another feasible method of recovering high-value substances such as metals, catalysts and anti-oxidants or removing problematic constituents such as heavy metals, phenol or biocides prior to biological treatment. They are also suitable for removal of silicates and phosphates which could impair downstream membrane stages. Depending on the composition of the water, ion exchangers with a variety of functional groups may be used, even to recover metals from water with a very high salt content. Molecularly imprinted polymers (MIPs) are currently attracting considerable attention. In terms of geometry and functional groups, these polymers have been processed so that they have an affinity with a specific template molecule, forming a key and lock combination. They are very selective and highly resistant to extreme pH, temperature and pressure conditions and organic solvents. By combining different process steps, fractionated recovery of various constituents such as polyphenols from olive processing becomes feasible.

### **Advanced Oxidation Processes (AOP)**

AOPs have a very broad application horizon. Free-radical reactions with high oxidation potential make AOPs particularly suitable for breaking down anthropogenic and toxic organic water constituents. Disinfection, decolorization and deodorization of the (waste) water normally take place in parallel. However, intermediates and by-products (transformation products) may form which can also create toxic effects. This makes analysis and design prior to actual deployment particularly important.

Compared to other techniques, AOPs have higher energy demand. AOPs are only cost-effective when the contamination level is relatively low, there are definite production benefits and the AOPs are used in combination with other techniques (biological, membrane-based, adsorptive, etc.). AOPs are normally very cost-effective for post-treatment of process effluent (polishing: elimination of trace elements, decolorization, disinfection, etc.) because the need for oxidation agents is relatively modest in these applications. Because AOPs are able to completely remove organic compounds, they may be used as a partial process in high-value substance recovery and water recovery, normally enhancing the quality of the recovered high-value substances and the reusable process water. The quality of

metal salts which are recoverable by precipitation can be improved by prior oxidation which minimizes the (co-)precipitation/flocculation of organic compounds.

Photocatalysis could become an increasingly attractive option, particularly in arid regions where solar radiation is often at its highest. However because current catalysts such as TiO<sub>2</sub> have a relatively low photon yield, the technique will initially be restricted to polishing.

### **Biological water treatment: complex and versatile**

Biological water treatment is an exceptionally important technique. It is more cost-effective than chemical and physical processing, and it can be tailored to the particular need using the large variety of microorganisms and reactor concepts which are available. Microbes which can be cultivated on a large scale are able to break down most organic constituents. Complete decomposition of inorganic salts or conversion to organic high-value substances (CH<sub>4</sub>, H<sub>2</sub>, lactate, oil, etc.) can take place when temperatures and salt content are relatively high, even outside the neutral pH range.

Using a variety of process management techniques, the parameters in the reactor can be adjusted to cultivate the target biomass (nitrifying organisms, methane forming organisms, etc.)

- Biomass growth or maintenance metabolism

- Suspended or carrier-bound growth

- Aerobic or anaerobic reaction conditions (availability of an electron acceptor)

With many water treatment techniques, aerobic and anaerobic processes take place in parallel. Aerobic processes are only initiated to a significant extent after oxygen has been actively introduced.

Biological treatment is used mainly in centralized water treatment plants where the various process effluent flows at a site are treated in one place to exploit synergies (economy of scale, balancing of mass flow and hydraulics, merging of C and N rich flows, avoidance of toxic concentrations). The insufficient biodegradability of certain synthetic low molecular weight substances and possibly inhibiting effects as well can cause problems. As a result, chemical/physical techniques are integrated into the treatment process, normally for partial flows.

Aerobic processes are based on specialized bacteria, algae or enzymes. They can also be immobilized on carrier materials with additional functions (membranes, sorbents). Multi-stage design can enhance the process. In place of a biocoenosis (biological community), individual specialized organisms are used at each purification stage under optimal conditions. Once the microbiological reactions are known, the bioreactors can be designed for cost-effective treatment of concentrate as well as process effluent which has low concentrations and contains trace elements. Algae-bacteria biotic communities are an established feature of industrial effluent treatment in sunny regions. Microalgae are used for selective sorption of specific effluent constituents and for recovery of substances such as heavy metals. They could in the future be used to recover oil as well. However to be cost-effective, the selectivity, regenerability and service life of the microalgae will have to be improved.

Besides the conventional water treatment plants, various types of membrane and biofilm reactors are also in operation. They are designed to effectively decompose effluent constituents and produce high-value substances and/or energy from the effluent matrix. Techniques where biomass is bound on a substrate play an important role in this context. They are less susceptible to problems and improve

process stability. Depending on the specific situation, anaerobic and aerobic fixed and fluidized bed reactors have proven to be effective for treatment of process effluent containing constituents which are difficult to break down. They operate with the aid of immobilized microorganisms.

### **Aerobic membrane reactors**

Besides taking up a lot of space, conventional biological techniques have other disadvantages. The dissolved effluent constituents have to be accessible to microbial decomposition under the given conditions and must not produce toxic or inhibiting effects under the actual operating conditions. With conventional process design, non-decomposed compounds and microorganisms have an “escape”, and that can have a negative impact on plant operations.

Aerobic membrane reactors/activation systems which to some extent do not exhibit these disadvantages have become an established process element over the past 20 years. They are reliable, compact and adaptable and deliver good purification performance. The range of applications includes deployment systems for internal water recycling and to close a gap in water recycling loops.

When an aerobic membrane reactor is used to treat highly contaminated industrial effluent or partial flows, different sub-processes can be combined in intelligent ways. The water composition is often very one-sided, and special reactor designs are developed to handle these situations. Efficient gas injection systems and intelligent control of those systems considerably reduce energy consumption. New and in some cases highly specialized membrane cleaning strategies are available. In choosing membrane materials and module designs, long-lasting, flexible and high-performance systems are preferable to low-cost mass-produced varieties. Aerobic membrane bioreactors are often linked to other physical or chemical treatment stages, creating highly specific, tailored hybrid systems.

### **Anaerobic techniques**

Energy release and reduced aeration energy consumption are major reasons why anaerobic technology is used on a widespread basis, normally as a pretreatment stage for effluent with high organic content which then passes to an aerobic stage. The conversion performance of anaerobic bacteria is very high, reducing the cost of sludge disposal and minimizing nutrient demand. This has distinct advantages, especially when the effluent is low in nitrogen and phosphorous.

Anaerobic water treatment is a good choice when the concentration of organic constituents is high, there is a constant inflow of effluent and the water contains few if any inhibitors. It is important to retain or return as much of the biomass as possible, because active biomass grows very slowly when conversion rates are low. This can be achieved through sedimentation techniques or biomass immobilization. Pilot testing is currently underway to evaluate the suitability of membrane bioreactors. The poor filterability of anaerobic sludge poses the main obstacle. Air cannot be used to control the thickness of the particle layer in the anaerobic stage. Substitution with biogas is not simple and raises safety issues.

### **A vision for the future? Microbial fuel cells**

Microbial fuel cells are one of the most interesting fields of current research. Basically, microorganisms break down dissolved or fine particulate organic matter through a process of oxidative decomposition while generating electricity at the same time. Because they aggregate at the anode forming a biofilm, they are able to release electrons directly. Effluent with relatively low levels of organic contamination,

for example municipal sewage, readily lends itself to energy-efficient treatment. Sewage treatment plants could even conceivably generate electricity.

The technology is currently at the pilot stage. Work is still needed on the materials and efficiency levels among other things. Experts are nevertheless convinced that technology will soon be available as an enhancement to anaerobic waste water treatment, as the process parameters such as temperature and duration of treatment are similar. MFCs also appear to be particularly suitable for waste water streams with high levels of organic matter which do not lend themselves to aerobic treatment due to high salt or sulfate contamination.

### **One step further: Integrated water management**

Water recycling is worthwhile when contaminated waste streams can be recovered at reasonable cost and with minimal effort. Water recycling is less efficient for waste streams that are highly contaminated and contain substances that have a very diverse range of chemical and physical properties. The basic prerequisite for water recycling therefore is the establishment of an efficient water management system to separate water that readily lends itself to recycling from water that is less suitable.

Optimization of the material streams is a highly complex task. The process and product implications, the impact on energy and personal resources and the economic context all must be taken into consideration. Because production-integrated water management involves considerable expense, retrofit of existing treatment plants is normally not cost effective. However on new build or extension projects, the designs can incorporate these aspects right from the start, and investors have the prospect of saving considerable amounts of energy and water over the long term. Recovery of high-value substances also becomes far easier, and a reduction of emissions at the source reduces post-treatment costs.

In contrast to integrated design, the additive approach involves the inclusion of additional downstream process stages. Seamless transition between internal additive and integrated design has been successfully implemented at a number of plants. Hot nano filtration, for example, follows directly after a dyeing or washing process. The water is recycled and less energy is consumed. Ion exchangers are used to treat rinse water in finishing operations. Other examples include membrane filtration for water recycling systems in the food & beverage industry. Most of these internal recycling processes are located at or near the source where the complexity of the constituents is low and additive techniques can be deployed with minimum effort and expense.

**Summary: Given the challenges China is facing, it could well become a pilot country for advanced process water management. A wide range of technologies are available. At AchemAsia on May 13<sup>th</sup> – 16<sup>th</sup>, 2013 in Beijing, the latest developments will be presented at the exhibition and in the congress program.**

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