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akvoFloat™ for refinery wastewater reuse – a flotation-filtration technology based on novel ceramic membranes

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The use of polymeric membranes (MBR, UF) as a pre-treatment before desalination has gained considerable acceptance and is generally a feasible method for refinery wastewater treatment and reuse; however, there are some important unresolved challenges.

These challenges are often in terms of increased fouling caused by oil and organics, scaling by metals and very expensive and frequent membrane replacements that significantly impair the economics of such solutions.

This article presents a full wastewater reuse project for a German refinery (250 m^3/h) and the water management study that has been carried out in order to assess the technical and economic feasibility of a solution based on akvoFloat™ – a novel water treatment technology based on ceramic membranes. The aim is to prove that this solution has the capability of avoiding the shortcomings of the above-mentioned 'state-of-the-art' technologies based on polymeric membranes with a positive ROI.

A novel technology

akvola Technologies is a water technology company that provides cost-effective and environmentally-friendly solutions based on akvoFloat™ – a proprietary flotation-filtration process – to clean hard-to-treat industrial wastewater containing high concentrations of oil (free, dispersed and emulsified) and/or suspended solids in harsh environments (pH, temperature, salinity, etc).

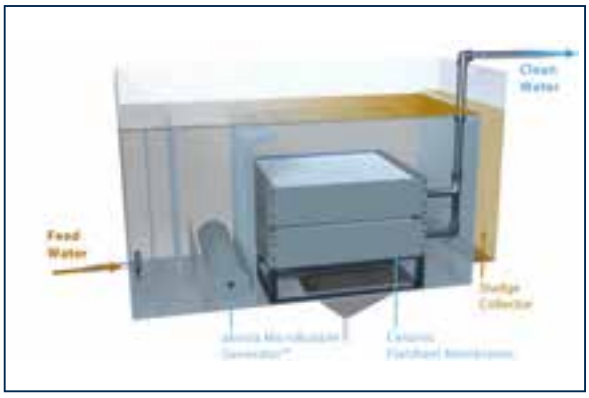

Figure 1: akvoFloat™ flotation-filtration process

akvoFloat™ is a separation technology based on a proprietary flotation-filtration process. The process leverages the akvola MicroBubble Generator™ and the company's special know-how in the design and operation of novel ceramic membranes, resulting in the most energy-efficient design on the market for oil and suspended solids removal in hard-to-treat waters.

The feed water first enters the flotation zone, where the akvola MicroBubble Generator™ induces fine gas bubbles (50-70 micron) using very little energy and equipment – without the need for a saturator or a water recycle stream, unlike DAF (Dissolved Air Flotation). These microbubbles attach to suspended matter, oils, hydrocarbons and organic flocs which are carried to the surface. The float layer that forms on the surface is skimmed off the tank at regular intervals. The partially treated water then enters the filtration zone, where submerged ceramic membranes are used as a polishing step. They provide high, constant permeate quality with very low pressure drop. (See a video here: http://vimeo.com/akvola/akvoFloat™)

The flotation in akvoFloat™ acts as a pretreatment, allowing for the submerged flat sheet ceramic membranes to be driven at high fluxes (up to 5x higher than polymerics) with very low transmembrane pressures (TMP < 0,2 bar) even in heavily polluted waters. This translates into systems with a very economical Capex/Opex balance, unlike the conventional cross-flow driven ceramic membrane systems in the market, which require more membrane surface, more equipment and have a higher energy consumption. The high chemical and mechanical robustness of ceramic membranes allow for very effective cleaning and longer lifespans that resolve the above-mentioned limitations of polymeric membranes.

Water management study: Drivers and results

The goal of the customer is to find a solution to treat 250 m^3/h wastewater effluent to be reused as boiler feed water with the following objectives:

- high resistance to influent variabilities,
- reliable, simple and cost-efficient operation and
- high recovery rate in order to minimise waste.

This project consists of a wastewater management study that includes a feasibility study (Q2 2016), a field project to validate the results obtained in the previous study (Q3-Q4 2016) and the design and implementation of a full-scale solution (2017).

Figure 2: akvoFloat™ pilot unit

Table 1: Crucial effluent parameters of existing WWTP and set RO feed quality targets

Parameter	Unit	WWTP normal operation	RO feed quality target
pH	[-]	7	-
Conductivity	[µS/cm]	1000	-
Turbidity	[NTU]	10	< 1
TSS	[mg/l]	20	-
SDI15	[-]	N/A	< 3
TOC	[mg/l]	10	< 3
COD	[mgO2/l]	35	< 6
BOD5	[mgO2/l]	< 3	< 3
CFU	[CFU/ml]	10000	< 10
O&H (Oil&Hydrocarbons)	[mg/L]	5	0.1
Nitrate	[mg/l]	45	-
Sulfate	[mg/l]	100	-
Aluminium	[mg/l]	0.07	< 0.05
Free Chlorine	[mg/l]	< 0.1	< 0.02
Iron	[mg/l]	0.5	< 0.05
Manganese	[mg/l]	0.15	< 0.05

The wastewater treatment plant (WWTP) in the oil refinery includes a flotation unit, an activated sludge process with secondary clarification and a sand filter as last treatment step to meet the current effluent limits for direct discharge to a nearby river. The favoured water reclamation option is to reuse wastewater as boiler feed water. The scope of akvoFloat™ is to treat the sand filter effluent up to RO feed quality, since an RO will be used for desalination. Comparing historical data sand filter effluent and RO feed quality requirements the wastewater impurities with the need of reduction were identified:

- Suspended solids and colloidal matter measured as Total Suspended Solids (TSS) and Turbidity

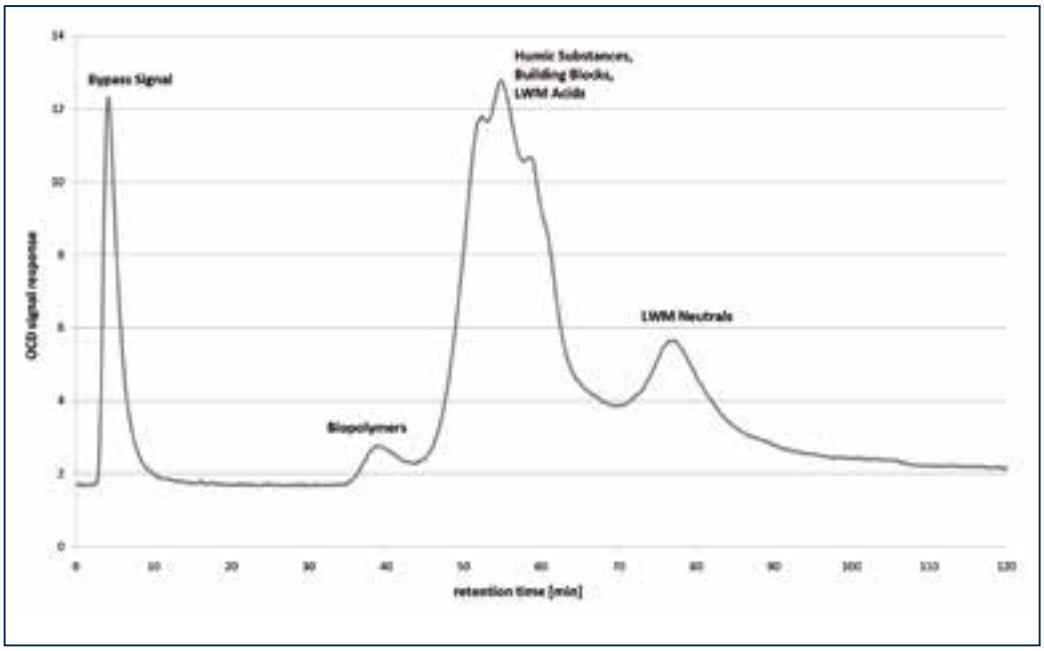

Figure 3: Results of the LC-OCD analysis to identify organic species

- Emulsified and dissolved oils measured as Oils & Hydrocarbons (O&H)
- Organics measured as Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC)
- Microbes measured as Colony Forming Unit (CFU)

Other contaminants, such as metals, free chlorine, nitrates and sulfates need to be removed prior to the RO with proper chemical treatment (pH adjustment, antiscalants, and so on). Table 1 lists the crucial effluent parameters of the existing WWTP (250 m^3/h) and the set RO feed quality targets.

The removal of the organics is a challenging treatment step as the efficacy of polishing technologies is highly dependent on the exact type of organic pollutants. For this reason a Liquid Chromatography - Organic Carbon Detection (LC-OCD) analysis has been carried out to identify the organic species. The results are shown in Figure 3.

It can be seen that the organic load mainly consists of high molecular weight humic substances (humic acids, fulvic acids), building blocks (breakdown products of humic substances) and low molecular weight (LMW) acids (oxalic, formic, acetic, propionic acids). Biopolymers (polysaccharides, proteins) and LMW neutrals (alcohols, aldehydes, ketones, amino acids, sugars) are present to a lesser extent.

akvoFloat™ is chosen as the first treatment step of the treatment chain because of its high resistance against inlet quality fluctuations. In case of upsets in the WWTP's sand filter effluent, such as breakthroughs of oil or high levels of suspended solids, akvoFloat™ acts as an absolute barrier for downstream units with high sensitivity against fluctuations. Within akvoFloat™ the two sub-processes complement each other in the removal of the key contaminants:

- **Micro-flotation**: Flocculation drives the agglomeration in flocs of humic substances as well as emulsified and a part of the dissolved oils so that the micro-flotation can remove them effectively. However, building blocks are not easily agglomerated by flocculation. Preliminary flocculation + flotation lab tests with Ferric Chloride showed a COD and TOC removal of about 50% and 30% respectively.
- **Flat sheet ceramic membrane filtration**: Due to the pore size of 0,1 micron of the ceramic membranes chosen for this application of akvoFloat™, a 3-log reduction (99,9%) of bacterial count measured as CFU/ml has been achieved during the lab tests. TSS and Turbidity were reduced to below the RO feed quality limits as well as SDI15 to < 3. The remaining emulsified and flocculated dissolved oils are removed by the membrane reaching the RO feed quality limits (O&H < 0,1 mg/L).

The lab test results with akvoFloat™ show that a polishing for the COD and TOC levels is required downstream. Several RO pre-treatment technologies are available for organic load reduction including adsorption, biological activated carbon (BAC) and oxidation (ozone, UV, AOP). After careful consideration, the use of ozone was preferred with the possibility of upgrading it to an AOP by the additional dosage of hydrogen peroxide. As an additional step, Granular Activated Carbon (GAC) was chosen as the adsorption technology.

In summary, the lab test results show that the novel akvoFloat™ technology has been able to almost completely remove the bacteria, turbidity, oils and TSS, and halve the refractory organics (like humic substances). The study results conclude that adsorption on GAC and oxidation techniques with ozone are applicable downstream of akvoFloat™ in order to decrease the organic load to appropriate RO feed levels. The pilot system for the ongoing field trials includes the following treatment chain:

- an akvoFloat™ pilot unit (2-3 m^3/h),
- a polishing step (GAC and oxidation with ozone will be tested), and
- an RO pilot unit (0,5-1 m^3/h), in order to validate a stable RO operation is possible.

Conclusion

The micro-flotation pre-treatment and the properties of ceramic membranes enable this technology to overcome the limitations that polymeric membrane based technologies have shown in the past ten years – ie, increased fouling,

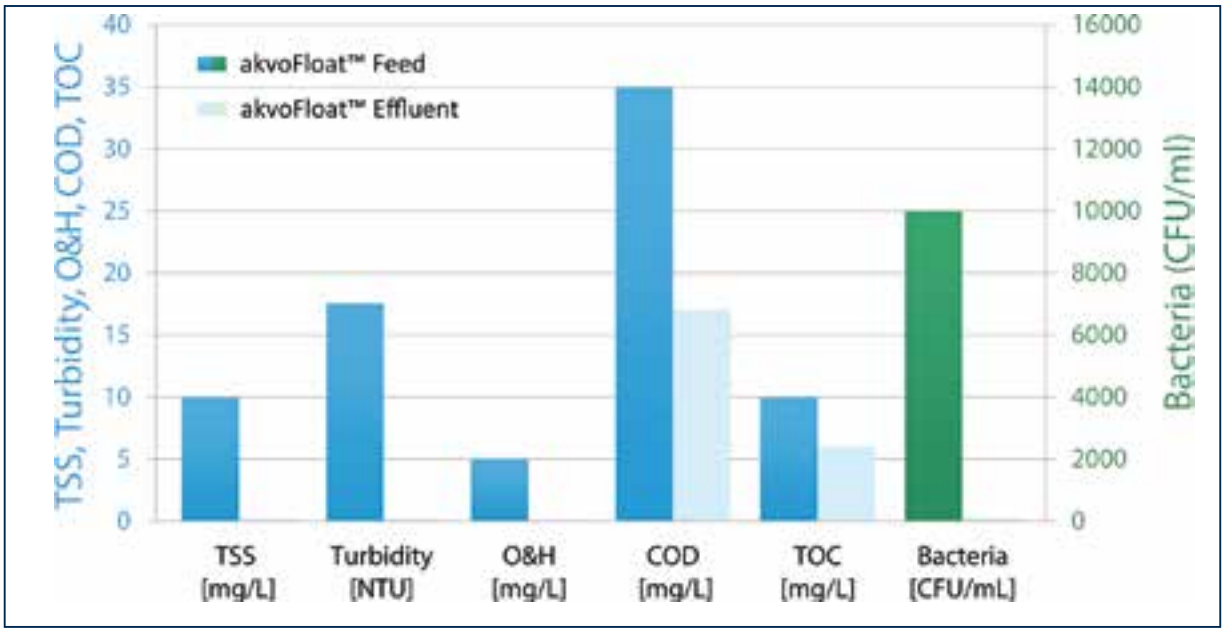

Figure 4: Lab test results of the use of akvoFloat™

frequent and costly membrane replacements.

Based on these promising results, the customer has decided to execute field trials at the refinery (ongoing). These long-term tests will reveal more about the technical and economic feasibilities of the proposed treatment trains. In particular, the operational costs of the polishing steps under consideration are a concern, due to the difficulty in the removal of the present recalcitrant organics.

Upon the successful completion of the field trials, akvola Technologies will start the design of a full-scale plant that will enable the refinery to reuse 100% of their wastewater, thereby reducing the costs of sourcing and discharging water as well as improving their environmental and water stewardship, thus meeting their internal corporate mandate expectations.

Five years of reverse osmosis membrane elements from LANXESS in Bitterfeld

"Our foray into the reverse osmosis (RO) membrane business five years ago has truly been a success story. We have almost reached the limit of our current capacity so we are going to double production capacity in the coming year," said Jean-Marc Vesselle, head of the LANXESS Liquid Purification Technologies (LPT) business unit, on the occasion of a celebration of the five-year anniversary of the Lewabrane plant operated by IAB Ionenaustauscher GmbH, a wholly owned subsidiary of the LANXESS specialty chemicals company in Germany.

"The Lewabrane brand has established a firm place for itself in the market, not least on account of its high quality and performance properties, which both we and our customers expect from 'Made in Germany' products," he added.

The market for RO membrane elements is currently projected to grow at an above-average rate of 10% annually in coming years (CAGR 2015-2020). Because the plant is already operating at almost the limit of its capacity, LANXESS has decided to double the corresponding capacity at the Bitterfeld site. The additional capacity is scheduled to come on line in the second half of 2017.

LANXESS is demonstrating its commitment to the Bitterfeld site in a number of different ways, including in Research & Development. In this regard, Vesselle said: "We are continuously conducting research in all areas of modern water treatment so that we can continue to provide our customers with the requisite expertise from a single source."

For that purpose LANXESS is cooperating with technical universities and other research facilities in the region such as the Fraunhofer Institutes for Factory Operation and Automation (IFF) in Magdeburg and for Microstructure of Materials and Systems (IMWS) in Halle.

LANXESS is one of only two companies in the world that offer know-how and products both in membrane elements and ion exchange resins. "With this comprehensive water treatment capability we can meet the requirements of customers all over the world," Vesselle remarked. The membrane element plant is the logical continuation of a tradition dating back almost 80 years in Bitterfeld-Wolfen. LANXESS operates additional production facilities for ion exchange resins in Leverkusen, Germany, and Jhagadia, India.

Because membrane and ion exchange technology frequently go hand in hand, the development and introduction of the LewaPlus integrated design software was a major contribution to optimally linking the strengths of both technologies.

Strands of different thickness are used for the novel, multifunctional feed spacers. These create space between the membrane surfaces for fast-flowing water, support the membrane in the process and cause turbulent water flow. (Photo: LANXESS AG)

For more information:
http://lpt.lanxess.com/en/home/