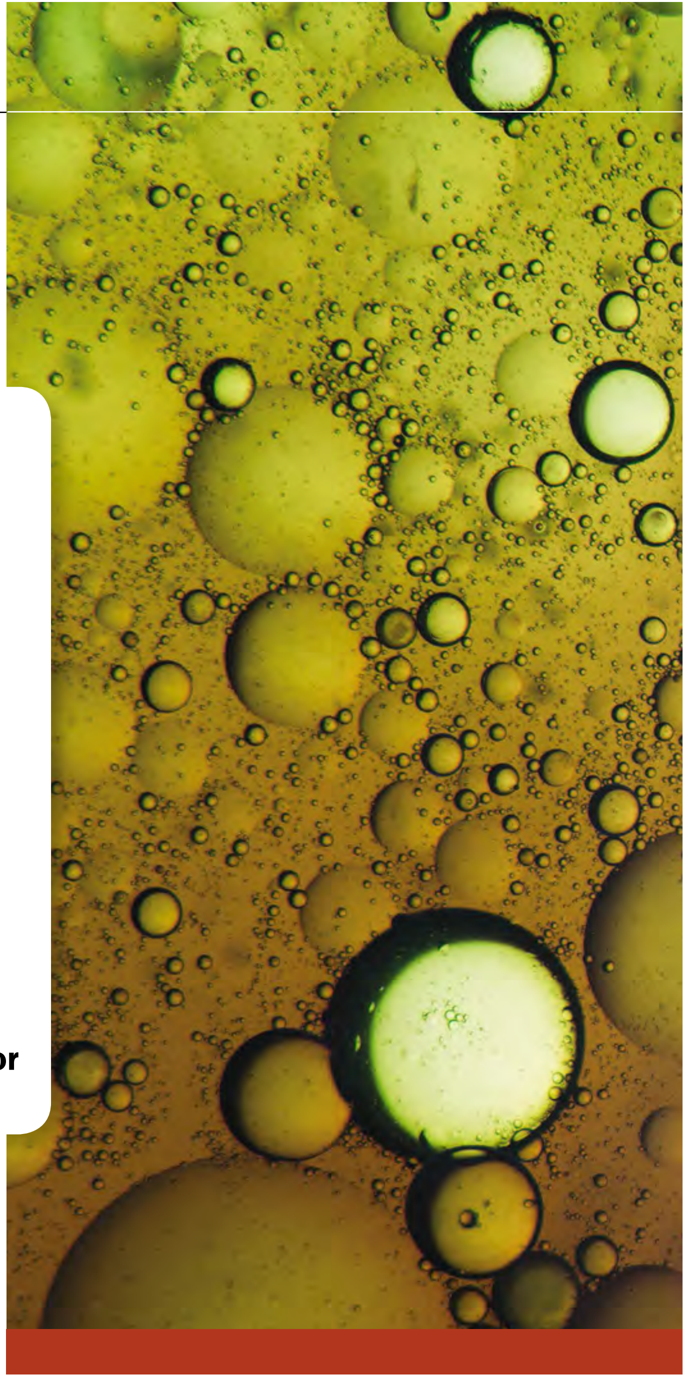
Hybrid flotation-filtration process for oil water separation based on ceramic membranes

by Dr-Ing M Beery, Dipl-Ing, J Ludwig, Dipl-Ing, L León, all of *akvolution* GmbH, Berlin, Germany

Microflotation and membrane filtration are two commonly used technologies in many fields of application. This article discusses how the two technologies were integrated and modified on a lab scale using new novel ceramic materials to technically assess their joined applicability for removing oil from water or water from oil.

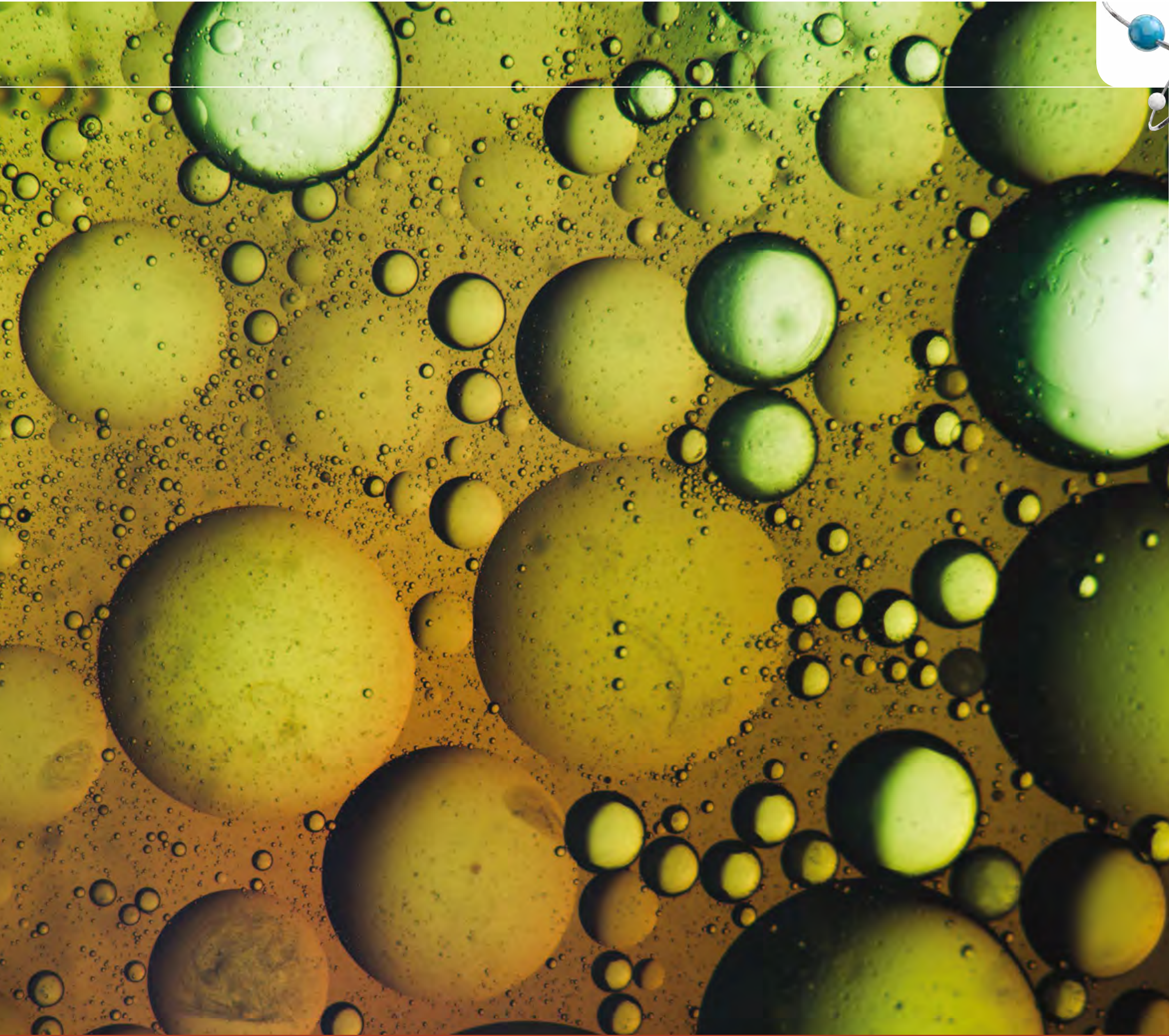


Abstract

Removing oil from water or water from oil is a challenging task which is relevant in many fields of applications such as food processing, pharmaceuticals, coatings, petrochemicals and oil and gas extraction. Two commonly used technologies, microflotation and membrane filtration were integrated and modified on a lab scale (10 l/h) using new novel ceramic materials to technically assess their joined applicability. In this article we present the results from testing this hybrid technology using produced water coming from both an onshore oil field and a refinery in Germany. The results are analysed in terms of both separation efficiency as well as market viability.

The use of advanced water treatment separations technologies for the removal of oil from water is becoming increasingly important in several industrial sectors. Especially in the oil and gas industry, the extraction and production of oil and gas is co-producing increasing amounts of oily industrial wastewaters commonly referred to as 'produced water'. This hydrocarbon-rich water must be sufficiently treated before being disposed of or reused in the production process. After a basic, gravity-based, three-phase-separation commonly referred to as 'primary treatment' the water is typically processed by a secondary (flotation/hydrocyclones) and possibly a tertiary (filtration by means of nutshell, cartridge or ceramic filters) treatment, in order to reduce the oil and suspended solids concentration before disposal or reuse. This article introduces and tests the concept of intensifying and integrating these processes for increased efficiency, low energy, compact solution, akvoDeOil (Figure 1).

The only way of successfully integrating the two processes requires the use of ceramic membranes for filtration (due to their robustness and high flux) and induced gas flotation (IGF). The use of IGF instead of dissolved gas flotation (DGF) in produced water treatment is beneficial in terms of energy consumption. Produced water is typically saline (100-300 000 ppm Total Dissolved Solids are possible ([1])) and warm (40-70 °C are common) and since the solubility



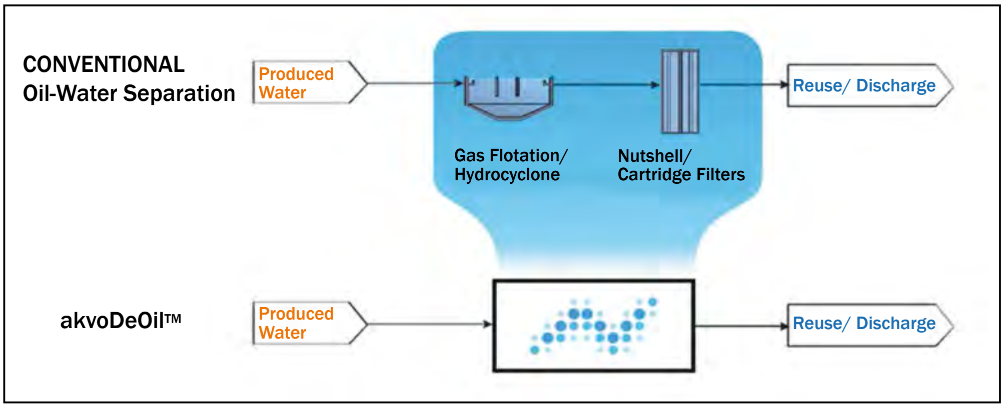


Figure 1: Integrating flotation and filtration for substitution of the secondary and tertiary treatment.

of gas in water decreases with increasing salinity and temperature, the energy required to recycle and introduce gas into a stream increases.

At the same time the use of cartridge filters and nutshell filters in the tertiary treatment step does not fully remove suspended solids, especially in the critical range of 1-10 micron that could cause formation damage and permeability issues in the reservoir when the water is re-injected for reuse ([2]). Therefore the use of porous ceramic membranes (pore size <1 micron) is preferred. The potential of ceramic membranes for produced water treatment is well documented in [3].

Materials and methods

Different fine bubble diffusors were screened for their microbubble generation efficiency. The use of flotation for

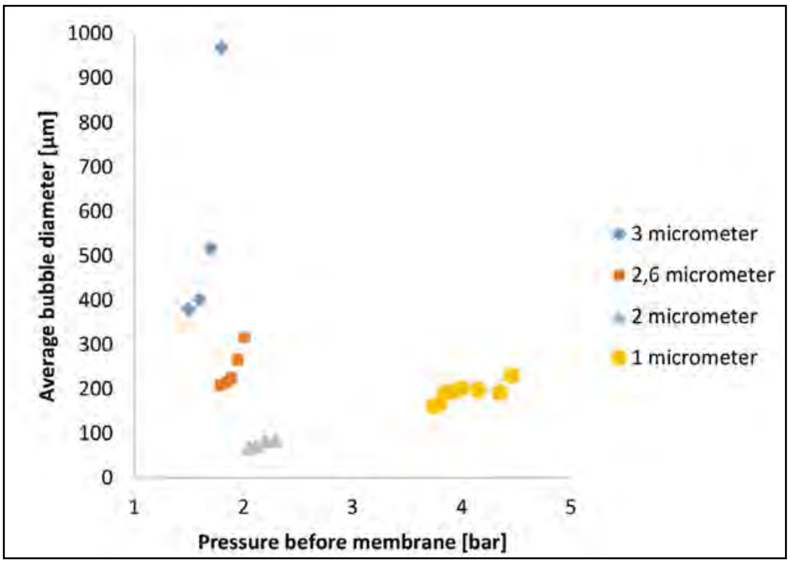


Figure 2: Average bubble diameter as function of the pressure drop for different diffusor pore sizes

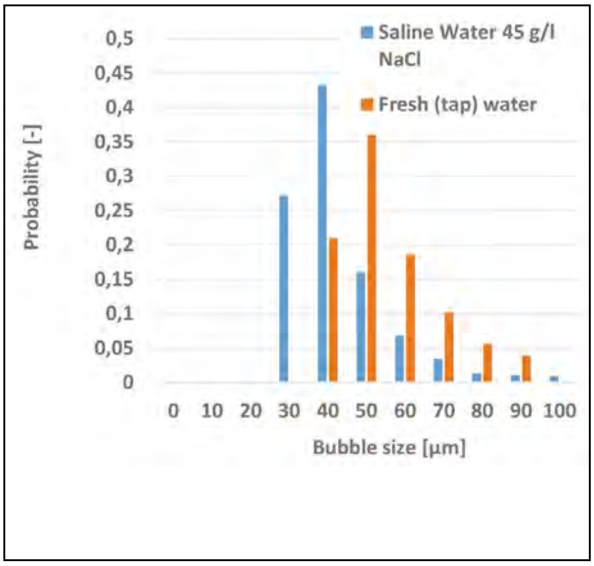


Figure 3: Difference in produced bubble size distribution resulting from increased water salinity

oily water treatment typically requires fine bubbles (<100 micron) and the needed chemical resistance called for the use of ceramic materials. Four different pore-sized ceramic diffusors were tested in a bubble column setup equipped with a CCD high-speed camera and automated image analysis software calculating the bubble size distribution. The relation between the required pressure (p), pore diameter (D), the contact angle (θ) and surface tension of the liquid (σ) is described by equation 1 with K as a correction factor for non-cylindrical pore shape:

$$\Delta p = K \frac{4\sigma \cos\theta}{D} \qquad (1)$$

Decreasing the required bubble size generally means reducing the diffusors' pore size down to a point where bubble coalescence begins playing a role and the overall pressure drop becomes too high. The effects of the applied pressure and pore size on the bubble size were measured (Figure 2). The ideal pore size was found to be 2 microns operating at a pressure of 2 bar producing an average bubble size below 100 micron.

Saline water, having higher density, viscosity and surface tension than fresh water has an effect on the bubble generation and formation. This effect is positive in the sense of producing finer, more narrowly size-distributed bubbles (Figure 3).

The experimental setup consisted of a continuously stirred feed tank with a valve and a pump feeding oil-water emulsion to the flotation-filtration unit. The unit consisted of a single ceramic diffusor fed by compressed air (2 bar) in a contact zone and a small 0,06 m² submerged ceramic membrane made of either Al_2O_3 or SiC run by an external gear pump in a vacuum driven mode (Figure 4). A weir collected the float hydraulically.

The air bubbles and oil droplets in the emulsion were analysed using optical methods (Figure 5).

Results

The setup was first tested with a mixture of motor oil and water at different concentrations and an alumina 0,2 micron filtration membrane. Each run lasted 6 hours with the goal of reaching steady state and preparing the system for 'real' produced water emulsions.

The results are shown in Table 1. It is clear to see that the higher the concentration of motor oil in the feed the lower the overall flow that one could reach (reduced permeability of the membrane). The oil concentrations in the filtrate were relatively high at 63-81 ppm practically independent of the feed concentration, which may indicate the formation of a stable emulsion that was not efficiently removed by the membrane. Nevertheless the removal efficiency increased with rising feed concentration. This trend must, however, be treated with caution as the fouling effects (higher transmembrane pressure (TMP), lower fluxes) also increase.

The actual produced water used in this study came from an onshore oil well in the centre of Germany characterised by a low oil-in-water content and high suspended solids concentration ('Feed A') and diluted crude oil dewatering wastewater coming from a refinery in Germany ('Feed B').

Feed A was processed at a filtration flux of 100 l/m²/h using alumina membranes with a pore size of 0,2 micron. The transmembrane pressure remained low during the entire duration of filtration at < 0,1 bar reducing the oil content to 9,5 mg/l and the suspended solids to 4,5 mg/l. A constant removal of the float layer could be hydraulically realized throughout the run. After the run the membrane surface showed a dark brown residue and an oily layer. Both could be removed by the use of a water jet.

Feed B was filtered by a SiC membrane with a 0,04 micron pore size and a flux of 100 l/m²/h. The pressure drop increased during the run from 0,2 to 0,4 bar. The filtrate quality and removal efficiencies were high showing almost no traces of organics or solids.

The results are summarized in Table 2. Figure 6 shows a qualitative comparison between feed, filtrate and float in A.

Conclusions and outlook

The results show that using a single ceramic flotation-filtration integrated unit (akvoFloat) results in an effective reduction of both suspended solids and oil from real produced water. As a result this integrated process could potentially

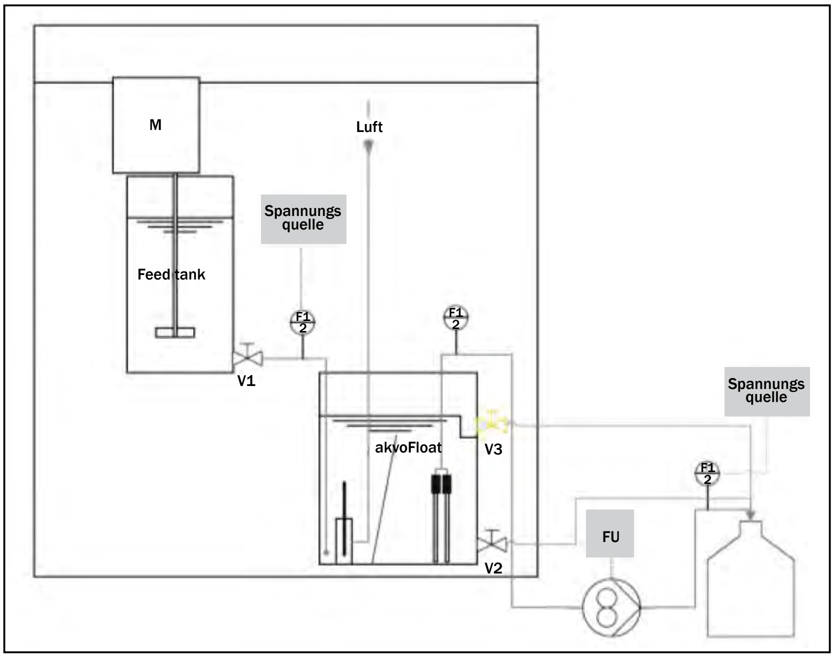


Figure 4: The small scale (20 l/h) flotation-filtration laboratory setup

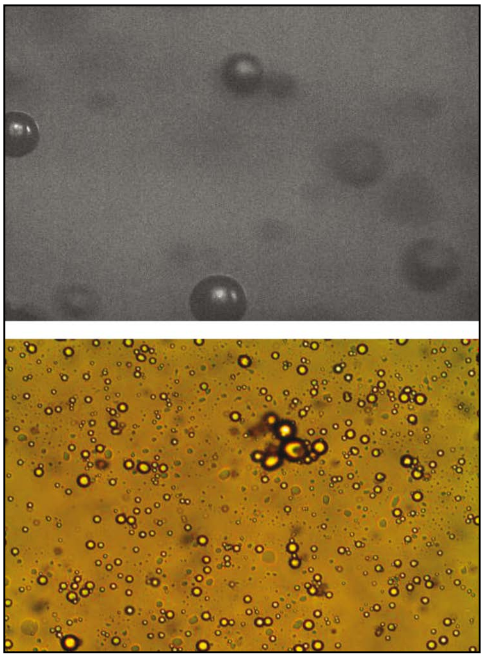


Figure 5: Microbubbles captured by a high speed camera (top) and oil droplets in an emulsion caught in a light microscope (bottom)

Feed (ppm)	Filtrate (ppm)	Removal (%)	TMP (bar)	Average Flow (l/h)
284	80	71.82	-0.2	22.5
457	81	82.22	-0.3	17
660	63	90.92	-0.4	16

Table 1: preliminary experimental results using motor oil in water emulsions

Parameter	Unit	Feed A	Filtrate A	Feed B	Filtrate B
Turbidity	NTU	335	0.4	-	-
Organic carbon	mg/l	20	9.5	253	0.5
TSS	mg/l	100	4.5	39	0

Table 2: Water quality parameters of feeds A and B and their corresponding filtrates

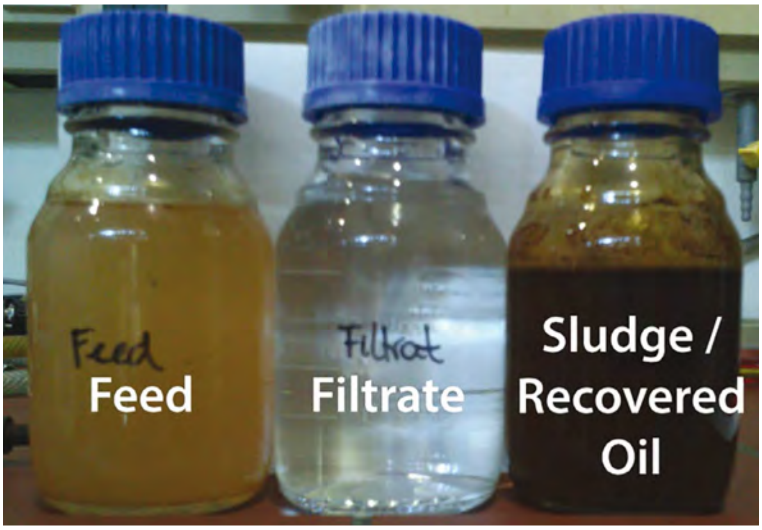


Figure 6: Feed A, permeate A and float A samples side by side.

replace the two process step currently used, yielding water that could be used for either discharge or reuse (Figure 7). The low pressure levels required both for flotation and for ceramic membrane filtration indicate a low energy consumption that fits well with the global water-energy-nexus agenda and could offset the higher capital costs associated with ceramics. Continuous field tests using a larger system accompanied by an exact cost analysis will follow later this year giving proof to these claims.

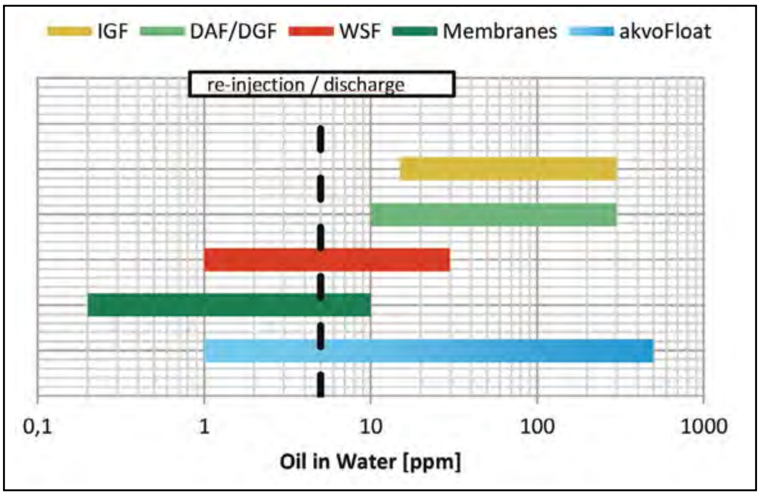


Figure 7: Operating Range (Feed to Effluent organics level) of different common technologies: Induced Gas Flotation (IGF), Dissolved Air/Gas Flotation (DAF/DGF), Wallnut Shell Filters (WSF), Membranes and akvoFloat

Literature

[1] M Stewart and K Arnold, Produced Water Treatment Field Manual, Gulf Professional Publishing, 2011.
[2] Personal communication, Baker Hughes Water Management 2014.
[3] S Alzahrania and AW Mohammad, Challenges and trends in membrane technology implementation for produced water treatment: A review, Water Process Engineering, 4, 2014, 107–133.