MANN+HUMMEL

Preface

Oily wastewater is classified as containing either free (floating) oils or oil/water emulsion. Many industrial processes could generate oily wastewater. Examples of these include petroleum refining, petrochemical, food, leather and metallurgy. Fats, oil and grease present in oily wastewater needs to be removed before reuse or discharge.

Sources of oily wastewater include produced water from oil refinery, wastewater from car washes, scouring baths for cleaning metal parts, cooling lubricants in metal process such as cutting, dry docks and wastewater stream from food factories. Oily water is usually in an emulsified form and this is a potential hazardous waste for most centralized treatment plant. Table 1.1 shows the typical oil concentration from the various industrial processes.

TABLE 1.1. Sources of oily effluents (Patterson 1985)

Industrial process	Oil concentration (mg/L)
Petroleum refining	20–4000
Metal processing and finishing	100–20000
Aluminum rolling	5000–50000
Copper wire drawing	1000–10000
Food processing (fish and seafood)	500–14000
Edible oil refining	4000–6000
Paint manufacturing	1000–2000
Cleaning bilge water from ships	30–2000
Car washing	50–2000
Aircraft maintenance	500–1500
Leather processing (tannery effluents)	200–40000
Wool scouring	1500–12500
Wood preservation	50–1500

Typical discharge limit for oil and grease is 10-15mg/L for mineral and synthetic oils and 100-150mg/L for other oils. Treatment of such oily wastewater can be via various techniques including gravity and centrifugal separations, chemical treatment, flotation, filtration, evaporation, biological treatment, membrane or hybrid processes.

Membrane processes, in particular, Ultrafiltration, has proven to be more effective and efficient as compared to conventional methods as a final treatment steps such as coalescers or filter media. However, one major drawback is the high fouling rate of Ultrafiltration membranes. This paper looks at the advantages of using Ultrafiltration for treatment of oily wastewater mainly emulsified oil separation and goes forth to prove that Polyacrylonitrile (PAN) membranes exhibits low fouling which is an ideal choice for treatment of such waters.

Background

Since over 70 years, quality, service and innovations make the MANN+HUMMEL Group a distinguished development partner and original equipment supplier for a wide range of products: automotive industrial filters, membrane filters for water filtration and filter systems.

The history for MANN+HUMMEL dealing with oily water can be traced back from the below cases:

1. Hydrocleaner Development

The operation of the advanced fuel injection technology for modern diesel engines requires the removal of free water and coarsely dispersed components from the diesel fuel. Ceramic ultrafiltration membrane is examined as a candidate to treat diesel water. The target for the hydrocarbon concentration in the permeate side is below 2ppm to meet the stringent European Union discharge standard.

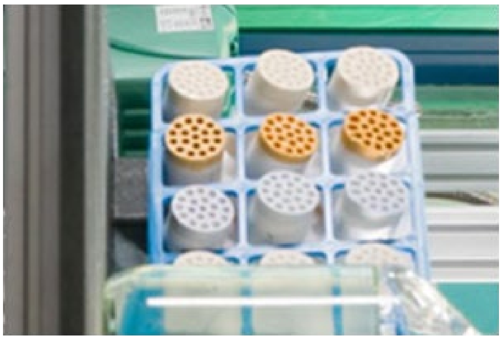


Fig: Ceramic UF membranes for diesel/water separation.

2. Hydromation Nutshell Filter

Hydromation is a division of Filter elements and systems for industry and trade in ANN+HUMMEL. The Filter Nutshell has been proposed as an alternative to polishing removal of oil and solids, ensuring the quality required for reuse of contaminated water stream in Duque de Caxias Refinery, Brazil. The final Quality of the contaminated water in terms of total TOG (5mg/L) and the turbidity (20NTU) are compatible with the raw water feed of ETA.

Fig: Nutshells filters for Produced water treatment, Brazil.

3. Water and diesel separation by coalescence filter media.

Emulsion stabilizing components – surfactants effect have been studied with different additive species and concentrations in various diesel fuels using hydrophilic filter media (coalescer). Interfacial tension drops with interfacial age by measuring contact angles. CFD Investigation – Water Droplet Separation from Diesel Fuel have been studied.

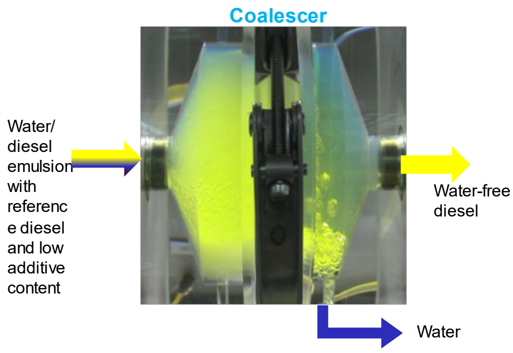


Fig: CFD Investigation – Water Droplet Separation from Diesel Fuel, Germany.

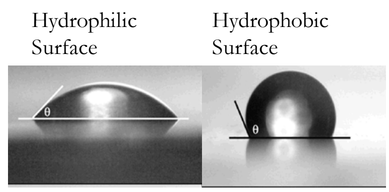
Conducting on-going researches, the established water business R&D center has the full capacity in Singapore, including water analysis, membrane development and cartridge/skid development.

Further reference on water/oil separation includes Edible Oil Refinery Treated Effluent in Malaysia, Mann Diesel Wastewater Treatment in Singapore and etc.

Oil-water separation mechanism

Effective separation of oil-in-water emulsions is controlled by several key parameters such as the *membrane pore size, surface energy, and wetting behaviour, size of oil droplets, surface tension, and pressure difference* across the membrane.

A membrane is a semi-permeable thin layer of material separating two fluids based on their physicochemical properties. The membrane surface can change their surface energy depending on the surrounding medium. This indicates that the membrane consists of functional groups on surfaces which differ in degree of hydrophobicity/hydrophilicity. The surface tension between the liquid phase, the surface material and the wetting nature defines the separation efficiency of oil-water emulsions.



	Hydrophilic Surface	Hydrophobic Surface
Contact angle	Low	high
Adhesiveness	Good	Poor
Wettability	Good	Poor

Fig 1. Water droplet and its wetting nature on

*Abbreviations: PVDF - poly vinylidene fluoride, PP - Poly propylene, PES- polyethersulfone, PAN- polyacrylonitrile.
IGF- Induced gas flotation; TC- total carbon; CPI – corrugated plate inceptor; O&G- oil & grease ; TSS-total suspended solids and *dispersed oil

Membrane surface

Membranes utilise the Laplace pressure inside the suspended phase to hinder access of the dispersed phase into the membrane. Hence the wettability differences between the immiscible liquids can be used to enhance membrane separation processes. According to Young's-Laplace equation,

$$\Delta P_{LP} = {}^{-4\gamma cos\theta}/_{d}$$

Where γ- Interfacial tension between liquids;
θ- Contact angle;
d- Pore diameter.

If the pressure difference across a hydrophilic membrane exceeds a certain critical pressure value, the oil phase will penetrate the membrane. Thus, for high separation efficiency, the transmembrane pressure (TMP) should be maintained at a value below Laplace pressure (ΔP_{LP}).

More Hydrophilic →

Material	PP	PVDF	PES	Modified PAN
Contact angle(θ)	108	85	54	30
Surface tension(σ) (mN/m)	25	29	41	44

Table 1. Water characteristics on membrane surface

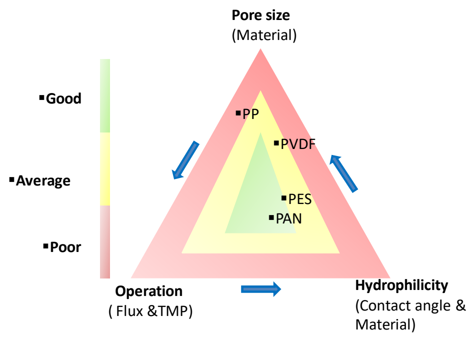
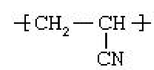


Fig 2. Ternary diagram explaining membrane behaviour

Table 1 and Fig 2 show that the performance and separation efficiency of the membranes is mainly based on the Material properties, operational behaviour and pore size of the membrane. Compared to all other polymeric membrane surfaces and their properties, it clearly shows PAN membranes are more hydrophilic and have higher affinity for the water filtration from the Oil-water mixtures.

A spectroscopy characterization of PAN interfacial interactions with water and oil, demonstrated that the nitrile (CN-CN) interaction is the main reason for the superior affinity to water and high chemical resistance property of PAN (ref-1). The acrylonitrile repeating unit of the polymer has the following structure:



As water being the wetting phase of the PAN membrane surface shows high hydrophilic to obtain larger fluxes of water. This is making back wash processes with water very effective and increases cleaning efficiency to achieve high selectivity compared to other membranes such as PES, PVDF and PP in the market.

Membrane treatment for oily water separation process

Large amounts of oily wastewater produced from diverse industrial, offshore/ onshore sources need to be treated before discharge to the sewage system or into the sea. Conventional wastewater treatment technologies such as coagulation, flocculation, and air flotation and gravity separation normally cannot meet the high discharge requirements.

By choosing the most efficient combination of material, pores structure and operation condition, membrane treatment for the removal of emulsions in water are very effective and the energy consumption is low, they are simple to scale up and the membrane properties can be controlled easily.

M+H Oily water case studies

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Emulsified oily water treatment – ONGC, India

Background: In 2012, M+H have supplied 1200 m^2 membrane area to one of the biggest petroleum companies in India for the removal of emulsified oil in produced water treatment (PWT) process.

The PWT process has multiple stages of conventional treatment steps (such as CPI, IGF, Nutshells and filter media or membrane).

Challenge: The feed oily water quality is dependent on the conventional pre-treatment systems placed before M+H UF system. The permeate water quality target is Oil & organic content should be less than 10 mg/l.

Results: M+H UF membrane system is used as a final polishing step in the PWT process. The discharge requirements have been achieved for the permeate water having oil content less than 5 mg/l.

As the M+H PAN UF membrane is highly hydrophilic in nature and it rejects the lowest oil content in the feed water (Table 2).This hydrophilic nature of membrane enhances the backwash process and achieves high separation efficiency for oily water filtration.

Parameter	Feed	Product	Reject
pH	7.24	7.4	7.51
Turbidity(NTU)	57	1.4	211
COD (mg/l)	933	533	--
TSS(mg/l)	62.5	4.0	240
O&G(mg/l)	35	5	100

Table 2.Quantitative measurements of water samples

Produced water Re-injection (PWRI) – Azerbaija

Background: Ultrafiltration Polyacrylonitrile (PAN) membrane was used to treat and meet the discharge standards of produced water for reinjection (PWRI) in Azerbaijan, **2007**.

Challenge:

To meet the <30 mg/l O&G discharge requirements of PWRI in permeate water with a feed water contains in total 500mg/l free and emulsified oil.

Results:

High volumes of produced water are treated 20m^3/h at 0.3-0.5bar transmembrane pressure (TMP) and the permeate water quality having <10mg/l of oil & grease content achieved to meet the discharge regulations for PWRI. The systems were regularly backwashed and the separation performance was achieved consistently.

Parameter	Feed	Product
TSS(mg/l)	-	< 2.0
O&G(mg/l)	500	10

Table 3. Re-injection water quality measurements

Fig 3. PAN- U860 Klar-20 series in Azerbaijan

Produced water treatment- IBPT, Germany

Background: M+H Membranes have been used for Industrial oily waste water treatment in the market for many years. An internal research project has been designed to get more insights for produced water treatment process using UF membranes in collaboration with a research institute.

Systematic trials have been performed to screen M+H Membranes for produced water treatment process. Current M+H PES and PAN membranes pilot modules were prepared and experiments were performed at external labs (Fig 5).

Challenge: Real produced water provided by major Oil & Gas Company, having emulsified oil is treated with M+H Ultrafiltration membranes modules.

Results:

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The performance of the membranes was tested at fixed criteria's of TMP-0.5bar and Feed flow velocity -2.5m/s. All the tests were performed without any cleaning steps in between the filtration time to observe the base character of the membranes with PW.

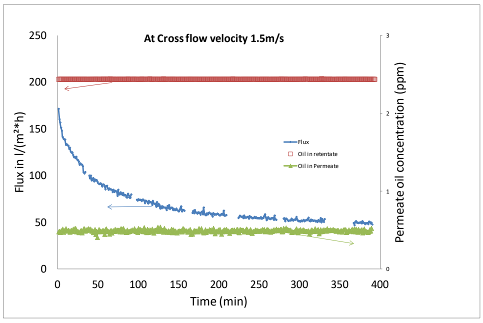

Fig 4. PAN membrane test with raw produced water having 1000ppm oil in feed.

The PAN membranes experiments results were shown above in Fig 4. It shows PAN membranes have high separation efficiency of **99%** oil removal even after 8hrs of filtration with no cleaning steps in between. Also shows almost 98% TOC retention.

The average flux of 90-100 LMH at 0.5bar TMP has been achieved. This performance is clearly much higher compared to other commercial membranes in market. After 8hrs filtration, a regular back wash with 1% detergent achieved 85% of flux recovery with PAN membranes.

Parameter	Feed	Product	Reject
COD (mg/l)	400	6.0	--
TC(mg/l)	122	3.0	143
Total Oil (mg/l)	126	1.0	154
Emulsified oil (mg/l)	35	1.0*	154

Table 4. Produced water samples quantitative analysis

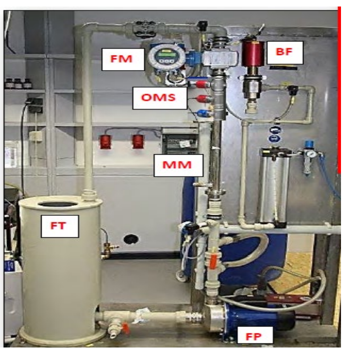

Fig 5. Pilot test system with in-situ measurements (where FM: flow meter; BF: back flush; FT: feed tank; FP: feed pump; OMS: oil measurement)

Whereas the filtration experiments with PES membranes performed with same feed flow rates and membrane area as PAN membranes to have fair comparison. Fig 6 show PES lower membranes separation efficiency for oil removal. After experimenting at different back washes pressures and back wash time the flux recovery was achieved only **~ 60%.**

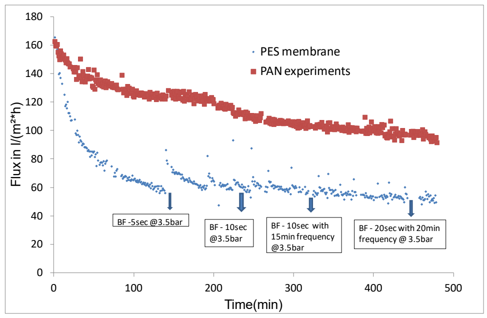

Fig 6. PAN & PES membrane test result for Flux

Conclusion:

Ultra filtration for produced water treatment using PAN membranes shows high separation efficiency compared to other membrane materials like PES. Together with sufficient operation protocol and optimized pore structure, PAN membranes unique nature having affinity of nitrile groups to water molecules on the surface helps to achieve high, constant permeate flux and cleaning efficiency.

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