Image Cover Sheet

CLASSIFICATION	SYSTEM NUMBER
UNCLASSIFIED	516431

TITLE

Studies on Micro and Ultrafiltration in oily wastewater purfication

System Number:

Patron Number:

Requester:

Notes: Paper #19 contained in Parent Sysnum #516410

DSIS Use only:

Deliver to: CL

This page is left blank

This page is left blank

Studies on Micro and Ultrafiltration in Oily Wastewater Purification

A.Y. Tremblay and T.H. Li
University of Ottawa, Dept. of Chemical Engineering
Ottawa, ON.

D. E. Veinot
Defence Research Establishment Atlantic
Dockyard Laboratory(A), Halifax, NS.

ABSTRACT

A series of ultrafiltration (UF) and microfiltration (MF) tests were performed on an oily wastewater mixture whose composition closely resembled that of wastewaters accumulating in a ship's bilge. The wastewater was found to contain a substantial amount of dissolved solids, defined as particles measuring less than 0.45 micron, which cannot be accounted for as dissolved salts alone. These oily wastewaters are by nature difficult to treat with membrane processes. The presence of used lubricating oils in a ship's bilges implies that particles of soot will be present in this wastewater. In order to offer a better representation of actual bilge water, synthetic wastewater mixtures were prepared using used lubricating oils.

Experimental results indicate that free oil is present in this type of wastewater. The wastewater was found to contain mechanical emulsions, chemical emulsions and particles of soot that can act as nucleating sites for oil. The size of the particles causing the flux decline was determined from cake filtration theory. Excessive pump shear was found to reduce the size of these particles by half causing a reduction in membrane performance. Once dispersed, the particles causing this further reduction in flux decline did not readily aggregate over a 24 hour period.

Tests were performed to verify that free oil was not irreversibly coating the surface of the membrane leading to this flux decline. A UF membrane was placed in a stir cell and free oil was poured directly onto its surface. The results indicate that new oil does not readily remain on the surface of the membrane. To determine the affinity of used oil for the membrane, the test described above was repeated with used oil. After a period of 24 hours in the stir cell, 90 % of the membrane surface was free of oil and just as clean as at the beginning of the test. These tests indicate that the membrane can recover from the de-phasing of free oil at its surface.

The oil content of the permeate was determined for a series of UF membranes placed in cross-flow test cells. The quality of the permeate was relatively independent of the molecular weight cut-off of the membrane. Contrary to expectations, membranes having the smallest pore size had the lowest oil retention. The UF membrane having the lowest pore radius of 2 nm should have retained oil emulsions expected to be two to three orders of magnitude greater. This suggests that some free oil is dispersed in the wastewater at a molecular level. In the presence of a cake, free oil is scrubbed clean from

solution as it passes through the cake. The results further support cake dominated filtration where the presence of a hydrophobic cake at the surface of the membrane enhances the separation of free oil by capturing it in its structure.

Objectives

- Determine factors that affect the UF and MF of oily wastewaters.
- Focus on wastewaters containing:
  - mixture of 50/50, fresh water:seawater
  - presence of new vs. used oils.
- New vs. Used Oil
  - Microscopic examination of bilge water
  - Particle measurements using light scattering
  - Solids content in used oil
- Study oil de-phasing at the surface of the membrane.
- Determine oil removal as a function of membrane pore size (MWCO).

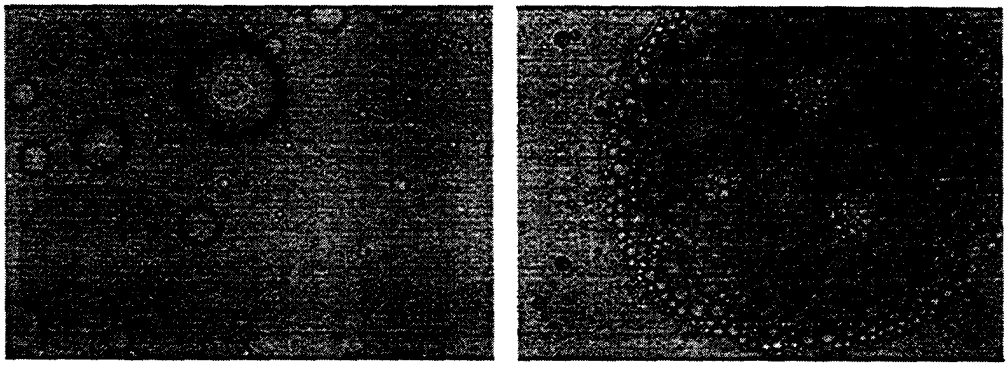
Oily Wastewater used in the permeation experiments – Synthetic Bilge Water

- oils – 2000 ppm;
  - 50% naval distillate (diesel fuel),
  - 40% naval diesel engine lubricating oil and,
  - 10% hydraulic oil.
- detergents and surfactants - 500 ppm.
  - 90% Canadian Navy standard oil and grease detergent (CLEANBREAK),
  - 10% Canadian Navy standard corrosion removal compound (OSTREM Rust Stain Remover).
- water - Composed of a 50/50 mixture of fresh and sea water.

New oil vs. Used oil

- New oil
  - oils are mainly aliphatic hydrocarbons (hydrophobic)
- Used oil
  - many oxidized chains (more hydrophylic)
  - contains soot
  - other particulates

Synthetic Bilge Water



New Oil Used Oil

50 µm

Microscopic examination of synthetic bilge water

- New oil - simple oil in water emulsion.
- Used oil - more complex water in oil in water emulsion.
- Used oil - possibility of forming reverse miscelles at the surface of the membrane

Determining the solids content in Used Oil

- Dissolve oil in hexane
- Filter using 0.45 micron PVDF filters.
- Particle content >0.45 µm = 4.9 % by wt. used oil.
- Particle content 0.02 to 0.45 µm = 0.72 % by wt.
- Total = 5.62 % by wt. used oil.

Bilge water can contain a large amount of dissolved solids in a range that is difficult to treat by membrane technologies.

- In a 6 % oil in water solution given very good dispersion,

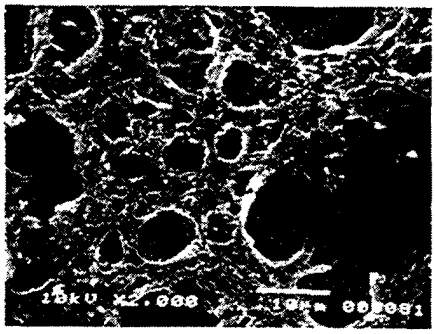
– there is a potential to have (6 *0.72 % = 0.04 % dissolved solids in solution)

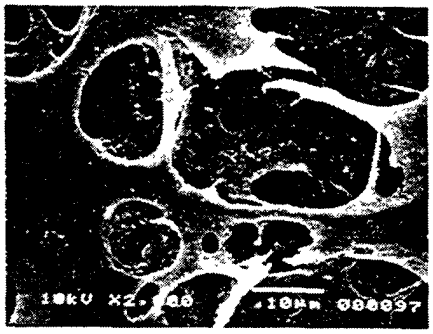
- assuming s.g. =1, gives 400 mg/L of dissolved particles in the 0.02 to 0.45 µm range.

Study effects of shear and aging on bilge water

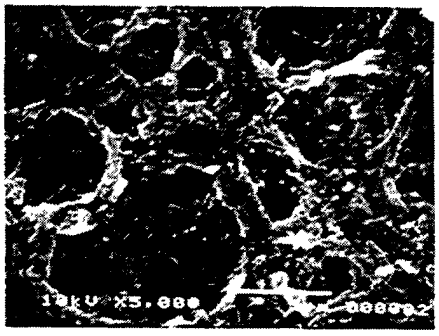
Study the effect of shearing - aging
Shear => circulating wastewater in a centrifugal pump for 1/2 hour
Shear wastewater - rest 1/2 hour - test
Take same wastewater 24 hours later - shear – test

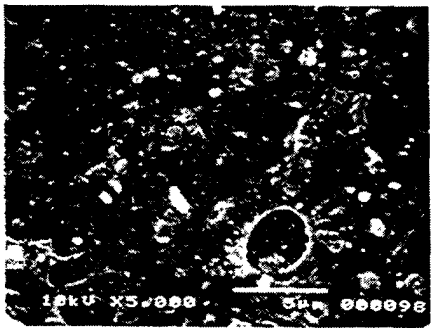
GN (10.0 kD) membrane
aging for
1/2 hour 24 hours



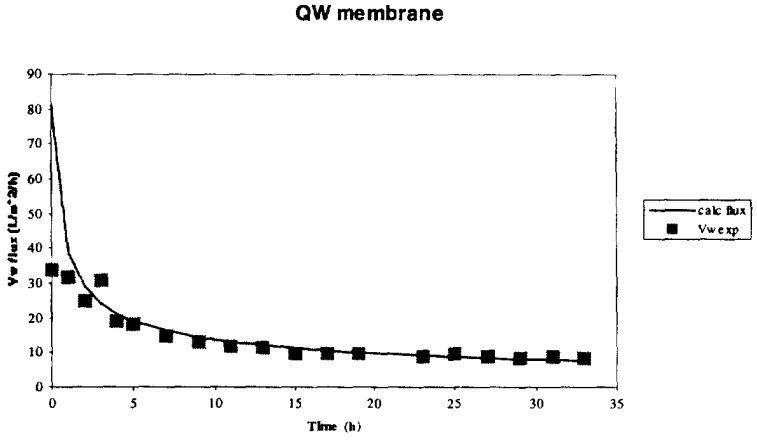


GN (10.0 kD) membrane
aging for
1/2 hour 24 hours



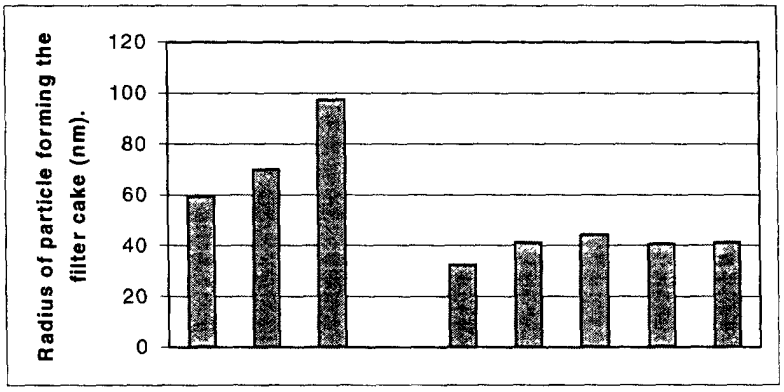


The size of the particles causing the flux decline was determined from cake filtration theory.



30,000 Daltons, MWCO, Radius = 6.4 nm

Shear effects on the radius of particles forming the filter cake at the surface of the membrane.



Conclusions from shearing and aging

- Shearing and aging reduced size of the particles found in synthetic bilge water.
- Once the bilge water was sheared, settling was not found to be a significant factor affecting the size of particles in bilge water.
- Excessive pump shear was found to reduce the size of these particles by half causing a reduction in membrane performance.

Tests to determine the influence of oil-membrane surface interactions

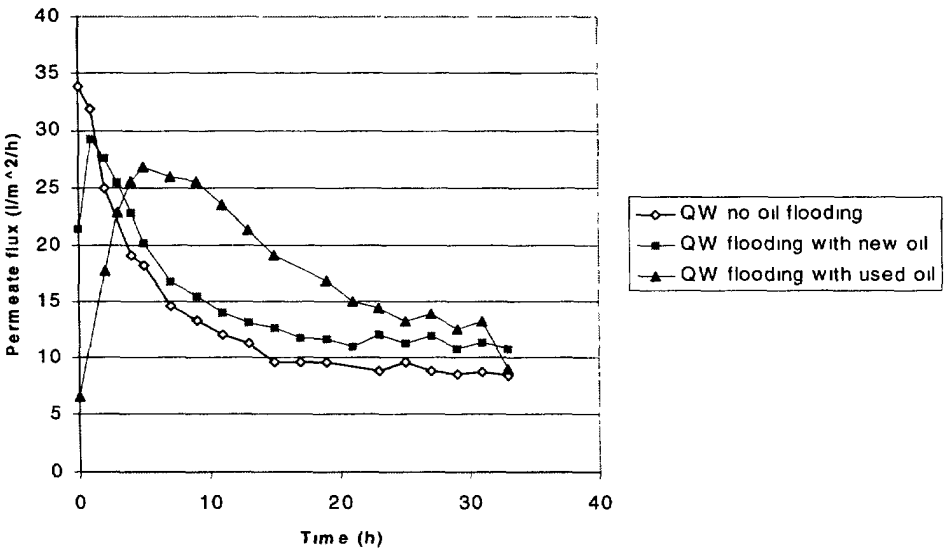
Objectives

- verify that free oil was not irreversibly coating the surface of the membrane
- perform experiments where free oil was poured directly onto the surface of the membrane prior to the permeation run.

Method

- Experiment conducted in a 7.0 cm diameter stir cell, QW (30 kD) membrane selected.
- The membrane was initially wet with water.
- Water droplets were completely removed from its surface.
- The membrane was placed in the stir cell and oil was poured directly onto the membrane until it was coated by a 1/8" thick layer.
- The oil covered membrane was then allowed to sit for 5 minutes.
- The stir cell was filled with synthetic bilge water and a standard permeation experiments carried out at 50 psig.

Plot of bilge water permeate flux vs. time for a membrane flooded with oil.



Plot of bilge water permeate flux vs. time for a membrane flooded with oil.

Conclusion- oil-membrane surface interactions

- The membrane can recover from a sudden exposure to oil.
- Hydrophilic membrane materials do exist, (QW membrane), that reduce or eliminate free oil as a cause of irreversible membrane fouling.
- These tests also indicate that the membrane can recover from the de-phasing of free oil at its surface.

The ability of membranes to separate oil and grease (O&G)

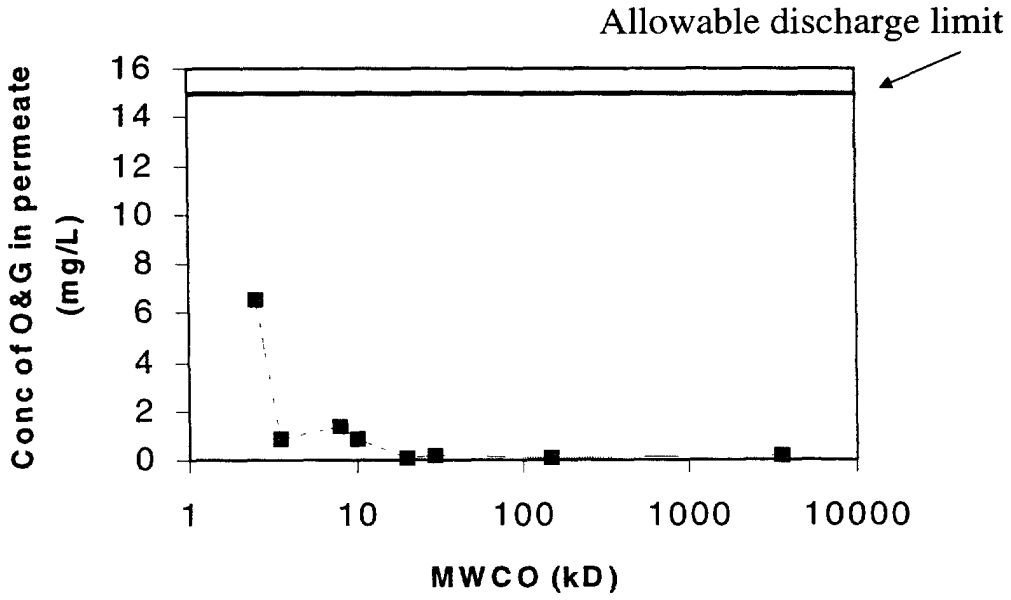
Analyze permeate from cross-flow tests

- operate test cells at a cross-flow velocity of from 1 to 1.8 m/s.
- Membranes were tested at 50 psig.
- Bilge water concentration of hexane extractable Oil and Grease EPA 1664 = 73 mg/L

Results from oil removal tests

- All membranes produce a permeate that meets and greatly exceeds the discharge regulation of 15 mg/L oil and grease for a feed concentration of 73 mg/L oil and grease.
- The quality of the permeate was relatively independent of the molecular weight cut-off of the membrane.

Plot of O&G Concentration in the permeate vs. MWCO of the membrane



- The pore radius of the GH membrane is 2.0 nm which should have separated 4.0 nm particles.
- The cake enhances the separation of free oil by capturing it in its structure.
- Suggests oil is dispersed at the molecular level or is destabilized on contact with the membrane but is scrubbed clean from solution as the feed passes through the cake.
- The state of the emulsified oil be it chemical or mechanical forming the cake will affect the separation process.

The cake layer acted as a dynamic membrane.

- This type of membrane can be formed dynamically and regenerated.
- Given proper conditioning of the bilge water, membranes having a large pore size can be used to treat this wastewater.

Conclusions Summary

- New oil - simple oil in water emulsion.
- Used oil - more complex water in oil in water emulsion.Used oil - possibility of forming reverse miscelles at the surface of the membrane
- Excessive pump shear was found to reduce the size of problematic particles by half causing a reduction in membrane performance.
- The membrane can recover from a sudden exposure to oil.
- These tests also indicate that the membrane can recover from the de-phasing of free oil at its surface.
- The wastewater was found to contain a substantial amount of dissolved solids, defined as particles measuring less than 0.45 micron, which cannot be accounted for as dissolved salts alone.
- The presence of used lubricating oils in a ship's bilges implies that particles of soot will be present in this wastewater.
- The results further support cake dominated filtration where the presence of a hydrophobic cake at the surface of the membrane enhances the separation of free oil by capturing it in its structure.

Acknowledgements

- Defence Research Establishment Atlantic (DREA/CRDA) - DND.