

PROTECTION FROM ORGANIC FOULING

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An ultra-low pressure drop oleophilic filter can solve problems associated with prefiltration of organics in crossflow membrane systems used in water treatment

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According to the latest reports, worldwide sales of cross flow filtration equipment and membranes were estimated to top \$4.7 billion in 2000. Reverse osmosis (RO) accounted for just under \$2 billion in sales, while Microfiltration (MF), Nanofiltration (NF) and Ultrafiltration (UF) accounted for the remainder (*Nonwovens Industry*, v.31, 2000-02-00).

RO is used in a variety of municipal and industrial water treatment applications. Almost half the cost of water filtration arises from clearing clogged and fouled filtration membranes (*Business Week*; February 26, 2001). The basic problem with filtration membranes is that they are composed of water repellent polymers. This causes them to attract and attach oily molecules and other organic compounds. In the past, attempts made to solve this problem using prefiltration have been unsuccessful due largely to the high pressure drop across oleophilic filters after they have captured and clogged with organic compounds and oils. Generally, the result has been prefilter organic fouling as opposed to crossflow membrane fouling, and in most cases membrane fouling still occurs.

Crossflow Membrane Technology

Cross current flow membrane technologies essentially work as molecular sieves and have been used to produce pure water in municipal and industrial applications. Cross flow operations typically fall into three categories:

- Ultrafiltration (UF)
- Nanofiltration (NF)
- Hyperfiltration (RO)

Particle size and molecular weight ranges are as follows:

- **Reverse Osmosis** -- Five to 15 angstroms (100 to 300 molecular weight (MW)); components retained are 99 percent of most ions and most organics over 150 MW; and process applications include brackish seawater, desalination, boiler feed purification, blow-down reclamation, pretreatment to ion exchange and ultrapure water production.
- **Nanofiltration** -- 10 to 80 angstroms (200 - 10,000 MW); components retained are 95 percent divalent ions, 40 percent monovalent ions, organics greater than 150-300 MW; and process applications include hardness removal, organic and microbiological removal, dye desalting, color removal.
- **Ultrafiltration** -- 100 to 1000 angstroms (1,000 - 100,000 MW); components retained are most organics over 1000 MW; and process applications include pre- and post-treatment ion exchange, beverage clarification, concentration of industrial organics and dilute suspended oils, removal of pyrogens, bacteria, viruses and colloids.

Commonly used is RO due to its high capability for removal of dissolved impurities. There are four major configurations for RO membrane modules: plate and frame units, hollow fiber, tubular and spiral wound. Membranes are available in a variety of materials. Some common ones are cellulosic and polyamide for RO and NF, and polysulfone, ceramic and fluorinated for UF. UF has molecular weight cutoff of 1,000 to 100,000. Pressure ranges are 25 to 400 pounds per square inch (psi) for UF; RO and NF generally operate in the 500 to 1000 psi range.

PS prefilters will allow crossflow membrane filtration feasibility in applications that are traditionally cost prohibitive.

All cross flow systems separate the influent stream into two effluent streams. These are the permeate (purified water which has passed through the membrane) and concentrate (pollutants rejected by membrane) which must be continuously flushed away. Crossflow is necessary in membrane systems due to the necessity of running continuously in a self-cleaning mode. Even a tiny fraction of foulant mass can have a severe effect on membrane performance.

Backwashing is not possible because the polymeric membrane is coated onto a support layer. Flow reversal causes membrane separation of membrane from the support layer.

The inherent tendency of RO membranes to catch all but the smallest particle sizes renders them susceptible to fouling by organic, inorganic and biological materials. Cross current flow does not suffice in keeping the membranes clean over time, and so they must be periodically washed. This can be tricky business, as membrane chemical compatibility may be similar to those of the fouling agent, in which case, the chemical cleaner will also dissolve the membrane. Short of dissolution, membranes can be denatured by solvents, high or low pHs and temperature extremes. At the very least, membrane/cleaner compatibility must be tested. It is unlikely that membrane cleaning will ever be totally eliminated even with the use of low concentrations of chemical cleaning agents in the process stream. Effective pre-filtration of particulate and chemical fouling agents should be considered when designing a membrane filtration system.

UF systems are not fine enough to capture ionic pollutants and therefore inorganic fouling has not been an issue. UF systems are able to capture most organic compounds over 1000 mw and are consequently susceptible to organic and biological fouling.

Effective protection of membranes is a complex matter and will require a multifaceted approach.

Organic Fouling

Membranes are very sensitive to fouling. Due to the large volume of feedwater containing potential foulants that pass through an RO system, even if a tiny fraction of the foulant mass is retained, the effect on membrane performance can be severe.

System performance is typically monitored through three parameters:

- Permeate flow normalized for temperature and pressure;
- Differential pressure between entry point of feedwater and exit point of brine concentrate; and
- Percent of feedwater salts passed into product.

A thin layer of foulant on the membrane surface can cause a noticeable increase in differential pressure. Fouling materials may generally be categorized as organic, inorganic or biological. Biological and inorganic foulants are adequately addressed through filtration and chemical treatment. Organic fouling is more problematic because chemicals that are effective in removing the organic fouling agents, especially in areas of accumulation where contact angle is high, tend to damage the membranes. This is because the membranes are chemically similar to the foulants themselves. Compounds effective in dissolving organic foulants tend to denature, swell, dissolve or otherwise damage the membranes resulting in decreased flux, service life and volumetric recovery. Consequently, effective prefiltration of organic foulants is crucial to the overall performance of RO and UF systems.

Prevention of Organic Fouling

A variety of prefiltration devices and techniques are currently used to protect membranes. Among these are clay, activated carbon prefilters, mechanical separation devices, such as oil water separators (OWS) and chemical additives. Chemical additives administered in low doses into the process stream can be very effective, as long the organic foulant is not allowed to build up. The effectiveness of chemical additives decreases with fouling buildup and with exposure of the membrane to concentrated slugs, which can cause irreversible damage.

Prefiltration, although a very good idea, has been ineffective to date due to very high pressure increases across prefilters when exposed to higher molecular weight compounds. This is true of

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traditional prefiltration materials like granular activated carbon (GAC) and especially true of typical polymer treated filters.

The ideal solution would involve effective prefiltration of higher molecular weight and insoluble organic compounds, coupled with effective chemical treatment of soluble and lower molecular weight organic compounds. To date, this has not been possible due to the high pressure drop across existing prefiltration technologies. We have attempted to solve this conundrum by developing an oleophilic filter which exhibits insignificant pressure drop even as it saturates with rheology-modified viscous organics. Saturation point of these filters is generally $\frac{3}{4}$ of filter weight with oil before breakthrough (generally with 99.99 percent first pass efficiency).

Chemistry and Performance of Low Pressure Drop Filters

As stated earlier, polymer treated oleophilic filters have generally been ineffective in organic prefiltration due to high pressure drop after capturing and fouling with organic compounds. This is due to the swelling of the polymer/organic foulant coagulate. We have developed a novel oleophilic polymer, which can be permanently cured into practically any filter substrate. What makes this molecule novel, aside from its high affinity for organic compounds, is that the polymer itself and its coagulate product with oil is viscoelastic. Generally, viscoelastic materials become more viscous and denser with shear. Essentially, the opposite of swelling occurs. Viscoelastic oleophilic curable polymer actually contracts when sheared, as is the case when water flows through a filter. This is a very important fact because as water passes through the filter the coagulate contracts allowing for essentially zero pressure drop across the filter to saturation.

The Solution

As stated earlier, viscoelastic oleophilic prefiltration technology is very effective at removing higher molecular weight non-aqueous phase compounds, however highly soluble organic compounds (i.e. ethylene glycol) are not captured by these filters. We have devised a composite solution for providing organic free feedwater to crossflow membrane systems.

With a composite unit, crossflow membranes can be totally protected from organic fouling. The RO membrane post polymeric surfactant (PS) will see clean water eliminating organic fouling and reserving flux. Membrane capacity is consequently reserved for what the membranes do best, namely removing soluble compounds with molecular diameters greater than that of water. These soluble materials, due to their low concentrations, low film thickness and high solubility, are then effectively treated using low concentrations of surface-active chemical dopants. Surfactants used in this way have very low impact on membrane integrity.

Case Study

A major industrial manufacturing plant extensively uses RO to recover precious process water due to its location in the desert where water is scarce. This facility initially attempted recovery of process waters utilizing membrane technology. They found that maintenance, cleaning and replacement of membranes only gave them 50 percent of their initial projected yield. The system was deemed effective but uneconomical. Consequently, viscoelastic PS filters were deployed as RO membrane prefiltration. After processing nearly a million gallons of water the facility has found that membrane service life has extended ten-fold, resulting in a 50 percent decrease in cost to treat and a 20-fold efficiency increase. The facility has implemented this composite technology plant wide, and has allowed the plant to be close-looped with their process water.

Even a tiny fraction of foulant mass can have a severe effect on membrane performance.

Conclusion

Composite membrane units composed of viscoelastic oleophilic prefiltration in conjunction with in-situ addition of low concentrations of surface-active dopants results in much more robust and economical membrane performance. Ultra-low pressure drop filters also generate substantial savings in energy and downtime.

The final result is reusable high-purity water with drastically lower operating costs, extended membrane flux and service life, and higher overall system performance. PS prefiltration will allow crossflow membrane filtration feasibility in applications that are traditionally cost prohibitive. PS prefiltration has similar benefits in deionizing water by protecting ion exchange resins.

PS technology is finding use in, and has gained extensive interest from, an assortment of industries, membrane manufacturers and technical societies for the removal of organic pollutants from water.

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