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Removal of polysaccharide foulants from reverse osmosis feedwater using electroadsorptive cartridge filters

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ABSTRACT

Fouling of reverse osmosis (RO) water filtration membranes is a common problem throughout the industry. Most membrane fouling has an organic component that is typically derived from planktonic transparent exopolymer particles (TEP). Polysaccharides are a major constituent of TEP that are produced both abiotically from organic colloid precursors and by a variety of organisms in marine and freshwaters. The microgel character of TEP makes them difficult to remove through conventional filtration other than by ultra filtration and RO membranes. However, removal of TEP by these membranes is also problematic. When the membrane surface is initially fouled with TEP, the TEP layer then acts as an attachment substrate for organism, colloids and other submicron particulates, further contributing to membrane clogging. We report on an innovative electroadsorptive, depth filter media that is shown to be effective in significantly reducing TEP from fresh water, sea water, and wastewater. This technology has significant potential to protect membranes from primary fouling due to both TEP and nanoparticle build-up. The electroadsorptive filter media removes TEP through a strong positive charge generated by nanofibers of the mineral boehmite and the torturous path created by the depth filter media itself. The filter media has a mean flow pore of about 0.7 microns and very high nanofiber surface area that produces a filter with low pressure drop but a high filtration efficiency and high loading capacity for TEP removal.

Keywords: Biofouling; Polysaccharides; TEP; Nanoparticles; Electroadsorptive; Disruptor

1. Introduction

Research work supported in part by Ahlstrom Filtration [1] strongly suggested that endotoxins (lipopolysaccharides) could be removed from water using Disruptor® electroadsorptive technology. This led to extensive internal research into dissolved polysaccharides, which coincided with a growing body of

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work identifying of transparent exopolymer particles (TEP) as a factor in membrane biofouling.

TEP are sticky, highly deformable organic microgels that are produced both abiotically [2] and by planktonic organisms [3]. These particles are present in large numbers in marine, freshwaters and municipal wastewater. TEP have been implicated as a potentially important factor in biofouling of membranes [4]. Since first described by Alldredge et al. [5] in 1993, the ubiquity and multiple ecosystem functions of TEP in many aquatic environments have been extensively documented in the oceanographic and limnological literature. TEP appear in many forms, from "dissolved" (0.05–0.4 μm) to "colloidal" (>0.4 μm) to "particulate" having a size of ~200–300 μm. [6,7] Because TEP are partially composed of highly surface-active polymers containing fructose and rhamnose they are about 2–4 orders of magnitude more sticky than phytoplankton or mineral particles and typically also have a net negative surface charge [2]. These two characteristics conspire to result in a high probability of attachment to submerged membrane surfaces upon contact to create primary biofouling [8–10]. In addition to polysaccharides, other substances, including nucleic acids [3], proteins [11] and trace elements [12] may be associated with these gel-like particles.

These well-documented characteristics of TEP provided a factual basis for the proposal that these particles play a significant role in biofilm formation. [13,14] Existing evidence from numerous studies as well as practical experience indicates that current pretreatment techniques do not sufficiently reduce TEP levels in the feedwater reaching reverse osmosis (RO) and ultra filtration (UF) membranes to provide maximum protection from biofouling. [6,15–22]

There are many possible benefits in membrane performance that can be obtained by reducing biofouling. These include: Energy savings through lower overall transmembrane operating pressure, higher flux rates requiring less membrane surface area per installation or system, reduced chemical use, reduced maintenance costs and downtime from increasing the time between clean in place (CIP) (which may be at least partially offset but the cost of Disruptor® filter changes), longer membrane life due to increased CIP cycles and less damage to membrane surfaces due to pressure damage.

This paper presents the results of several independent studies that examined various aspects of the functioning of Disruptor® technology, an innovative electroadsorptive, depth filter media. Challenge waters came from diverse sources: the North Sea, two locations from the Mediterranean Sea, a river in Europe, Lake Kinneret, the Jordan River, and two waste water (WW) treatment plants.

The first study using North Sea coastal water indicated that the electroadsorptive and physical characteristics of the Disruptor® technology may minimize membrane fouling by reducing polysaccharides from the feed water stream [17]. Experiments with two freshwater sources established that the Disruptor® technology could reduce both TEP and chlorophyll (Chl) in these waters. Studies with treated wastewater evaluated the ability of the electropositive filter to remove nanoparticles from microfiltration (MF) membrane filtrate in order to improve process performance. The fourth trial using river water that contained high levels of TEP and iron evaluated biofouling reduction of a spiral wound RO membrane that was protected by Disruptor®.

2. Results

2.1. Disruptor® media as pretreatment for SWRO

A study conducted by El-Azizi et al. [17] used unfiltered water from the North Sea and Mediterranean to compare the ability of a 1 μm prefilter and Disruptor® media to reduce biofouling of RO membranes. The study found that the greatest decrease in flux was produced by the raw water. Use of the 1 μm prefilter increased the flux rate of both water sources while the greatest increase in flux was produced by the combination of a 1 μm prefilter followed by the Disruptor® media. This evidence suggests the benefit of appropriated stages of filtration to improve overall membrane flux rates.

The fouled membranes were evaluated after the trial, along with a new membrane. The membranes were examined for surface contamination using Attenuated Total Reflection—Fourier Transform Infrared Spectroscopy (ATR-FTIR) to identify any functional groups present in the fouling layer. The contamination present on the fouled membranes which produced the highest absorbance had a wave number in the range of 750–1,100 (cm^{-1}) which is indicative of polysaccharides and silicates. Further examination of the membrane surfaces using a scanning electron microscope showed obvious buildup of globular contamination as well as crystalline structures, confirming the results of the FTIR analysis.

2.2. Disruptor® media efficiency in removing TEP and Chl from two freshwater sources

Initial studies indicated that Disruptor® was effective in removing polysaccharides from seawater and could protect RO membranes from biofouling [17]. In order to determine if the media would perform equally in different types of water four source waters with very different characteristics were tested to evaluate removal efficiency of TEP and Chl. The water sources were: Coastal Mediterranean sea water collected from the intake of the Hadera Desalination Facility, Lake Kinneret (LKW) coastal water, Secondary treated wastewater from the Shafdan WW Treatment Plant, Upper River Jordan (RJ) water, taken near the inflow to Lake Kinneret. (Note, although L. Kinneret is freshwater, the salinity level is relatively high; ∼280 ppm Chloride).

For each test run, the source water was filtered under low vacuum pressure through a single 47 mm Disruptor® disc with flow rates of 14/L/sq.m/min (0.35 gal/sq.ft/min). The volume filtered varied by source water with the filtered volume being recorded to provide an indication of the capacity of the filter media for removal of TEP prior to fouling. The concentration of the TEP and Chl were measure din both the unfiltered source water and in the filtrate. The Alcian blue staining method [23] was used to measure TEP concentrations. Chl *a* concentrations were determined by the method of Holm-Hansen et al. [24].

The efficiency of the media in reducing the initial levels of TEP was highest for RJ Water (avg. 81.8%), decreased somewhat for the secondary treated Wastewater (avg. 73.8%), Lake Kinneret water was lower (avg. 62.7%) and lowest for coastal Sea Water (avg. 58.5%). There was fairly high variability in the filtration efficiency of Disruptor® for different samples of water from the same source at different dates. For example, the percentage reduction for Lake Kinneret Water ranged from 36.1 to 82.4%; for Wastewater from 60.6 to 81.6%; and for Sea Water from 43 to 75%. This variability in% reductions was to be expected, given the wide range of initial concentration of TEP that most likely reflects the dynamic changes in TEP composition and gel structure which are known to occur in natural waters [2,23]. These data are shown in Fig. 1.

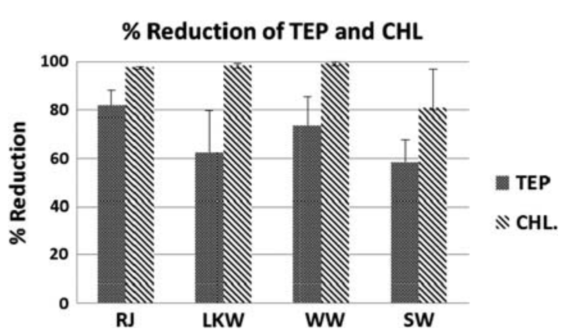

Fig. 1. The average and standard deviation of percentage reduction of TEP and Chl.

Only in the cases of Lake Kinneret water and Sea Water were there a fairly large number of samples from different dates tested ($n = 7$ and 8, respectively). This allows us to ascertain that there was no statistically significant difference (*t*-test) in the performance of the Disruptor® in removing TEP from Sea Water or from freshwater of Lake Kinneret. Since only a very few experiments were run with RJ Water and Wastewater ($n = 2$ and 3, respectively) we can only state that Disruptor® possibly was more effective in removing TEP from these source waters than from Lake Kinneret water and Sea Water. More tests would be required to be certain of this.

For all four water types tested, Disruptor® was much more effective than other filtration media for which data are available. For example, Bar-Zeev [21] reported that, on average over a month period, a Rapid Sand Filter at an operational desalination facility removed only about 30% of the TEP in the supply water. Villacorte et al. [6] also found that TEP was not effectively removed from source waters by existing pretreatment methodologies.

2.3. Hollow fiber backwash study: HF fouling reduction

In water treatment plants, nanoparticles present in backwash water are frequently a major cause of fouling on HF membranes. These nanoparticles commonly found in water reuse streams are largely produced in upstream biological reactors (e.g. activated sludge) through cell lysis; however, inorganic (e.g. calcium phosphate) and manufactured nanoparticles are also present in substantial quantities. In many cases filtrate from the Micro Filtration MF is used to backwash HF membranes, and nanoparticles in the filtrate as well as contamination from the holding tanks and back flush lines cause fouling on HF membranes.

This study examined if higher quality backwash water produced by Disruptor® mitigated the extent of fouling on HF membranes.

2.3.1. Quantification of nanoparticle removal from complex media: West Basin MF feed water

Experiments were conducted using MF feed water from West Basin Municipal Water District to determine what, if any, impact would be realized on the performance and fouling behavior of the membrane process when treating the MF backwash water with the Disruptor® filter. The MF membranes studied operate in an outside-in configuration. These experiments were conducted in a cross-flow mode of operation. Two sets of experiments were done, the first

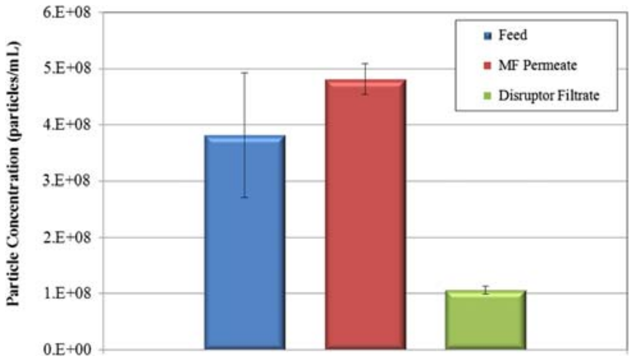

Fig. 2. Particles ($d_h < 500$ nm) per unit volume of water for three different source waters: MF feed from West Basin spiked with 0.5 mg $L^{-1}$of 57 nm nanoparticles, MF filtrate, and MF filtrate filtered through the disruptor filter ($n = 3$; pH = 7.8; $T = 20$°C).

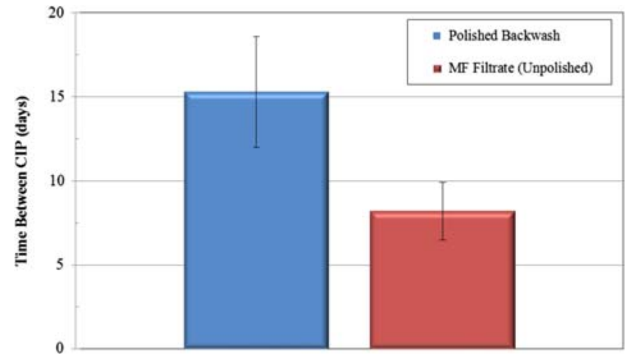

Fig. 3. Average time between CIP events for MF membranes being backwashed with MF filtrate or with MF filtrate that had been treated using the Disruptor filter. The source water was MF feed collected from West Basin spiked with 0.5 mg/L of 57 nm ($n = 3$; pH = 7.8; $T = 20$°C).

used MF filtrate as the backwash water, while the second used MF filtrate that was filtered through the Disruptor® filter as backwash water.

The source water contained both naturally occurring/present in addition to 0.5 mg/L of the fluorescent nanoparticles ($d_h = 57$ nm) used in other experiments. Samples were collected from the raw/spiked feed water, the MF filtrate and the Disruptor® filtrate. Samples were collected from the Disruptor® filtrate line that supplied the backwash reservoir for the hollow fiber membranes. This water was used to backwash the hollow fiber membranes during their normal operation cycle.

Results from the analysis are reported in Fig. 2 which reveals that the MF feed and MF filtrate are characterized by relatively similar concentrations of particulate matter ($d_h < 500$ nm). The West Basin samples are complex and contain both organic, particulate and nanoparticulate materials. For this reason it is difficult to isolate only the nanoparticulate ($d_h < 100$ nm) fraction. Nevertheless both the MF feed and MF filtrate contained approximately 5×10^8 particles per mL having a diameter of less than 500 nm. In comparison, the Disruptor filtrate contained approximately 1×10^8 particles per mL having diameter less than 500 nm. This represents a reduction of nanoparticles of roughly 80%.

2.3.2. MF performance from treatment of backwash water using the disruptor® filter

Performance statistics (run time or time between CIPs) for the experiments are presented in Fig. 3. Using the polished MF filtrate (i.e. that which had passed through the Disruptor® filter) to backwash the MF membranes extended the run-time for the MF membrane process. This observation is attributed to a reduction in the fouling of the interior of the hollow-fiber MF membrane when the polished backwash water was used.

During these tests the increase in trans membrane pressure over time (psi/hr) that was required to maintain a constant permeate flux rate was greater when using the unpolished MF filtrate, relative to that for the polished MF filtrate, to backwash the membranes. Results indicate that using the polished backwash water can extend the operating time for the MF membranes between CIP events. Disruptor® media effectively removed nanoparticles and organic matter in both simple electrolyte and complex aqueous water with removal efficiencies at or exceeding 80%, while also demonstrating removal of nanoparticles and/or organic matter significantly reduces the fouling of downstream MF membranes and reduced flux decline for MF membranes by at least 98%. Polishing MF filtrate prior to its use as backwash water for MF membranes treating a complex feed stream from West Basin Municipal Water District and spiked with 0.5 mg/L of carboxylated nanoparticles ($d_h = 57$ nm) increased the duration between CIPs from an average value of 8.2–15.2 days (154% increase). The reduction in CIP frequency or increase in operation time to reach terminal TMP is attributed to the removal of nanoparticles and other contaminants from the MF backwash water by the Disruptor® filter and a corresponding decrease in membrane fouling on the permeate side of the membrane.

3. RO prefiltration study: river water

This trial was conducted to obtain field data to learn how well it could be correlated with data obtained from the previous trials. The source water for this trial was the Ebro river having high levels of iron and polysaccharide contamination. The river water is first conventionally treated at the intake point by flocculation, settling, sand filtration, and activated carbon before entering a long distribution pipeline. The trial ran in two phases, first to establish baseline performance of an RO membrane using standard mechanical prefiltration techniques with phase two of the trial using a Disruptor® cartridge filter as the final polishing filter before the RO membrane.

A baseline trial was first run using a 2.5″ × 14″ low energy BWRO element protected by first a 20 µm bag filter followed by a 5 µm cartridge filter. The flow rate through the membrane was held at 104 gallons per day (16 l/h or average operational flux of 23 LMH) with pump pressure being increased as fouling occurred. The baseline trial ran 66 days until reaching a flux loss equal up to 60% from initial membrane performance.

A second trial was then run using a new RO element of the same size and the same flow conditions but with a 2.5″ × 10″ Disruptor® prefilter having approximately 0.29 square meters of surface area. During the course of this trial it was necessary to change the Disruptor® prefilter on average, every 7 days (41,210 gallons or 156 m^3 of water). The trial

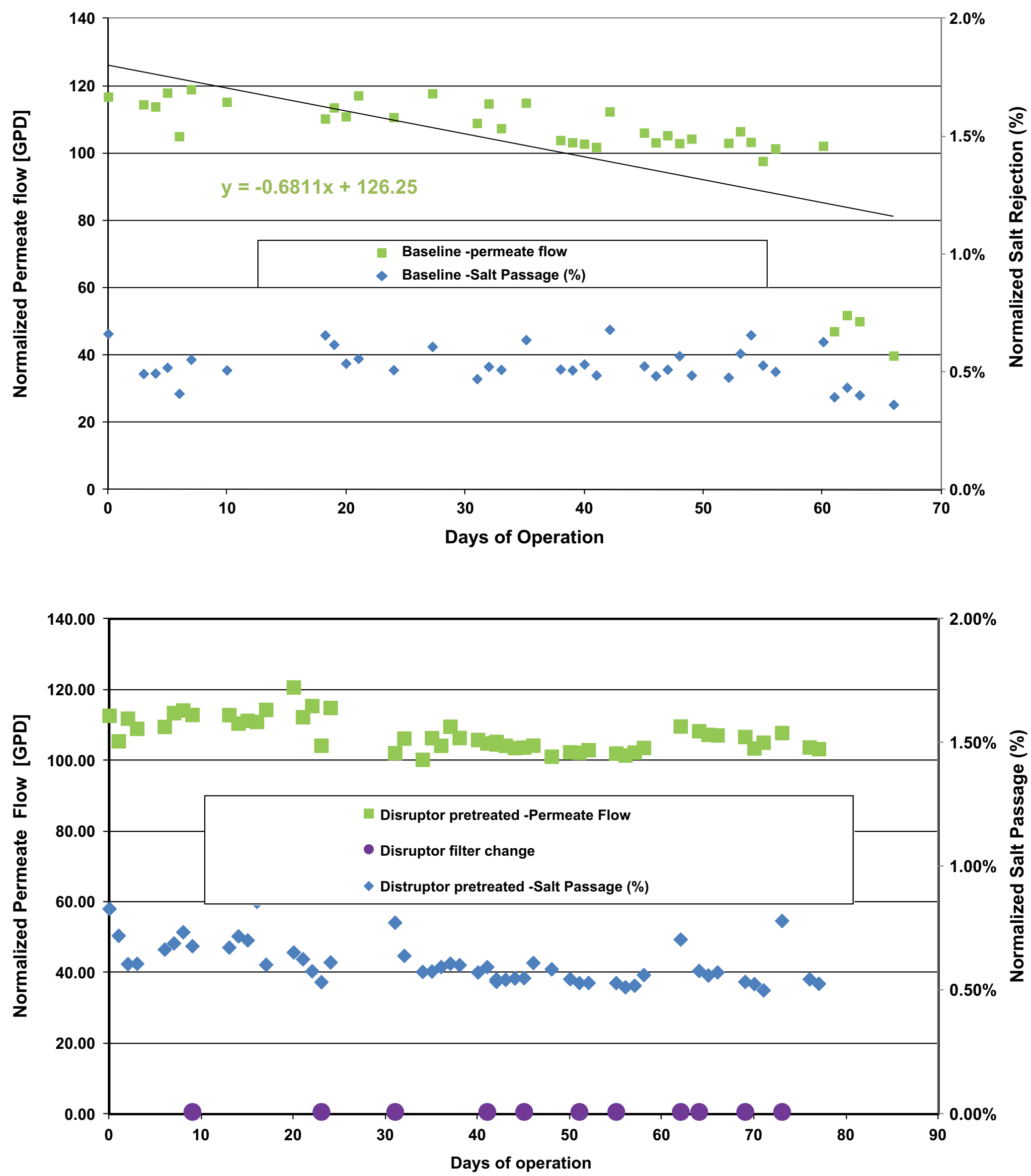

Fig. 4. Normalized permeate flow and salt passage of conventional pretreatment (above) and disruptor pretreatment (below).

continued for 80 days, during which the membrane performance stayed very stable, indicating low fouling. Use of the Disruptor® prefilter increased the time between CIP by a minimum of 150%.

Fig. 4 shows the performance of both trials as compared to days of operation vs. normalized permeate flow and salt passage, and the change out frequency of the Disruptor® prefilters.

During both trials eight samples of water were taken before and after the 20 + 5 micron prefilters for TEP testing. Samples were also taken after the Disruptor® filter during the second trial and tested for TEP content. It was found that the first trial TEP levels were reduced on average by 26.2% by the 20 + 5 micron pre filters. The second trial showed a decrease of TEP after the 20 + 5 micron prefilters of 38.2% while the TEP decrease after the Disruptor® filter was 63.1%.

4. Discussion and conclusions

Of particular importance are the data presented showing that TEP and nanoparticles can be efficiently removed from fresh, salt, and highly complex WW by using simple cartridge filters as part of effective membrane pretreatment systems. Reduction of nanoparticles and TEP using the Disruptor® electroadsorptive technology was shown to be equally effective as, or more effective than, MF of the same water source. The principle removal mechanism for TEP, nanoparticles, and natural organic matter was through attractive charge-charge (negative-positive) interactions between the foulant materials and the Disruptor® filter media. Size exclusion for all the said foulants is considered to be a secondary removal mechanism, which likely increases in importance as the filter becomes conditioned or loads with contaminants over time. Recall that the organic debris and the nanoparticles are many times smaller than the nominal pore size for the filter media. Therefore, the electropositive filter media are capable of high removal efficiencies for nano-scale materials with minimal pressure drop, which is in contrast to pressure-driven membrane processes like UF and MF. The data also showed that reduction of TEP and nanoparticles had a direct impact on reducing membrane fouling and subsequently extending time duration between CIP's for both MF and RO membrane processes.

Further study is needed to validate the value proposition of using these filters in large volume applications such as power plant boiler feed water, cooling tower water, and large scale desalination or suspended solids removal applications, such as municipal wastewater treatment and reuse.

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