UF/NF TREATMENT OF ORGANIC LADEN WASTEWATER IN INDUSTRIAL PULP AND PAPER WASTEWATER

Craig R. Bartels, PhD, Hydranautics, 401 Jones Road, Oceanside CA 92058, USA,
Email: cbartels@hydranautics.com Phone: 760-901-2617

Wayne Bates, Hydranautics

Abstract

The pulp and paper industry converts massive amounts of wood pulp into bright white paper. During the chemical processing of the pulp, bleaching and caustic extraction are used to remove the lignin molecules which give a brownish color to the paper. As a result, though, the process generates large quantities of wastewater which have high pH, high temperature, and high organic load. A unique sulfonated polyethersulfone NF membrane was chosen for this application since it was suitable for high pH operation and could reject the organic material, while passing much of the inorganic ions. This would allow the membrane process to operate at high recovery.

Initial lab trials with this color removal NF membrane and plant wastewater proved that the color could be removed at high recoveries, but when trialed at the plant, it was found that the NF elements readily fouled. Further experiments proved that very fine colloidal material was the cause of the fouling. A capillary UF pretreatment system was instituted prior to the NF membrane, and resolved the fouling problem. Operating data from the test are reported and show stable operation and the ability to clean and recover performance. The NF was run at up to 90% recovery and was able to reduce color from 12,000 PCU to 20 PCU, while only rejecting about 50% of the inorganic ions. Evaluations were underway to consider the feasibility of reusing the permeate and the concentrate in the papermaking process.

Introduction

There are many industrial wastewater treatment processes which employ nanofiltration (NF) or reverse osmosis (RO) membranes. Nearly every application is unique, depending on the processes and water sources employed by the industrial client. The treatment of the inorganic constituents tends to be more straight-forward, while the treatment of the organic contaminants can be very complex and difficult. This is a result of the vast array of organic chemicals that may be present, and how they interact with the membrane. For example, some organic contaminants may adsorb on the membrane surface and foul the membrane, while other organics may chemically degrade the membrane or element materials, and still others may change in nature during processes and become problematic. One counter measure to treat organic laden wastewaters is to use more robust membranes, which can tolerate higher chemical concentrations or can be cleaned more aggressively.

One industry that has historically had difficult industrial wastewater is the pulp and paper industry. In the mid-nineteenth century, technology was developed to convert wood to pulp for paper-making. This spawned a rapid growth in the papermaking industry as it grew by a factor of 10 in the 19^{th} century, and by a factor of 50 in the 20^{th} century (Biermann 1993). There are now an estimated 565 manufacturing facilities in the USA alone. (EPA Fact Sheet Nov. 1997) The basic process of making the paper is shown in Figure 1. The two major components of wood pulp are cellulosic fiber and a material called lignin which holds the fibers together. Wood is cooked in the digester at high pH and high temperature, screened and then washed to remove lignin and digestion chemicals. During the ensuing bleaching process, the brown colored fiber is transformed to the typical white color associated with paper. Typically, this is done with bleach. As the remaining lignins are broken down, they can be extracted from the fiber with caustic or other chemicals. (Figure 2). This step can be repeated several times until the fiber reaches the brightness of white color that is desired. (Biermann 1993). The fiber is then filtered from the chemical solution in each of these successive steps and further treated. The wastewater from each of these steps is collect for treatment and disposal. This wastewater can typically have a pH in the range of 10-12 and can be at a temperature of 90-110 C. Additionally, the wastewater can contain large amounts of very small, colloidal fiber which can make further processing more difficult.

It is reported that approximately 20,000 gallons of water required to bleach one ton of pulp. To minimize the use of water, the wastewater from the latter stages of processing can be re-used as wash water for the former stages of washing. This minimizes the water use, but increases the concentration of lignins in the wastewater. Also, there is a great deal of caustic used in this process, along with some acid that is used to drop the pH of the effluent. As a result, there is a need in the papermaking industry to reclaim the high pH water from the wastewater so that it can be reused. Also, there is some value to the organic material in the wastewater if it can be concentrated. Finally, treatment of the wastewater to lower the BOD demand, COD demand, and in some cases color for addition to surface bodies of water is required to meet NPDES permit requirements.

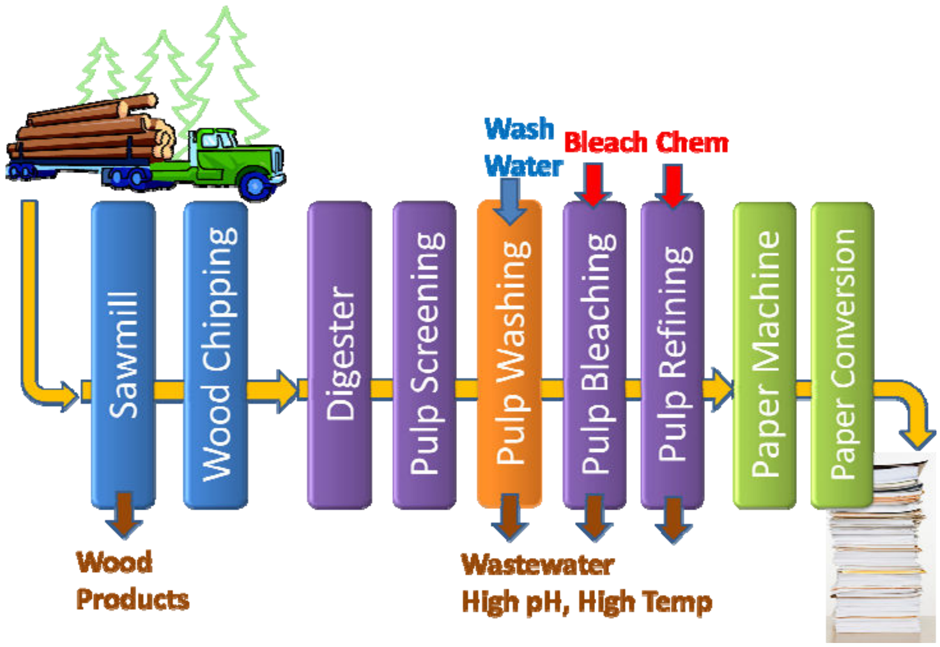
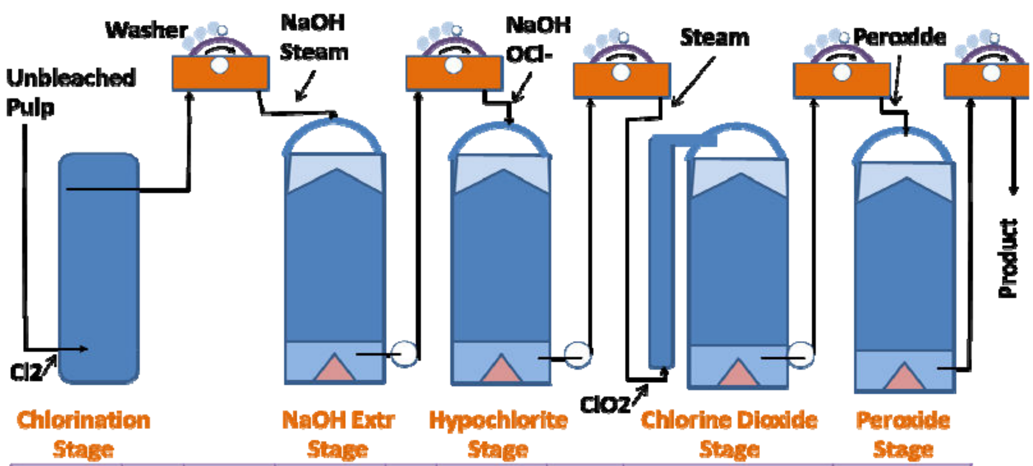


Figure 1. Papermaking Process



Temp (F)	85		160		90		160	160
Conc	3%		12%		12%		12%	12%
pH	1.5		10.5		9		3	10.5
Brght	22%		33%		70%		88%	91%

Figure 2 Typical process used to bleach pulp (Biermann 1993)

One way to treat this wastewater is by the use of chemical treatment. Various coagulants, oxidizers and other materials can be applied to recover purified water by conventional settling or media filtration methods. However, this can result in the generation of large amounts of sludge and can be very expensive. Additionally, this results in make-up water which again needs much chemical to be used for the washing process. Alternatively, membrane process could be ideal if they were able to remove the organic material, while still allowing the caustic solution to pass through to the permeate.

Membrane Selection

The selection of membrane for this application was critical. The membrane had to be thermally and pH stable for the chemical environment listed in Figure 2. Additionally, the separation characteristics needed to be very selective, such that the hydroxide would not be rejected, while the color-causing lignins would be removed. The rejection of the lignins would have to be very high to make the process viable, and the rejection of the caustic would have to be very low so that the process recovery would be very high and concentrate the organics to a useable level.

To meet this requirement, we chose a class of chemically robust NF membranes (Bartels 2002) which are a composite membrane made of a polysulfone support and a sulfonated polyethersulfone (SPES) barrier layer[1] (Figure 3). This specially formulated layer can be controlled to achieve porosity in the range of 500-3000 molecular weight cut-off (MWCO) and is highly negatively charged (Figure 4). The negative charge comes from the sulfonate groups present at the membrane surface. These help increase rejection of negatively charged ions, organics and color-bodies by charge-charge repulsion. The rejection of various ion pairs has been measured for each of the SPES membranes which we manufacture (Figure 5). It is evident that the rejection is strongly influenced by the size and charge of the anion, although the size and charge of the cation have an effect as well.

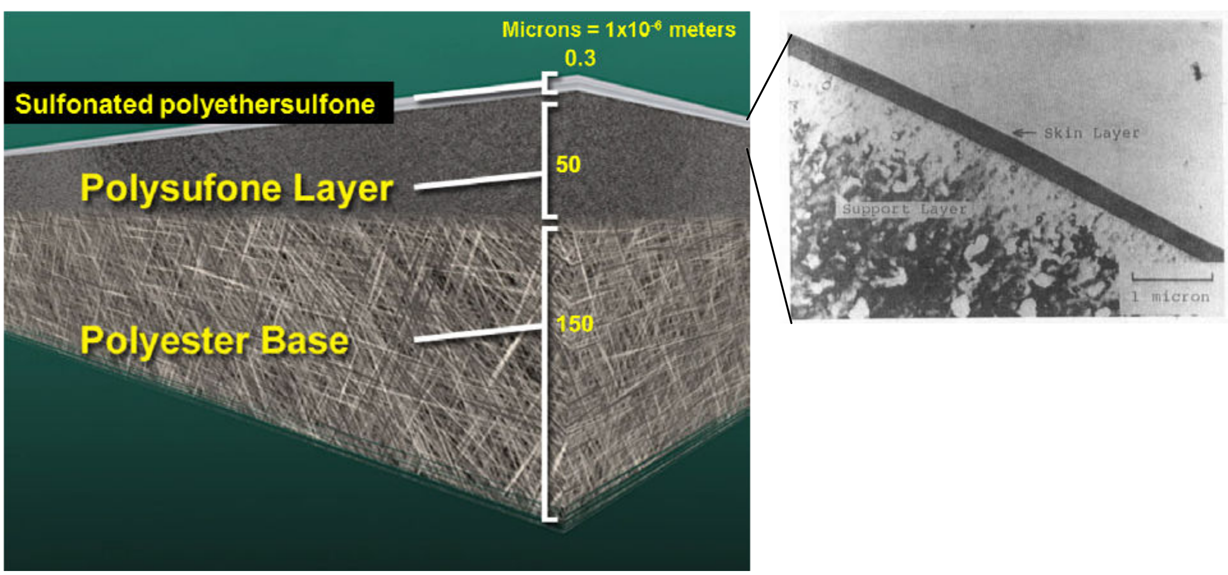


Figure 3. Composite Sulfonated Polyethersulfone Membrane

[1] Hydranautics' HYDRACoRe50 Nanofiltration membrane.

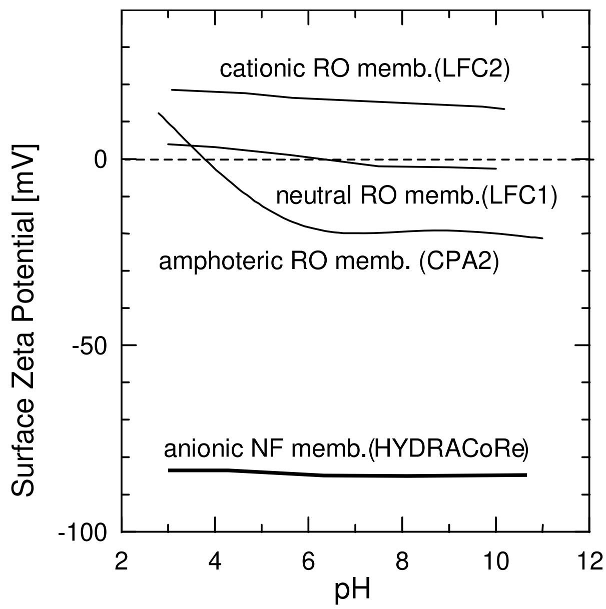


Figure 4. Surface Zeta potential measurement for typical polyamide membranes and the S-PES membrane.

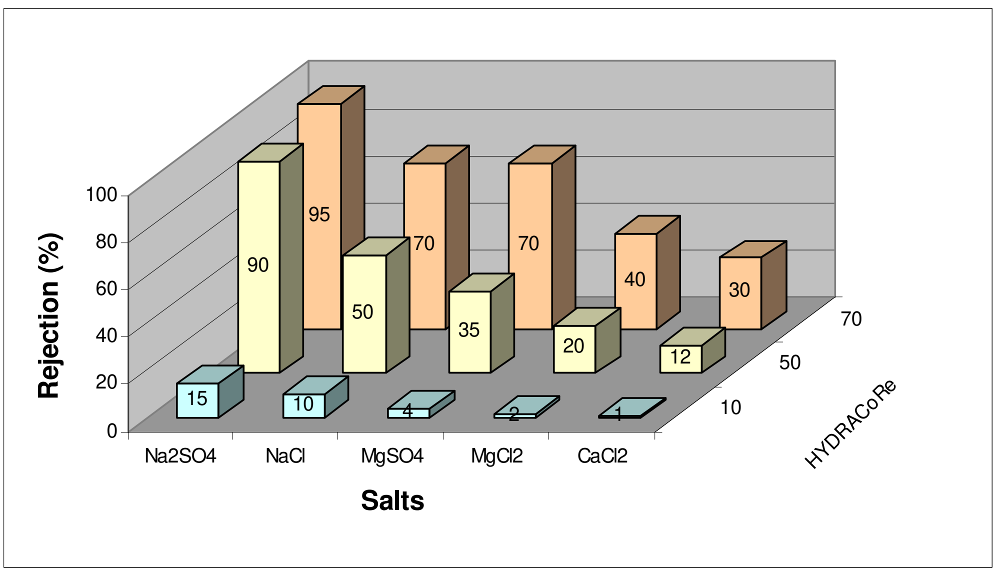


Figure 5. Ion pair rejection values for 3 different SPES membranes

However, the rejection will typically be lower when treating mixed ion feedwaters. This is believed to be due to divalent cations (Ca and Mg) forming ionic bridging with the negatively charged sulfonate ions. This in turn masks the effect of the negative charge repulsion and makes the overall salt rejection much lower. For HYDRACoRe50, the typical total dissolved solids (TDS) rejection for natural water is around 25-30%. Since it can remove larger molecular weight organics that impart color, but pass most of the inorganic ions, it is classified as a "color removal membrane". Also, the greater the concentration of ionic species in the water, the lower is the rejection of the membrane. This again is likely due to ionic shielding due to the high concentration of ionic species in the feedwater. These will shield the ionic repulsion and thus lower rejection. An example of this is shown in Figure 6, where rejection of NaCl is measured as a function of the feed NaCl concentration.

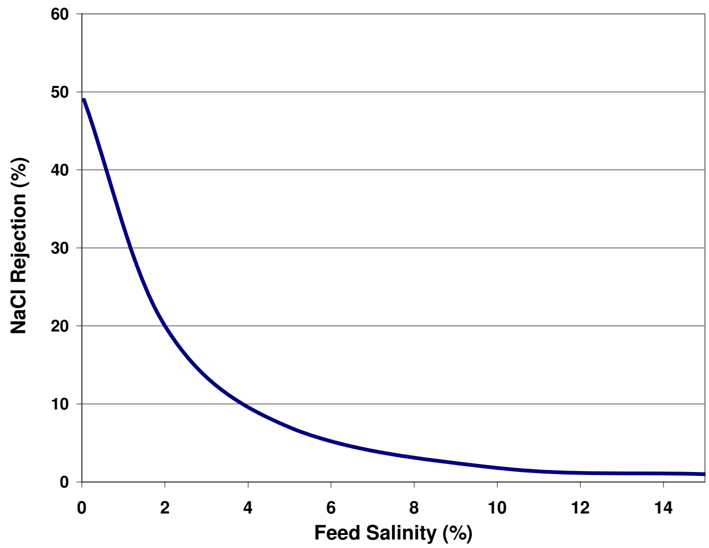


Figure 6 Effect of feed salinity on the rejection of SPES membrane

Another unique feature of the membrane is that it has robust chlorine tolerance. This makes it valuable for these industrial applications. Because there is no polyamide separating layer, this SPES membrane is not very susceptible to chlorine damage. However, it should be noted that chlorine in combination with a transition metal catalyst can still oxidize the membrane in a matter of months. A comparison chlorine tolerance of various membranes as measured in the lab is shown below (Figure 7). Additionally, the SPES membrane is very stable at high pH, and can thus be cleaned very aggressively. Both of these features are essential to treat papermaking effluent, due to the process steps described in Figure 2.

Laboratory Testing

A potential application was identified at a pulp and papermaking plant in the USA. Discussions with the client indicated that they were looking for improved treatment technology for the colored wastewater from their papermaking process. They were also looking for opportunities to save cost by reclaiming the caustic wash waters for reuse in their manufacturing process.

A sample of one of their waste streams was sent to our laboratory for small scale testing. A quick cell test of the fluid demonstrated that the HYDRACoRe50 SPES membrane had sufficient organic rejection to provide either a reusable wash stream or one for discharge to a local river. The as-supplied waste stream had a color index of 2,730 PCU, while the permeate from the HYDRACoRe50 was measured to be 21 PCU (Table 1). This is a 99.2% reduction of color and met the target of less than 50 PCU. The conductivity and

TOC rejections values are also shown in Table 1. Although the conductivity rejection was a little higher than desired, it was believed that the rejection would drop as the feed concentration goes higher with the increased recovery. In general, these values also seemed suitable to this application.

Table 1 Analysis of Water Quality from Lab Testing*

Parameter	*Units*	*Feed*	*NF Permeate*	*Rejection %*
Conductivity	uS/cm	2,260	790-1020	60-65%
Color	PCU	2,730	21	99.2%
TOC	mg/l	600	126	79%

*Feed conditions include: pH 10.3, Turbidity 6 NTU, TSS 10 mg/l, 49 C

Pilot Testing at Site

As a result of the positive lab studies, a pilot was proposed to demonstrate the membrane at site. A 2-stage array pilot was provided which consisted of two pressure vessels in series, each holding three pieces of 4" x 40" NF elements. The elements used for the test were HYDRACoRe50 elements having 75 ft2 of membrane area. The pilot was capable of producing 4.5 gpm of permeate flow when operated at a flux of 14 gfd. A concentrate recirculation line was installed to allow us to test the NF system at higher recoveries at 80-96%, which would more closely mimic the commercial process. The wastewater was trucked to the pilot unit and transferred to a 1000 gal tank. The water temperature was lowered to 40-49 C using a heat exchanger due to the thermal limits of the element.

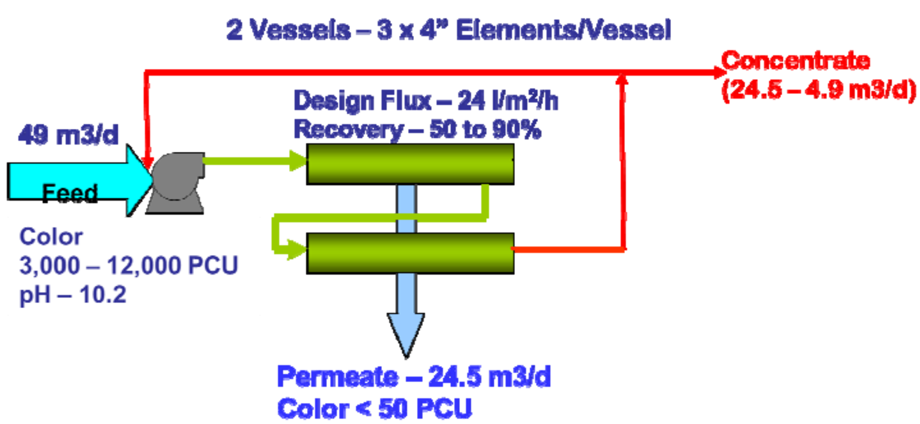


Figure 7 Pilot Schematic for field testing of pulp and paper wastewater

Initially, the NF system treated the wastewater directly. Although the rejection during this test was good and consistent with the lab study, the flow from the system dropped over a one week period. Therefore, it was agreed that more pretreatment was required. A 1 micron cartridge filter helped lower the fouling rate, but did not stop it, and required changing more than once per day. Even though the feedwater had good clarity, measurements indicated that SDI was in the range of 6-7, which is too high for a spiral element. One of the fouled elements was retested and autopsied in our labs. The differential pressure had increased from 5 psi to nearly 30 psi. Also, the weight of a lead element increased by almost 50%. Once the element was opened, it was found to have a heavy orange-brown organic foulant on the surface.

Ultimately, we elected to install a UF membrane[2] to pretreat the water before the NF. The capillary UF was a PES membrane fiber with 1.3 mm outside diameter and 0.8 mm inside diameter and a 100,000 Dalton molecular weight cut-off.   This membrane has 200,000 ppm-hrs chlorine tolerance and can operate at pH of 4-11 continuously, and the module had 500 ft2 of surface area in one 60” long module.

Table 2 UF Feed and Filtrate Quality*

Parameter	*Units*	*Feed*	*NF Permeate*	*Rejection %*
Turbidity	NTU	6.1	0.24	
TSS	mg/l	8.7	<5	
TOC	mg/l	580	530	9%
Color	PCU	12,000	12,000	0%
pH	Units	10.2	10.2	

*Feed conditions include: pH 10.3, Turbidity 6 NTU, TSS 10 mg/l, 49 C

The UF pilot system was designed to operate at a peak flux of 32 gfd (54.4 lmh) and an average flux of 26 gfd (44.2 lmh) and was capable of filtrate flow of 11.1 gpm at peak flow condition. With the backwash flux and frequency, the overall recovery was 83%. The system was operated at a typical flux of 24-30 gfd at a pressure of 4-11 psi, depending on temperature. A picture of the entire pilot set-up is shown in Figure 8.

Figure 8 Pilot system for field testing of pulp and paper wastewater

[2] Hydranautics’ HYDRAcap Capillary UF membrane

Operation of the NF membrane with UF pretreated wastewater was resumed. The pilot was operated on and off for 7 months to collect data at different conditions as required for system design information. A graph showing the flux and TMP for the HYDRAcap UF module is shown in Figure 9 and the flux and dP of the NF membrane in Figure 10.

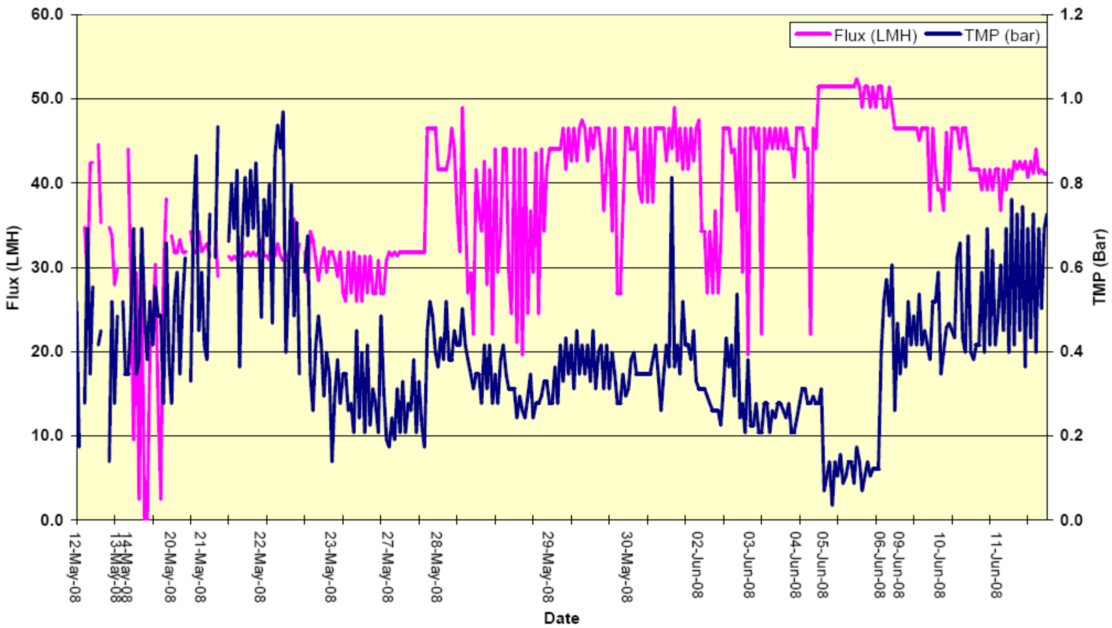


Figure 9 UF Pilot performance

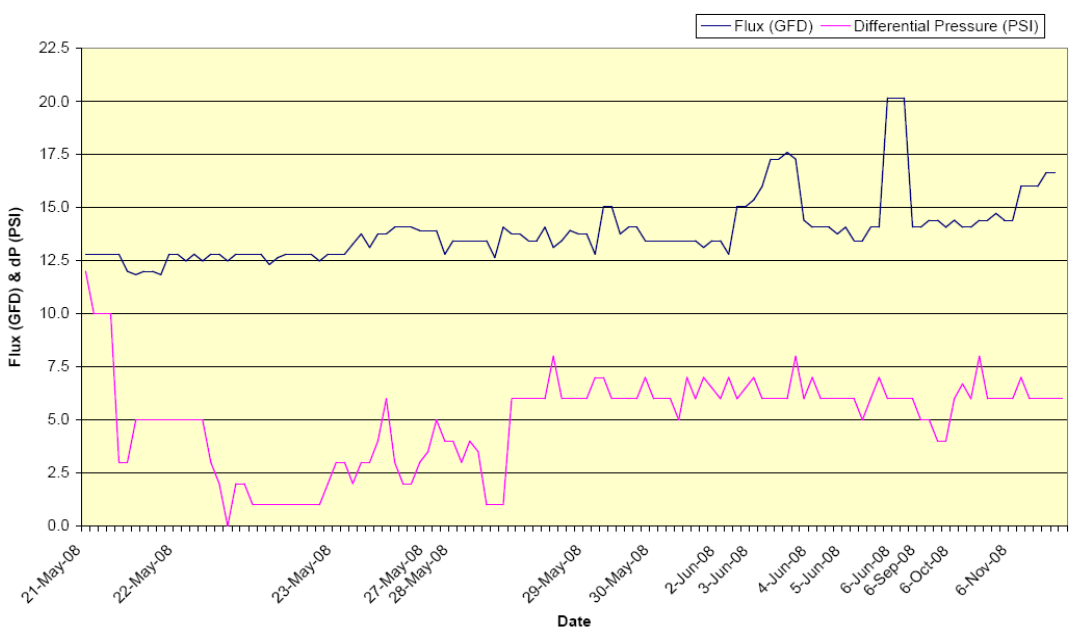


Figure 10 NF pilot performance

The NF was able to run at 15-30 gfd flux, and most of the time, around 25 gfd. The recovery was typically in the range of 80-90%. This is a very aggressive condition for operating NF, but was chosen to determine how robust the process would be and see how rapid the fouling would be. Normally, with 6 elements in series, the recovery would not exceed 50%. Despite these aggressive conditions, the fouling on the NF membrane was well within acceptable values.

The water quality was determined at each step of the process to assess the membrane performance. The results are listed in Table 3. It can be seen that the UF effectively removed the fine particulates, while the NF removed almost all of the color from the wastewater (Figure 11). Also, the NF permeate was only 50% of the feed TDS. The detailed permeate quality is shown in Table 4. Operation at the high NF recovery condition highlights the value of the novel SPES NF membranes. Because they are not concentrating the salts

Table 3 Typical Analysis of Water Quality from Pilot Testing*

Parameter	*Units*	*UF Feed*	*UF Filtrate and NF Feed*	*NF Permeate*	*Softened City*
TDS	mg/l	2,345	1,928	973	338
Color	PCU	12,000	12,000	20	10
TOC	mg/l	580	530	53	<1
TSS	mg/l	8.7	<5	<5	<5

* Operating parameters: UF Flux – 23 gfd (39 LMH) UF Recovery – 90%
NF Flux – 9 gfd (15.3 LMH) NF Recovery – 86%

Table 4 NF Performance Detail

Parameter	*Units*	*Feed Value*	*Permeate Value*	*Concentrate Value*
Feed Pressure	psi	84-100		
Differential Press	psi	5		
Feed Temperature	C	30-35		
Ca	mg/l	10	<0.5	
Na	mg/l	660	340	
CO3	mg/l	790	310	
SO4	mg/l	110	13	650
Cl	mg/l	270	250	340
Silica	mg/l	80	59	
TDS	mg/l	1928	973	

At the end of the pilot testing, the performance was used to evaluate various commercial designs which would fit into their process. The initial consideration was for a 2.7 mgd treatment system. The NF design was based on 96% recovery, which would concentrate the organics by almost 20 times. Detailed discussions were held with the customer to determine the suitability of the permeate for reuse in their process, as well as options for the reuse of the concentrate. However, the plant requirements for both of these aspects is quite specific and strict, so further information was needed before deciding to proceed with the commercial plant. Test marketing of modified or new paper products can take years to accomplish before full production can occur.

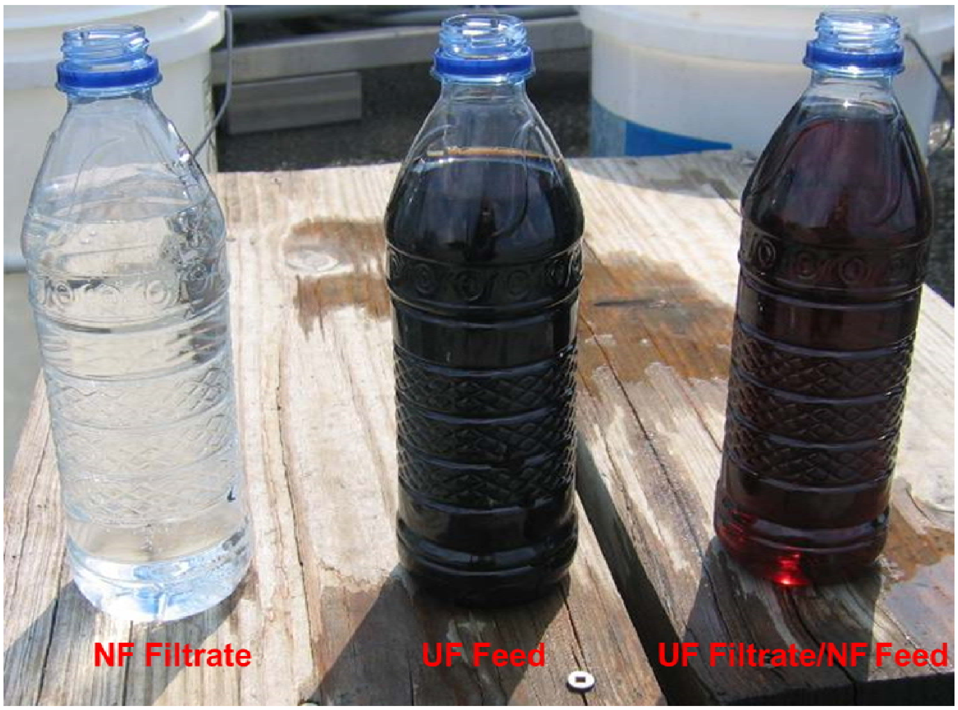


Figure 10 NF pilot performance during test period

Conclusions

The integrated membrane solution comprising UF and NF membranes successfully treated highly colored water from the pulp and paper plant. Because this water had high levels of TOC, high pH and high temperature, the NF membrane was chosen to be a SPES novel product that can also give unique separation performance. This membrane was able to highly reject the organic material that caused color in the water, while also passing most of the ions in the feedwater. This allows the membrane to run at high recovery.

Due to the high amount of colloidal fiber in this pulp and paper wastewater effluent, the fouling on the NF was very high. As a result, a capillary UF membrane was used to pretreat the wastewater prior to the NF. This effectively reduced the SDI below 4 and allowed the NF to run stably, with minimal fouling.

A pilot system was installed and operated for 7 months at various design conditions. The NF was able to operate at high flux of 25 gfd and high recovery, 90%. The resulting permeate was collected and evaluated. The color was reduced from 12,000 PCU in the feed to 20 PCU in the permeate, while the conductivity was reduced from 1928 to only 973 uS/cm. This design information was used to design a full-scale system for consideration by the plant. Further evaluations are being done to evaluate the potential for reusing the permeate and concentrate in their process.

References

EPA Fact Sheet, November 1997, The Pulp and Paper Industry, the Pulping Process, and Pollutant Releases to the Environment

Biermann, Christopher, J (1993) "Essentials of Pulping and Papermaking", Academic Press, Inc.

Bartels, Craig, R (2002), "Selective color removal Nanofiltration membrane for the 7 mgd Irvine Ranch water treatment project" Proceedings of the MDIW Conference in Mulheim, Germany.