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Paper Title:

"New Membranes for Specialty Separations in the Pharmaceutical, Food & Beverage, Dairy, and Sweetener Industries"

Abstract

Hydranautics, the world leader in membrane technology, develops, manufactures, and sells membranes for specialty applications in a wide variety of industries. This paper discusses a number of membrane products recently developed by Hydranautics, including the HYDRACoRe-70pHT membrane to remove color from high pH brine solutions in the sweetener industry. The HYDRACoRe membrane technology incorporates low-pressure flat sheet composite membrane with a strongly negatively charged surface. The membrane is tolerant of free chlorine and exhibits stable performance at high pH and high temperature. Data shows successful color removal at 60C.

Introduction

Since its commercial introduction in the late 1960's, the spiral wound membrane has become a prominent unit operation in natural water and process water desalination. No device is as economical as the spiral for bulk salt removal over a wide range of uses; including municipal drinking water, pharmaceutical process water, industrial boiler feed water, beverage make-up water, and others. Hydranautics, one of the founding spiral companies, continues to be a pioneer in new industries beyond water treatment, developing and commercializing specialized membranes that save energy, purify proteins and sugars, reclaim chemicals, and remove compounds from the environment which are harmful to our health.

Hydranautics' patented HYDRACoRe product line is a durable, chlorine resistant nanofiltration (NF) membrane developed to purify salts and chemicals, operate at low pressure, and reject high molecular weight organic compounds such as colorants. The HYDRACoRe was initially used to treat chlorinated industrial wastewater, including highly colored streams from pulp and paper manufacturing (Ikeda, 1988). HYDRACoRe membranes have also been used to remove color from soy sauce and color from highly colored ground water (Spangenberg, 2002).

Membrane Characterization

The HYDRACoRe membrane consists of a sulfonated polyether sulfone polymer with a typical thickness of 0.3 µm. The surface charge of the HYDRACoRe membrane is strongly negative due to the presence of the sulfonate functional groups. Streaming potential measurements (**Figure 1)** show the anionic HYDRACoRe to have a constant surface zeta potential of -85 mV over a pH range of 3 to 11. In contrast, the conventional amphoteric polyamide RO membrane (CPA2) varies in charge from +10mV at pH 3 to -20mV above pH 6. The strong negative charge of the HYDRACoRe can be advantageous in that it will repel negatively charged organics present in certain waters and thus minimize membrane fouling by organic adsorption.

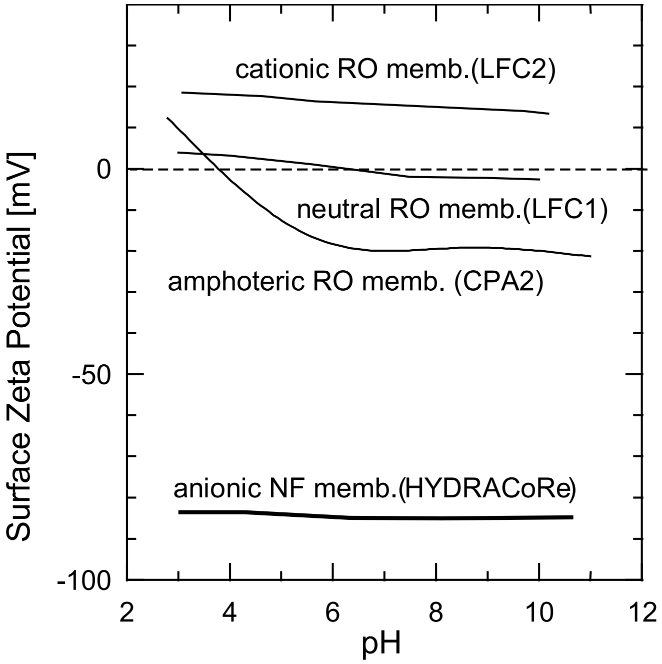
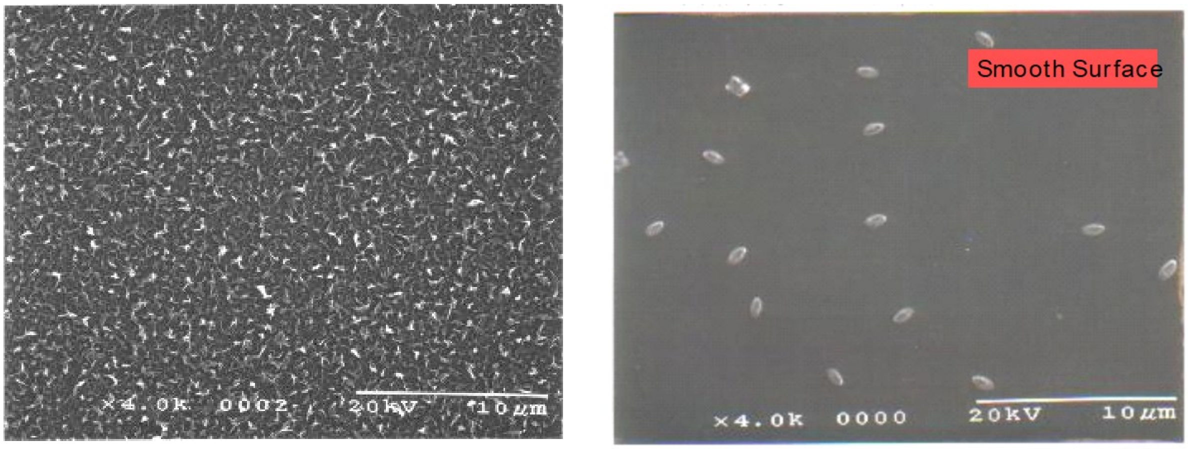


Figure 1. Surface Zeta potential measurement for typical polyamide membranes and the HYDRACoRe membrane.

Another important characteristic of the HYDRACoRe membrane is its smooth surface relative to a typical polyamide membrane surface. **Figure 2** below compares a scanning electron microscope photo of a polyamide membrane with that of the HYDRACoRe membrane. The surface roughness for the polyamide is clearly greater than that of the HYDRACoRe. The smooth surface can be advantageous in that a smoother surface suppresses colloidal fouling and biofouling by reducing the number of sites for the deposition of colloids or microbial cells. (Elimelech, 1997, Vrijenhoek, 2001, Subramani, 2005).



Polyamide Membrane

HydraCoRe Membrane

(a) (b)

Figure 2. Characterization of surface roughness of a) a typical polyamide membrane b) the HYDRACoRe membrane.

Ion separation properties

With a molecular weight cutoff of 1,000 Daltons, the HYDRACoRe is classified as a loose NF membrane deriving a significant degree of its dissolved salt rejection from the repulsion between the negatively charged membrane and negatively charged ions within the feed solution. The composition of the feed solution and the presence of certain ions within that solution therefore have a dramatic affect on the resulting selectivity of the membrane.

The effect of ion valance and charge on the selectivity of three variations of the HYDRACoRe is seen in **Figure 3**. The three membranes tested included the HYDRACoRe 10, 50, and 70 with a sodium chloride rejection of 10%, 50%, and 70% respectively. The rejection of each of the inorganic salts in **Figure 3** was determined in cell tests by applying 1 Mpa (144 psi) to a flat sheet membrane. The ionic mixture was prepared at a feed concentration of 2000 mg/L and a pH of 6.5 at a temperature of 25 C. The moderate rejection of sodium chloride compared to the much higher rejection of sodium sulfate can be explained by the negative charge of the membrane surface exerting a weaker repulsive force on the monovalant chloride ion compared to a stronger repulsive force on the larger divalent sulfate ion.

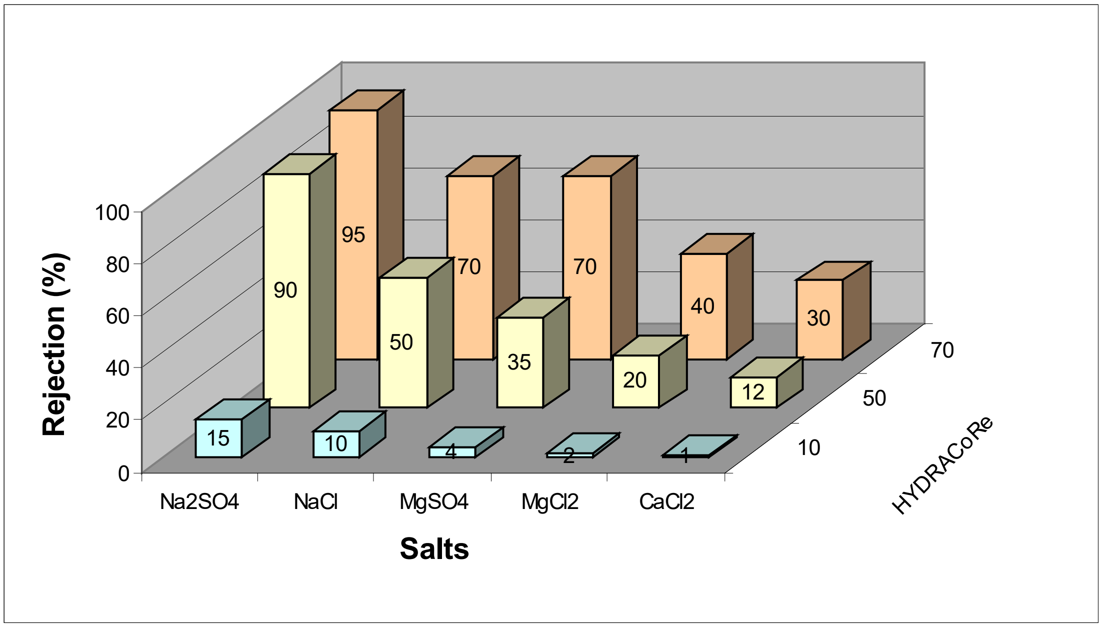


Figure 3. Rejection of inorganic salts by HYDRACoRe 10, 50, and 70 membranes at 1.0 Mpa, 2000 ppm, 25 C, and pH of 6.5.

In contrast to the high rejection of sodium sulfate, the calcium chloride rejection was much lower due to the strong attraction between the positively charged, divalent calcium and the membrane surface. In this case, the negative charge at the membrane surface is believed to be shielded or neutralized by the positively charged calcium thus weakening the repulsive force of the membrane on the chloride ion. Compounding this increase in overall salt passage is the fact that, for every calcium ion that passes through the membrane, two chloride ions must be "pulled" through the membrane to maintain electro neutrality on the permeate side of the membrane.

Another effect of the strong negatively charge HYDRACoRe is the decrease in rejection associated with increasing feed salinity. As the feed salinity increases, the increase in concentration of positively charged ions at the membrane's surface serves to shield the repulsive force of the negatively charged membrane resulting in an overall reduction in rejection. Experiments done on actual waters have shown a NaCl rejection of 40% at 500 mg/L TDS, while the rejection drops to 20% at 2000 mg/L TDS. In a full scale system, where recovery is generally greater than 80%, the brine stream will be 4 to 6 times more concentrated than the feed. Because of the loss of rejection at high salinity, the final permeate concentration will therefore approach that of the initial feed. Thus, a full-scale HYDRACoRe system will not significantly alter the ion composition of the feed water. In applications where it is desirable to maintain the ion composition of the feed while rejecting large organic or color, the HYDRACoRe is ideally suited.

Chemical stability

Another advantage of the HYDRACoRe is its greater stability toward pH and chlorine compared to conventional polyamide membranes. Chlorine is especially harmful to polyamide membranes at concentrations above 0.01 ppm due to the hydrolysis of the polyamide which leads to an increase in salt passage. A general rule is that the salt passage of a polyamide membrane will double after an exposure of 2000 ppm-hours of free chlorine. As a result, even low doses of free chlorine can not be used to control or clean biogrowth on polyamide membranes. Though not as severe, chlorine can have a detrimental effect on cellulose acetate membrane as well.

In contrast to the polyamide and cellulose acetate membranes, the HYDRACoRe is tolerant to chlorine. **Figure 4** demonstrates the chlorine tolerance of the HYDRACoRe relative to the cellulose acetate membrane (Ikeda, 1988). A sample of HYDRACoRe membrane was soaked in a 1000 ppm sodium hypochlorite solution. After 50 days (1,200,000 ppm – hours) the HYDRACoRe membrane maintained a stable sodium chloride rejection. In contrast, a cellulose acetate (CA) membrane was exposed to a 100 ppm sodium hypochlorite solution for 10 days (24,000 ppm-hours) and showed a doubling in salt passage. Thus, the HYDRACoRe is ideally suited for low doses of chlorine to control biofouling and higher doses to enhance the removal of organic foulants.

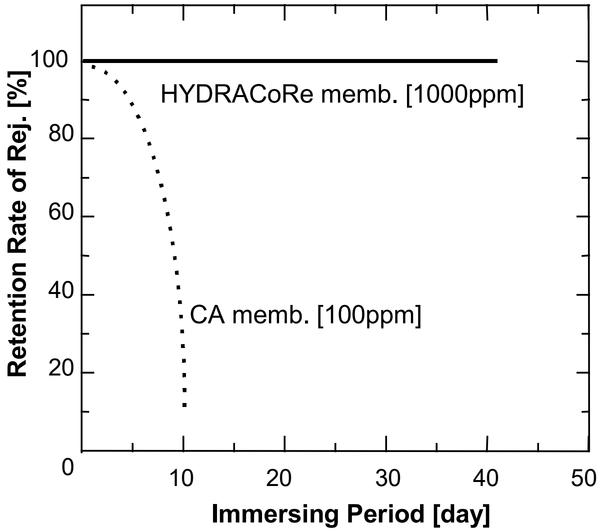


Figure 4. Chlorine tolerance of the HYDRACoRe membrane as compared to cellulose acetate membrane.

The HYDRACoRe membrane has been exposed to many aggressive agents to test its chemical durability. **Table 1** shows a list of some of these agents which had no negative effect on HYDRACoRe performance.

Table 1. Chemicals tested for compatibility with HYDRACoRe membrane.

Chemical Agent	Condition
Sulfuric Acid	pH 2
Hydrochloric Acid	pH 2
Nitric Acid	pH 2
Acetic Acid	1%
Oxalic Acid	2%
Citric Acid	2%
EDTA	2%
Sodium Hydrogensulfate	2%
NaOH	pH 13
Sodium hypochlorite	200 ppm
Formalin	0.5%

HYDRACoRe Commercial Application- Cane Sugar Purification

Most consumers in developed countries are familiar with sugar in its white crystal form. This common form of sugar is derived from the raw, brownish or yellowish crystals obtained from the crushed stem of the sugar cane grown in tropical regions of the world. The off color of the natural sugar comes from a thin film of molasses as well as organic and inorganic impurities. The process of refining sugar, including the process of decoloring, is shown in **Figure 5**.

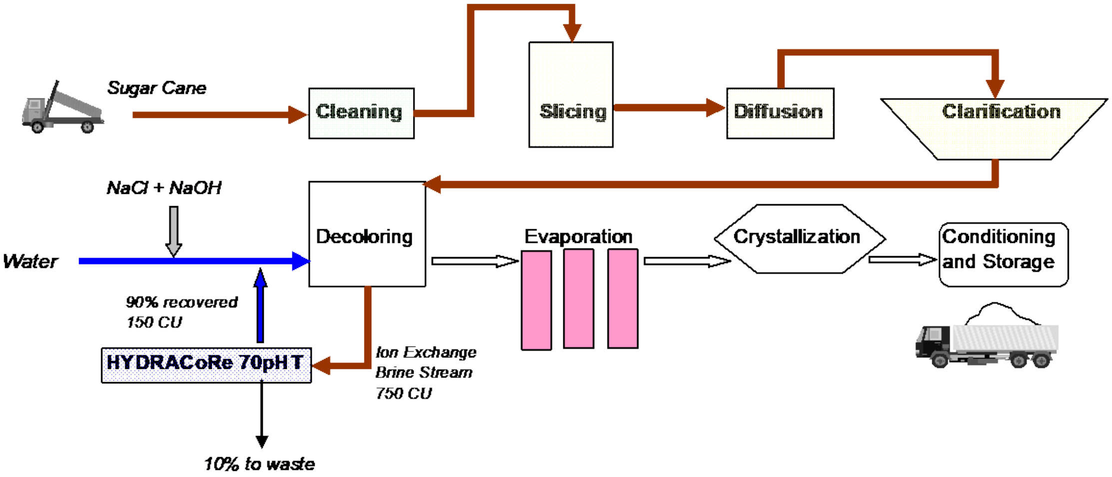


Figure 5. The sugar manufacturing process using HYDRACoRe 70pHT membrane to reclaim the regenerative brine stream in the decoloring portion of the process.

A traditional method of color removal from sugar relied on adsorption of the color onto charcoal created from crushed animal bones. Modern methods employ ion exchange, allowing the color and impurities to adsorb onto the ion exchange resin. When the resin becomes loaded with the sugar impurities and color, it is regenerated with a high pH, high temperature (60 C) sodium chloride (10 to 14%) and sodium hydroxide (0.5 to 2%) solution. After regenerating the resin, this brine solution is typically sent to drain. However, with the introduction of the HYDRACoRe 70pHT into this portion of the sugar refinement process, the brine regeneration solution can be purified and reused, saving acid neutralization, sewer discharge, and fresh chemical costs.

HYDRACoRe 70pHT

The HYDRACoRe 70pHT was developed with new materials of construction to meet the specific needs of the sugar industry and to allow operation at high pH and high temperature. The standard HYDRACoRe, used for natural water decolorizing, with its polyester components, can withstand a maximum temperature of 50 C and a pH range of 2 to 11. The HYDRACoRe 70pHT, with its caustic resistant materials, is rated for temperatures as high as 80 C and pH as high as 13. The HYDRACoRe 70pHT reclaims the ion exchange brine by rejecting the color and allowing the highly concentrated salts to pass. In this way 75 to 90% of the stream can be recovered and reused in subsequent ion exchange regeneration. The permeate stream will contain less than 10 to 20% of the original color and a dissolved salt concentration nearly identical to that of the feed.

Pilot Qualification Tests

A lab scale pilot test on organic and color loaded brine regenerant was conducted on a single HYDRACoRe 70pHT membrane, at 55-65 C for a period of 80 days. After pilot startup, as the membrane fouled, permeate flow dropped by as much as 75% (**Figure 6**). Analysis showed that biofouling and multivalent cation precipitants at high pH were the primary foulants. Because of HydraCoRe 70pHT's ability to withstand harsh chemicals, a very effective cleaning regime was developed, utilizing a high pH chlorination step with 200 ppm free chlorine at pH 13, and a separate acid cleaning step.

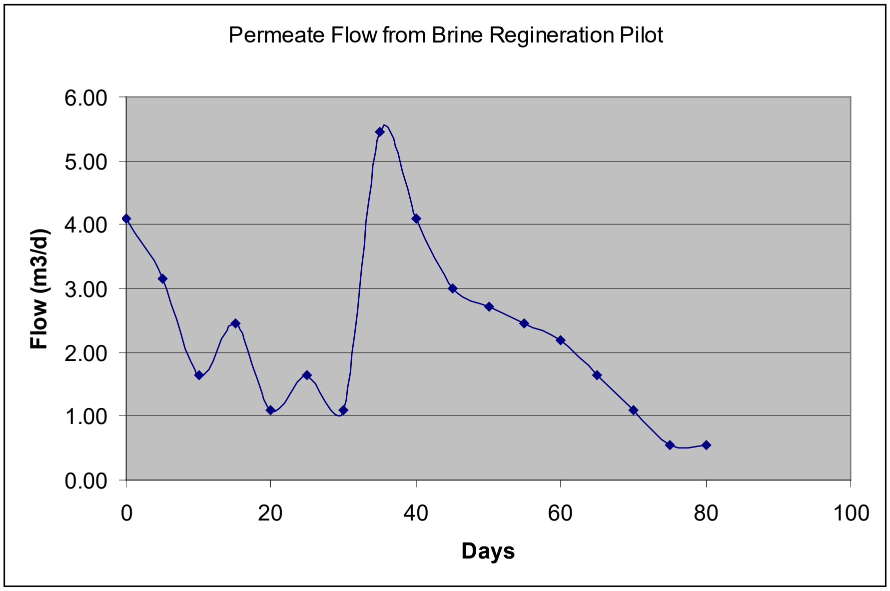


Figure 6 . Permeate flow from HYDRACoRe 70pHT pilot during 80 days of operation.

As expected, the pilot showed that the HYDRACoRe 70pHT membrane removed color and large organics while allowing smaller organics and dissolved salts to pass. Based on analysis of the pilot's feed and permeate streams as presented in **Table 3**, 88% of the color was rejected by the HYDRACoRe 70pHT while 43% of the largest sugar molecule, raffinose (594 Daltons) was rejected and 23% of the fructose (180 Daltons) was rejected. Molecular weight clearly plays an important role in the rejection of large organic molecules. Less evident is the role that molecular structure plays in organic rejection. More detailed studies have been done elsewhere to characterize the relationship between molecular size, shape and passage through the HYDRACoRe membrane (Kiso, 2001).

Table 2. Rejection of organic molecules and color by HYDRACoRe 70pHT.

Analysis		Rejection (%)	molecular weight (Daltons)
Raffinose	g/100g ds (HPLC)	43.37	594
Fructose	g/100g ds (HPLC)	23.08	180
Color	ICUMSA	88.08	

Commercial HYDRACore-70pHT Systems and Process Economics

After the HYDRACoRe 70pHT was successfully piloted, a number of plants of various sizes were installed. Based on plants currently in operation and the extensive piloting, a cost analysis can be done relating membrane performance to processing a metric ton of raw sugar to product. This analysis assumes a pretreated feed stream of 750 ICUMSA

(International Commission for Uniform Methods of Sugar Analysis) color units and an 80% color removal through the color adsorbing ion exchange resins. The salt recovery is assumed to be a conservative 82%. Amortized capital costs are not included in this analysis as these can vary significantly by region. Based on these assumptions and the values presented in **Table 3**, the nanofiltration membrane process saves approximately $0.50 per metric ton of raw sugar processed.

Table 3. Brine Regeneration System Economics.

Cost Basis

	$/ kg
NaCl	0.05
NaOH	1.01
HCl	0.24
	$/KwHr
Power	0.05

Cost of decolorized sugar produced w/o HYDRACoRe 70pHT = $0.77 / metric ton

	$ / metic ton
NaCl	0.30
NaOH	0.47
Total	0.77

Cost of decolorized sugar produced with HYDRACoRe 70pHT = $0.27 / metric ton

Chemical cost of sugar produced with HYDRACoRe 70pHT = $0.15 / metric ton

	$ / metic ton
NaCl	0.06
NaOH	0.09
Total	0.15

Membrane energy cost = $0.015 / metric ton
Membrane replacement = $0.10 / metric ton
Membrane cleaning cost = $0.0033 / metric ton

	$ / metic ton
NaOH	0.0020
HCl	0.0002
Hypochlorit	0.0006
Surfactant	0.0005
Total	0.0033

Cost savings with Membrane System = $0.50 / metric ton

Conclusions

The HYDRACoRe 70pHT, based on proven HYDRACoRe membrane technology, has been developed and proven to benefit the sugar industry in several ways:

- The HYDRACoRe 70pHT membrane effectively decolorizes, and purifies brine regenerant under high pH and high temperature conditions while generating considerably less waste and less caustic to be neutralized.

- The HYDRACoRe 70pHT saves a minimum of $0.50 / metric ton of raw sugar processed, based solely on non-regulatory, non-feed discharge assumptions. In the event that the plant was charged for discharge, and brine neutralization is required before disposal, savings would be much higher.

- Plants of 1,000 to 4,000 metric tons /day refining capacity could realize a payback on the membrane system equipment within one year.

- Additional brine can be used for regeneration and recycled at the lower cost, further improving the decolorization process.

Reference

Elimelech, M, Zhu, X., Childress, A., Hong, S., *Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes*, Journal of Membrane Science, 127, (1997), pp 101-109.

Ikeda, K., Nakano, T., Ito, H., Kubota, T., Yamamoto, S. *New Composite Charged Reverse Osmosis Membrane*, Desalination, 68, 1988, pp 109-119.

Kiso, Y., Sugiura, Y., Kiato, T. and Nishimira, N., *Effect of hydrophobicity and molecular size on rejection of aromatic pesticides with nanofiltration membranes*. Journal of Membrane Science 192 (2001) 1 – 10.

Spangenberg, C. W., Duranceau, S., Kutilek, J., *Membrane Manufacturer and Utility Implement Non-Traditional Membrane Acceptance Testing*, American Water Works Association – Water Quality Technology Conference, 2002.

Subramani, A., Hoek, E., *Direct observation of biofouling of RO/NF membranes in wastewater reclamation*, American Water Works Association – Membrane Technology Conference, Phoenix, Az., 2005.

Vrijenhoek, E., Hong, S., Elimelech, M., *Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes*, Journal of Membrane Science, 188, (2001), pp 115-128.