

NANOFILTRATION; HIGH POTENTIAL, HIGHLY MISUNDERSTOOD

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ABSTRACT

The membrane mediated process termed nanofiltration (NF) is *currently enjoying heightened attention*, some of it due to *erroneous assumptions* that it arose out of the recent nano-materials advances, or that it performs based on the characteristic of nanoparticles. But NF has been employed commercially for nearly three decades, *predating today's popular concept of nanotechnology*. The main objective of this paper is to define and illustrate the process of nanofiltration in the context of its better understood sibling membrane processes. Three more specific objectives include a) improve the common view of nanofiltration by exposing several misconceptions that have grown in the popular understanding and often in the literature, b) document a brief history of the poorly understood origin of the nanofiltration process, and c) highlight the broad potential for applications of nanofiltration.

Keywords; Nanofiltration, definition, history, applications, commercialization

INTRODUCTION

Due to space limitations, this paper assumes the reader has a working knowledge of the pressure-driven membrane processes, and also of the general morphology of these man-made membranes; to help put the information in context. The pressure-driven membrane processes are divided into four separate classes; reverse osmosis, nanofiltration, ultrafiltration and microfiltration (RO/NF/UF/MF). While some popular misconceptions apply to all four processes, and some only to individual classes, nanofiltration seems to have the most confusion in the popular literature, and occasionally in the scientific literature as well.

Nanofiltration is both a noun (a separation process) and an adjective (it qualifies a class of membranes). This can be confusing-when learning from the general literature. When the term NF appears by itself, it should be assumed the process is being described.

HISTORY OF NANOFILTRATION

Understanding the history of NF helps put several other points of this paper into context, especially in explaining the "nano" prefix. Keep in mind that the term nanofiltration preceded by over 15 years the realization and popular embrace of the potential of "nanomaterials".

Membrane Filtration

Filtration processes driven by hydraulic pressure differential are nearly as old as technology itself. Deliberately filtering water would have been practiced sometime after gathering and growing food and using fire

for cooking and heating. Therefore, filter media is nearly that old too. Membrane filtration probably began a millennia ago using animal tissue, but was not well defined until the 18th century. Use of artificial filter media that would filter in the micron range followed, and the modern *microfiltration* membrane was developed in the early 1900s. The next class of membranes to appear, *reverse osmosis*, was conceived in the 1950s, developed in the 60s and commercialized in the early 1970s. [1] Soon thereafter ultrafiltration was developed and commercialized, and both RO and UF needed to run in the crossflow mode to be commercially viable. The industry became comfortable with the RO and UF definitions, and it was both commonly understood and codified in accepted standards that RO would remove down to ionic species using a more complex mechanism than UF, which would allow the passage of ionic species and retain larger solutes through simple sieving (or "steric hindrance"). [2]

While most of the commercial focus was on the obvious and relatively simple application of water purification, some membrane companies and many academic researchers focused on process separations, as well as waste treatment or pollution control. [A useful way of categorizing membrane applications is into water purification, wastewater treatment and process separations.] The most novel and lucrative applications in the 1970s involved process separations in industry, pharmaceuticals and biotechnology. This distinction continues.

Need for Nanofiltration

As soon as the broader industry was comfortable with the definitions of RO and UF, researchers and application technologists began recognizing a large number of applications that could not be performed with either class membrane. They looked for membranes with separation capability that fell between these two classes, and they found imperfect versions of either available, which was important to helping develop the new membrane class. This brings up the interesting question: were NF membranes developed specifically for applications, or were they first simply invented, with applications for them sought after the fact? The answer is both, although the applications-driven membrane inventions dominated. The record shows that first removal of hardness from water was employed (water treatment), then removal of salts from chemical and food products were identified as valuable (process applications). These occurred separately, developed by different companies NF membranes were developed specifically for both these applications.

There are two distinct major categories of NF applications, important to understand since some of the major players in NF commercialization focus on one or the other, skewing

their literature, other communication and therefore what they teach the industry. One separates ions by their charge, the other separates uncharged solutes by their size.

This bias and the confusion it can cause is readily apparent to this author, most glaringly in the differences in the terminology definitions being written into formal “neutral party” and credible standards groups, evidenced by the differences between the standards written by the AWWA and by ASTM.[2,3] These differences appear to be based on experience narrowed by the committee members industry. Drinking water treatment professionals tend to view NF only by ionic charge mediated separations, whereas as industrial process technologists will focus on the size of the uncharged solutes (saccharides, pharmaceutical intermediaries, flavor and color bodies, etc.).The latter group acknowledges the ionic difference, but fails to put it into a context that drinking water professionals can use. The former group has been pushed a narrow definition into formal standards that appear to define the entire universe of NF, but in fact miss much of it. Therefore respected standards now abet confusion are making the way into important references. A broader view is called for.

Origination of the Term NF

Besides the use-oriented term “softening membrane,” probably coined by drinking water utility engineers [4] membrane industry insiders were using the clumsy terms “loose RO” and “UF/RO” and “RO/UF hybrid” membranes, and less often, “tight UF” [1,4,5,6].

At the time, a sizable portion of the industry agreed with the concept of pores in RO membrane barrier layers, or at least in the presence of uniform “inter-stitial spaces” amongst the polymer molecules. The size of these pores or “spaces” was generally described as 3 to 5 Ångströms “in diameter” (probably *inter-stitial spaces* - one quickly realizes the temptation to defer to the pore concept). Such spatial sizing explained the removal of uncharged small solute molecules such as sucrose. Although to some theorists these pores or gaps were not essential to explain salt rejection, but did fit the theoretical spatial size of a hydrated sodium or chloride ion, or their apparent charge density size. If an RO pore was 3-5 Å and retained glucose and 200 mw pesticides, for instance, then a membrane that passed these molecules but retained Red Dye #40, lactose and divalent ions was probably twice the size; approximately 10 Ångströms, or 1 nanometer

The FilmTec Corporation, looking for a more market-friendly descriptor for their new membrane (which did not reject a high percentage of monovalent ions), settled on a catchy term that evoked the theoretical pore size that would affect such a separation. The year was 1984 and the coining of “nanofiltration” came from Dr. Peter Eriksson, then at FilmTec, and now working for another major membrane company [6] Nanofiltration is a more palatable term than, say, “decaÅngström filtration” so it was an obvious choice once spoken, written down and examined by the market-

driven FilmTec Corporation. Despite multiple incorrect citation of the origin and timing of the NF term, sales literature dated in late1984 and 1985 prove several personal memories. [7,8]

First NF Membrane Use

The first use was led by the concept of membrane softening, or using NF membranes to remove the hardness ions (all multi-valent) but allowing the monovalent ions to pass through (they were of no concern in drinking water and represented an additional cost to remove). Reverse osmosis works just as well except it requires higher pressure, creates a more salt-laden concentrate stream to dispose of, and its purity can create an objectionable taste. It is probable the first NF membranes were conceived as these so-called “softening membranes” which were put to use for 6 to 8 years prior to the coining of the term nanofiltration.[1,4] These softening membranes were further made popular by the discovery that ultrafiltration membranes, although capable of some color removal of water sources in Florida, were not capable of removing the organic precursors which produce the carcinogenic group of tri-halo methanes (THM's) which result from reaction with the necessary chlorine biocide in the drinking water. James Taylor’s group published the data showing that UF membranes would not remove the THM's, but both the RO membranes and the so-called “loose RO” membranes did an excellent job.[4]

If you accept membrane softening as an NF process (as this author does) then the NF process was first used in 1976, just not with membranes that were labeled as nanofiltration. Applications development activities in the records show that several companies were either developing membranes that fell between RO and NF, or identifying and describing processes that could use such a membrane.[5,9] Although other ionic separation water purification applications and some waste treatment applications were developed, by far the ones with most interest for process applications

Figure 1 is the *gold standard* (most copied) of the several membrane vs. solute/particulate size comparison charts

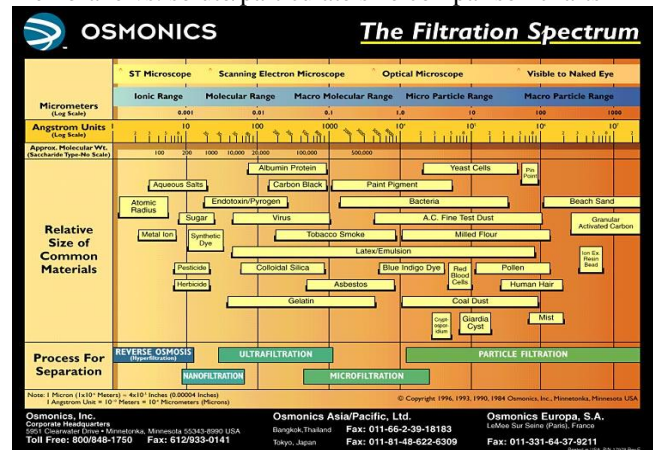


Figure 1: Osmonics classic 1984 version of their Filtration Spectrum, used with permission.

Nanofiltration's first use in an industrial process is more difficult to determine since many of these processes were not made public, widely published or written for publications that are Internet-archived today. One candidate for the first application in this category is described in detail in this paper because the author was directly involved in developing it, and it progressed into the source of a patent and US Supreme Court decision.

Nanofiltration goes to the US Supreme Court

In early 1984, two rival companies seeking new membrane solutions to old problems were, unknown to each other, simultaneously trying to develop the same application in the Applications Lab of membrane company Osmonics. These rivals were Warner Jenkinson, a major producer of dyes and flavorings for the soft drink industry, and Hilton-Davis, a major dye manufacturer. Hilton-Davis (H-D) had the most success, and not least because they patented the process they co-developed with Osmonics, and turned into a major customer due to their high consumption of membrane for this process.[10]

Warner Jenkinson (WJ) did not want to be shut out of this valuable process, so they interpreted the H-D patent claims literally and developed the ability to operate at pH 5.0, below the perplexing limitation of 6.0 Hilton Davis had added to a major independent claims during the patent prosecution. After years pushing lawsuits through both the lower and the appellate courts, the appellate decision loser would not give up and, through some fluke or oversight, a question of patent law regarding how to apply the so-called Doctrine of Equivalents brought this NF process and its patent to the Supreme Court (SCOTUS). This was the first time for decades the SCOTUS heard a case regarding patent law, and none has been heard since. If one wants to get the attention of a patent lawyer onto membrane, just mention this decision.

Although the membrane in question is clearly in the NF class, that term did not exist at the time the patent was filed, and the erroneous term ultrafiltration used in of the patent carried through all the way to the Supreme Court decision. [10,11] Therefore a search of decisions that include *nanofiltration* + *US Supreme Court* will not yield this case, whereas use of *ultrafiltration*, either of the litigants' names or *Doctrine of Equivalents* will. Hilton Davis prevailed in the final decision, written by the somnolent Justice Thomas, who declared that, even though the limitation of operation at above pH 6.0 was written into an independent claim, the theory of estoppel could not be enforced because the record did not hold the reason for adding this limitation. Thus the Doctrine of Equivalents was interpreted broadly, and a previous act of Congress cited by WJ was held not to narrow interpretation of that doctrine. This decision did not hinge directly on the definition of NF, although the invention could only occur due to a true NF membrane. The case provides a cautionary tale about careful cleanup of a patent's claims wording before allowed to issue.

Documented Legacy

Perhaps the first written description of the NF process and NF membranes in a surviving legal document is in the H-D patent filed in 1984 (relevant wording reproduced below). The patent did not use the term NF, but the inventor Cook, using the pore size information the Osmonics R&D department had speculated about to him, did define the same pore size range that later compelled Dr. Eriksson to coin the term "nanofiltration". [10] As the chain of ensuing patent, protracted lawsuit and eventual US Supreme Court decision attest to, this was an important process. Although it hardly discovered a new basic concept, the process was novel enough in detail to be patented, and to provide a complex legal question which justified a seminal decision on the application of the Doctrine of Equivalents:

US patent #4,560,746 *Detailed Description Inclusive Of the Preferred Embodiments:*

"The membranes used in the practice of the present process, and generally referred to as reverse osmosis/ultrafiltration membranes, have a nominal pore diameter of 5-15 Angstroms, a preferred range being from 7-11 Angstroms. Membranes useful in the practice of the present invention are manufactured by Osmonics Inc. of Minnetonka, Minn.The filtration is carried out under a hydrostatic pressure of approximately 200 to 400 p.s.i.g. applied to the upstream side of the membrane. By use of a membrane having the appropriate critical pore size, those impurities of a molecular size smaller than the nominal pore diameter of the membrane, along with a large quantity of water, are thus forced through the membrane ..., while the desired product molecules, as well as impurities of a molecular size larger than the nominal pore diameter of the membrane, are rejected by the membrane and remain on the upstream side thereof where the product becomes more and more concentrated...."

OUTLOOK FOR NF

The NF Market

There are no precise numbers or methods for determining the size of the NF marketplace. However, there is near-universal agreement among professional prognosticators that NF is growing at from 2 to 5 times the rate of its sibling membrane processes. Annual element-only sales (i.e. excluding related hardware and equipment- the purest measure) of US\$300 million seems a reasonable estimate, and represents a 5 to 10 multiple increase over 10 years ago. Ceramic NF represents a miniscule portion of this. This author believes that from 5 to 8% of the total RO/NF pool goes to NF, with that percentage higher in the process applications, and the percent of profit made on the membranes and membrane equipment considerably higher for the NF class In 2013 a major data aggregator placed the NF sales growth at 27% cumulative annual growth rate (CAGR), as compared to the accepted range of 8-12% for RO membrane.

Applications and Suppliers

While membrane softening is a simple process, it represents the most potential for use of the membrane measured by volume, and the number of companies selling NF for water treatment supports this assertion. Of the 9 companies worldwide that manufacture polymeric NF membrane at present, eight offer water treatment models and/or promote water treatment applications. But several of the same companies seek to develop and support process and waste reclamation applications as well, and nearly all target the common foodstuff applications. Fractionation as a concept can be applied to many industrial processes, with more potential than fractionation by UF, at least in number of distinct uses and probably in terms of volume or area of membrane used. These applications include:

- Recovering catalysts from metals, fine chemicals and pharmaceuticals.
- Separating saccharides by molecular size, and from proteins or salts.
- Purifying and concentrating amino acids
- Desalting food and textile dyes
- Purifying intermediates in chemical processes
- Separating and concentrating metals from extractant acidic solutions (mining, refining)
- Purifying acids prior to concentration and reuse (mining, refining, food processing).

The USA has a newly recognized and set of wastewater disposal/reuse challenges, which are increasing in scope with its dramatically increasing domestic production of oil and gas. Water shortages at many well sites call for rigorous reuse efforts, and the fate of chemicals from fracking solutions and contaminants naturally occurring in “produced water” have deservedly generated much concern. There are multiple applications for use of membrane separation treating what is often highly saline produce water and fracking “flowback water”. These can be broken down into four categories: Purification for beneficial use on the surface, reuse in secondary and tertiary oil and gas recovery, downhole disposal injection, purification for surface discharge.[12]

Ceramic NF Membranes

Fulfillment of the promise of nanofiltration class ceramic membranes has been a long time coming, and its realization has yet to be proven. While ceramic and metallic MF and UF membranes have carved out niches in the marketplace, NF ceramic has not. Pure ceramic NF membranes have also not really been achieved, or at least commercialized., resins are added to a UF or MF ceramic substrate, typically treated to give produce an charged surface. A tough proposition long-term. After twenty years later, the marketplace still waits for the proof, although not for a lack of trying. A recent review by the author concluded that there are four companies worldwide offering so-called NF ceramic membranes, and none show a specification for salt rejection. They do, however, offer a molecular weight cutoff value, for practical purposes a pore size specification.

This survey shows that ceramic NF is both a very difficult proposition to achieve, but that there remains a belief in their potential. There is some definitional value in the attempts at NF class ceramic membranes, it forces the mechanistic question of ionic separation: Is it the solution diffusion or pore flow mechanism that rules?

The Technology of NF Membrane

While more interesting and varied applications exist for crossflow MF membrane, there is no inherent characteristic in this class of membranes that will change the manner in which they are operated. As with RO, NF must be operated in crossflow, limiting system design and economic viability. Until NF made in a hollow fiber configuration, which will enable cleaning by permeate backflushing, like RO, it is constrained by the crossflow mode. On the other hand, NF membrane is where the most action is occurring in terms of new materials and new morphology. The only commercially viable advances toward non-aqueous polymers in the last 15 years has been in the NF class. In addition to the so-called ceramic NF membranes, liquid crystal “lyotropic” and other exotic chemistry formulations are in development more than in the RO and even UF class. It is likely that the tweaking of pore size and other morphology in the commercial cellulosic and polyamide membranes will yield the advances. History teaches this. Nevertheless, with the weight of research money and new ideas the NF class, so this is the field that is right for the most breakthroughs.

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