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Nanofiltration membranes and processes: A review of research trends over the past decade

Darren L. Oatley-Radcliffe \textsuperscript{ab*}, Matthew Walters \textsuperscript{ab}, Thomas J. Ainscough \textsuperscript{ab}, Paul M. Williams \textsuperscript{a}, Abdul Wahab Mohammad \textsuperscript{c}, Nidal Hilal \textsuperscript{a}

a. Centre for Water Advanced Technologies and Environmental Research (CWATER), College of Engineering, Swansea University, Fabian Way, Swansea SA1 8EN, UK.
b. Energy Safety Research Institute, College of Engineering, Swansea University, Bay Campus, Swansea, SA1 8EN, Wales, UK.
c. Centre for Sustainable Process Technology (CESPRO), Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Ehsan, Malaysia

*Corresponding author: d.l.oatley@swansea.ac.uk

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Abstract
Nanofiltration technology has come a long way since first inception in the late 1980s. Research activity in this area covers a great many topics and the aim of this review is to quantify the level of interest in each of these areas. The number of annual publications directly related to nanofiltration technology has been harvested from ScienceDirect since 2007. This quantification of research has shown that interest in nanofiltration technology has grown over the past decade, particularly over the past five years. The primary journals reporting articles on nanofiltration are the Journal of Membrane Science, Desalination and Separation and Purification Technology, although articles have been spread across a further 139 journals. Unsurprisingly, the major topics of interest have been water processing, membrane fabrication and membrane surface modification. There has been clear growth in the areas of organic solvent nanofiltration, pharmaceutical and biological applications, design and economics of nanofiltration processes and review articles. Nanofiltration modelling has received less support over the period reviewed and has experienced a steady decline. Clearly the overall growing trend in nanofiltration research indicates that the technology remains popular and this interest should materialise into further applications for a robust and sustainable future.

1.0 Introduction
Nanofiltration membranes have come a long way since inception in the late 1980s. With properties between those of ultrafiltration (UF) and reverse osmosis (RO) membranes, nanofiltration membranes continue to see increasing interest due to their versatility as a separation tool. Their pore size is typically of the order of 1 nm, which corresponds to a molecular weight cut-off (MWCO) in the range of 100–5000 Daltons. Nanofiltration membranes also exhibit a moderate level of charge due to the dissociation of surface functional groups or the adsorption of charged solutes. For example, polymeric NF membranes contain ionisable groups such as carboxylic and sulfonic acid groups which result in charged surfaces in the presence of an aqueous feed solution. Nanofiltration membranes operate with no phase change and typically have high rejections of multivalent...
inorganic salts and small organic molecules at modest applied pressures. This makes the separation process highly competitive in terms of selectivity and cost benefit when compared to traditional separations. Thus, NF has found wide application across a range of industrial sectors including water and wastewater treatment, pharmaceutical and biotechnological processes, and food engineering to name a few. Various aspects of NF membranes have been explored in a number of recent review papers [1-3], these include treatment, pre-treatment, modelling, atomic force microscopy, and some of the pitfalls of NF technology. In addition, a comprehensive account of NF membranes has been provided in several reference books [4, 35-37]. The aim of this review is to collate and highlight the trends in research progress related to nanofiltration membranes and processes over the past decade, from 2007 onwards. To this end, the ScienceDirect platform has been used to collate academic papers across the spectrum of journals available. The subsequent processing of articles has removed any papers that claim keywords or text such as ‘nanofiltration’ but does not actually include work in the respective field. For example, the term nanofiltration may appear quite legitimately in the text of a paper, but on closer inspection the paper actually deals specifically with ultrafiltration. Where this is the case, these papers have not been included in this review with the goal to only include relevant research specific to nanofiltration.

2.0 General research trends since 2007

The trend in nanofiltration research has been generally increasing since 2007 and is illustrated in Figure 1. At the time of writing, there have been 1902 journal articles published on Science Direct related to the topic of nanofiltration. Due to the versatility of nanofiltration membranes, these articles cover a range of topics, for example membrane fabrication, membrane modification, desalination, and Organic Solvent Nanofiltration (OSN – formerly known as Solvent Resistant Nanofiltration [SRNF]) all showing that nanofiltration is an innovative technology that has a wide range of applications.

In total there have been publications across some 142 journals spanning the topic of nanofiltration. In 2007 there were 148 articles published related to nanofiltration membranes and processes. This number, barring small spikes in 2009 and 2012, was almost constant until 2013; beyond which there has been a significant year on year increase to 266 papers in 2016. The spike in 2012 is most likely attributable to publications arising from the Euromembrane Conference of that year. Figure 2 indicates the major journals that have published articles related to nanofiltration. The data clearly shows that main journals publishing nanofiltration papers are The Journal of Membrane Science (27.39%), Desalination (22.97%), Separation and Purification Technology (10.78%). Collectively these three journals account for more than 60% of all nanofiltration publications with the remainder of articles spread across a further 139 different Journals.

A breakdown of the publication topics from the total amount of publications from 2007 to present is provided in Figure 3. The majority of the research reviewed has dealt with waste water applications, this may however include publications that also cover other topics such as membrane fabrication or fouling studies that have been applied to waste water applications. Waste water applications total some 18.30% of the papers reviewed, the trend is then: Pharmaceutical and biotechnology (14.04%), economics and design (13.72%), membrane modification (12.83%), solvent nanofiltration (11.25%), membrane fabrication (10.52%), desalination (8.94%), fouling studies (7.83%), modelling (6.78%), reviews (5.47%) and food (2.52%). Given that waste water applications and desalination could be
grouped together as ‘water processing’ then this combined subject area is the predominant area of research interest and represents some 27.24% of publications, i.e. a quarter of all published nanofiltration research. Similarly, given that membrane modification is a subset of membrane fabrication, the combined total for this subject area becomes 23.35% of papers and is the second most significant subject area. Thus, water processing and membrane fabrication represent more than a half of all research interest in nanofiltration in terms of direct publications.

The data illustrates that nanofiltration has a wide range of applications, but research trends are more focussed in certain areas. For example, the largest single industrial application for nanofiltration seen in this review is that of water applications, both waste treatment and desalination. The water industry has used membranes for a considerable period of time and has a great deal of capital invested in the technology. However, for clean water production, nanofiltration is replacing or working alongside reverse osmosis which provides the cost benefit of lower pressure operation. Retrofitting in this sense is simple and is in essence replacement of the membranes only. Thus, research is clearly being conducted as inclusion of NF technologies is a straightforward task and the cost benefit/process improvement can easily be exploited. By contrast, the food industry is the lowest observed area of research found in this review. Parallel to the water industry, the food industry has used membranes for a considerable period of time and therefore one could easily expect similar levels of research. However, in this sector the membrane applications utilised have been predominantly microfiltration and ultrafiltration (e.g. removal of bacteria from products [5]). Retrofitting to include NF processes for this industry requires substantial capital investment to upgrade the pumps and pipework to take the increased operational pressure. This required capital investment to upgrade pressure systems for NF processes can prove to be a major obstacle in the industrial setting. So while the trend in publications related to nanofiltration in food applications is increasing, the net deployment in terms of real applications in industry in this sector remains low. One would suspect that as existing plants reach their end of life, then the opportunity to select NF processes will become more widespread and further research to compliment the technology uptake should be expected.

3.0 Specific research trends since 2007
3.1 The dominant research areas
3.1.1 Water Processing
As stated in section 2, the majority of research interest related to nanofiltration technology is in water processing and membrane fabrication. Waste water processing is the single largest area of research interest found in this study. This is unsurprising in the modern world where pollution prevention and control is a key objective of governments and is forcing industry and academia into action. For example, in Europe water policy is now governed by the Water Framework Directive (Directive 2000/60/EC [6]). The directive constitutes the culmination of water legislation within the European Union and is aimed at establishing a framework for action in the field of water policy, i.e. improving and maintaining water standards across the region. Other regions of the world have similar legislation either in place or in the pipeline. The level of research interest in this field has remained almost constant across the period studied, as illustrated in figure 4, and has only seen an increase in activity since 2013. Between the period 2007 to 2012 there were approximately 30 publications annually and since this point the number has increased to 52 publications in 2016. There are several different subtopics within the waste water area and these are highlighted in figure
5. Within these subtopics, the removal of organic matter from water is the most published area of research with 29.31% of the total publications reviewed. The vast majority of urban and industrial waste water plants are focused on the removal of organic matter (as well as other materials), so this high level of interest is completely understandable. Similarly, the wastewaters generated from the textile industry are among the most polluting of all the industrial sectors and have been considered as a significant environmental problem for several decades [7]. Therefore, the high level of interest (16.95% of the publications released from 2007 onwards) in this area is also quite expected. Within this sub-topic studies include removal of dyes from actual textile industry waste waters [8] and the study of synthetic systems representative of the industrial effluent such as the removal of Congo Red from water samples [9]. Of the 16.95% (59 publications), over 40% of these publications are directly related to textile industry processes, with the other publications covering characterisation of membranes for use in this field [10] and hybrid-technology evaluation [11]. While some of these latter applications have only been proven at bench scale, further development into large scale processes would be expected.

Desalination is another area of water processing that has shown increased growth in nanofiltration research over the period reviewed, see figure 6. The desalination sector is expected to become a $50 billion industry by 2020 and the technology still uses multi-stage flash (MSF) and multi-effect distillation (MED), but in more recent times predominantly employs reverse osmosis (RO) technologies to remove the salt from saline waters producing clean fresh water suitable for consumption or agriculture and industrial purposes. Table 1 illustrates the levels of salt typical to different input feed water streams to the desalination process. Nanofiltration can be used to remove divalent ions and small organic materials and is finding increased use for pre-treatment operations prior to the reverse osmosis stage [12]. Nanofiltration allows some salts to pass through the membrane and thus has a reduced operating pressure to reverse osmosis. This leads to economic savings in terms of operational costs and a reduction in fouling. This shows that nanofiltration membranes have their place in clean water applications either as a replacement for or in combination with traditional technology, microfiltration and ultrafiltration for the pre-treatment process [13] or in some cases as a replacement of reverse osmosis [14]. There has been a steady supply of papers in this area at the level of 10-12 papers per year from 2007 to 2012 and then a significant increase year on year to 32 papers in 2016. Out of the total publications in this area, seawater desalination is the most published topic (40.43%) followed by desalting waste water (30.5%), then brackish water (18.44%), pure water (9.22%) and finally river water (1.42%).

3.1.2 Membrane Fabrication and Modification

The manufacture and subsequent modification of nanofiltration membranes to enhance performance (increase separation capability) and reduce cost (increase flux, decrease hydraulic resistance and fouling) is also a dominant area of research. Figure 7 shows the number of publications for both membrane fabrication and modification. The trend for membrane fabrication shows a definite and significant increase from only 2 publications in 2007 to around 50 publications in 2015 and 2016. Interestingly, fabrication papers doubled between the years 2012 and 2013 and then doubled again between 2014 and 2015. These spikes in publication trend may be attributable to the establishment of the International Conference on Desalination using Membrane Technology, inaugurated in April 2013 (papers from this event were published in a special edition of the journal Desalination in 2014) and then held again in 2015, which has a firm focus on membrane fabrication. Similarly, there has been a recent surge in activity related to the development of nanocomposite
membranes [15-17] which may have contributed to the 2014 to 2015 trend and indeed maintained the level of activity. Papers on membrane modification have followed a similar upward trajectory, but with less significant increases. The number of papers published in 2007 was 17, significantly more than membrane fabrication. The number of papers then gradually increases over time to 40 papers in 2016. Thus, in the period 2015 and 2016 membrane modification was overtaken in terms of the volume of publications by fabrication, although the net quantity of papers is similar in magnitude. Over the period reviewed, nanofiltration membranes have been fabricated from a variety of different materials. These include different materials for the active layer and support layers (and various combinations of the two) and variations in the materials used to modify the resultant membrane. The most popular material for the fabrication of nanofiltration membranes was polyamide (14.12%), which is typically the active layer of the membrane [18,19]. The most common support layer found in this review was polyether sulfone (7.17%) that may be used in pure form or combined with other materials [20]. A list of the top 25 materials for fabrication and modification of nanofiltration membranes, ranked by number of papers, is provided in table 2. In total there were 101 different materials identified. This shows the enormity of the task at hand and the sheer variation in membrane properties and performance that can result from fabrication processes. By the same token, 101 different chemicals is only the very tip of the iceberg in terms of available materials for fabrication and modification and demonstrates that there is potentially a huge amount of research still to be completed in this area. The key question dictating how much of this future potential will be realised is related to the effort and cost expired in relation to the improvements in membrane performance gained and the supply of new applications for nanofiltration technology to justify the experimental cost. Similarly, the vast majority of new or modified membranes identified in this research have only ever been fabricated at bench and pilot scale. There are no research papers that detail a membrane travelling from concept to an available marketed product. This is an obvious issue and for the impact of this colossal amount of research to be fully realised, then a new generation of commercially available NF membranes translated from this early research should be expected soon.

3.2 Increasing research activity

While the majority of activity related to nanofiltration research is in the area of water processing and membrane manufacturing, there are a number of research areas that are increasing in terms of publications generated. These include OSN, pharmaceutical and biological applications, design and economics of nanofiltration processes and review articles. OSN has seen quite a pronounced increase in research activity over the period reviewed, see figure 8. From 2007 to 2011 the number of papers in this area was consistently between 7 and 10. However, from 2012 and onwards the rate of publications in this area has increased to a level of 41 publications in 2016. OSN has a wide variety of sub-topics which can be summarised as solvent recovery [21], solvent exchange [22], solute purification [23], fabrication and modification [24,25]. Marchetti et al. [26] have reviewed the field of OSN, and while at 72 pages their review is not particularly ‘critical’ as the title would suggest, the review is certainly comprehensive and provides a full overview of this area. There has been a growing trend in publications for thin film nanocomposite nanofiltration membranes [27,28] for OSN applications. These membranes are commercially available and are proving popular mainly due to their customisation abilities where the polymer system can be created and modified to be optimised for a given separation [29,30].
Pharmaceutical and biological research has also shown a steady level of increase over the period studied. Figure 9 shows the number of paper published in the period 2007 to 2011 is approximately 20 per annum (varies between 14 and 22) and for the period 2012 to 2016 the publications jump to 30 to 40 papers per annum. This trend shows a marked increase from 2012 and is similar in nature to the trend observed for OSN. As OSN deals to a large extent with pharmaceutical applications then this apparent synergy seems sensible.

As nanofiltration technology and applications grow, naturally there will be attempts made in order to design more effective and efficient separations with the ultimate aim of reducing costs. Figure 10 shows the trend in papers published related to design and economics of the nanofiltration process. There was a slight dip in the number of papers from 21 publications in 2007 to 14 in both 2008 and 2009. Since then the number of papers has risen steadily to 42 papers in 2016, while the total numbers are modest this change represents a 300% increase in research activity!

As research activity in any area grows and progresses over time, then naturally there will be review papers written. Nanofiltration is no exception and figure 11 shows that the number of reviews for nanofiltration topics has been steady with between 5 and 10 papers published each year for the period 2007 to 2013, with a year on year increase following this date to 28 papers in 2016. Possibly the most recent and general review of nanofiltration membranes is that of Mohammad et al. [3].

3.3 Decreasing research activity
Not all aspects of nanofiltration technology research are experiencing growth. In this review, the only area of nanofiltration that has experienced stagnation or decline is the topic of modelling nanofiltration processes. Figure 12 illustrates the trend of publications in this field and while the publication rate is somewhat erratic, the general trend is one of a slight decline. The number of publications in 2007 was 13 and in 2016 was 11. This is not that significant a decline, however, the number of publications in 2009 was 21 and from this point forward there is a clear gradual decline. Accurate models for nanofiltration are required for the ab initio design, optimisation and scale up of effective industrial processes. The current state-of-the-art in nanofiltration modelling has been outlined [3,31,32] and the typical solution methodology explained. While a decline in publications may not be attributable to a single cause, the decline may well be the result of a lack of interest in this field due to the fact that the established models of nanofiltration membranes are as accurate as possible given the limitations in physical measurement technology available for the nanoscale. Moreover, as models increase in complexity (as knowledge and understanding build) then they become significantly more computationally complex and difficult to solve and in some cases quite abstract from reality. There are other factors that affect nanofiltration modelling. In a recent paper, Oatley-Radcliffe et al. [32] point out that not only are the physical properties of the membranes difficult to measure, but the interactions between the solvent(s), solutes and the membrane itself are often unclear, particularly for OSN systems. For example, the pores of the membrane may shrink or swell depending on the interaction with the solvent [33]. There have been some attempts to model OSN systems (such as OSN designer used in conjunction with MATLAB [34]) but these are still in their infancy and need to be improved to take into account physical reality such as fouling etc. Thus, nanofiltration modelling is inherently coupled to measurement technology and until there is a step change in measurement at the nanoscale, interest in modelling nanofiltration membranes is likely to amble along or decline yet further.

4.0 Conclusions
The area of nanofiltration research is clearly gaining interest by measure of academic papers published. While the number of papers published remained steady at approximately 150 from 2007 to 2011, since then the trend in publications has increased to more than 250 papers per annum. The vast majority of these articles lie within three international journals, namely: The Journal of Membrane Science (27%), Desalination (23%) and Separation and Purification Technology (11%). The other publications span some 139 journals. The major topics of interest within the scope of nanofiltration are water processing, encompassing waste water treatment and clean water production, membrane fabrication and membrane surface modification. Each of these four topic areas currently receive similar numbers of papers annually, around 50 publications, and all have shown growth over the last five years. There are other topics not as well reported that have also shown quite significant growth, especially over the last five years, these are: organic solvent nanofiltration, pharmaceutical and biological applications, design and economics of membrane processes and review articles. Each of these topic areas has at least doubled in the number of articles published over the period reviewed with particular growth in the last five years. The picture is not the same for modelling of membrane processes. While this subject is key to improve the technical understanding of the science and operation of nanofiltration membranes, this area of research has shown a steady level of decline since 2009 to only a handful of papers annually. Overall, the interest in nanofiltration technology as measured by publications is growing annually and recent activity suggests that this trend can only continue.

Acknowledgment:
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Figure and Table captions

**Figure 1**: Number of nanofiltration research articles published since 2007 according to ScienceDirect.

**Figure 2**: The major journals publishing articles related to nanofiltration.

**Figure 3**: The research topics covered in the articles reviewed.

**Figure 4**: Research trends in wastewater applications for nanofiltration (348 total papers).

**Figure 5**: Topic areas in wastewater nanofiltration research.

**Figure 6**: Research trends in desalination using nanofiltration (170 total papers).

**Figure 7**: Research trends in membrane fabrication and modification (total papers: 200 fabrication and 244 modification).

**Figure 8**: Research trends in organic solvent nanofiltration (OSN/SRNF) from 2007-2016 (214 total papers).

**Figure 9**: Research trends in pharmaceutical and biotechnology applications for nanofiltration technology (267 total papers).

**Figure 10**: Research trends related to design and economics of nanofiltration technology (261 total papers).

**Figure 11**: Review articles for nanofiltration technology (104 total papers).

**Figure 12**: Research trends in modelling of nanofiltration membranes and processes from 2007-2016 (129 total papers).

**Table 1**: Levels of dissolved solutes in different waters.

**Table 2**: The top 25 chemicals identified to fabricate or modify nanofiltration membranes found in this review (total of 1339 papers).

References


Figures and Tables

Figure 1

Number of papers

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Figure 2

- Journal of Membrane Science: 27%
- Desalination: 39%
- Separation and Purification Technology: 23%
- Others: 11%
Figure 8

Figure 9
Table 1

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<th>Water type or origin</th>
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<td>Brine or concentrated seawater</td>
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Table 2

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<th>Abbreviation</th>
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