TFC	Thin film composite
TMS	Teorell-Meyer-Sievers
TOC	Total organic carbon
UF	Ultrafiltration
XPS	X-ray photoelectron spectroscopy
W	Weight

Other symbols

∇	Nabla-Operator

1. INTRODUCTION

Membrane technology has turned out to be a state of the art technology in important processes for mankind such as seawater desalination, dialysis in artificial kidneys and wastewater treatment. Membrane processes have been used in drinking water production from seawater over 40 years [1]. In addition, since 25 years they have a permanent place in food and beverage industries [2], within production processes for clarification and enrichment and also to treat wastewaters and process effluents [3]. Currently, biotechnology and chemical industries benefit from this versatile technology owing to the developments of new membrane materials, advanced module designs and better antifoulant agents.

Attempts to utilise this technology for the imperative industrial growth are especially strengthened by process intensification studies, in which the target is to enhance the efficiency of the industrial processes. Some approaches are the recovery of partially used raw materials, extraction of interesting by-products, along with a reduction in waste generation, energy consumption and overall costs [4]. In this regard, membrane processes with their appreciable energy savings, compatibility between different membrane operations in integrated systems, easy control, large operational feasibility and as being environmentally benign, ensure an important answer for the realisation of these approaches [4]. In comparison to the standard membrane processes such as reverse osmosis (RO) for water purification or ultrafiltration (UF) in food industry, nanofiltration (NF) offers a variety of functions implementable in a plethora of applications. Therefore, it is convenient in intensification studies of various industrial processes such as in the feed pre-treatment of RO seawater desalination.

While RO and UF membrane processes were mainly established in most of the industrial fields, the applications such as whey processing, water softening and fractionation of sugars were in need of membranes, which exhibit better selectivity than UF and show higher fluxes than RO. Till 1980, researches were carried on integrally asymmetric cellulose acetate (CA) RO membranes and its modifications to achieve the desired performances. Nevertheless, the deficiencies of CA membranes in terms of pH instability as well as unstable flux and rejection performances moved the investigations to the search for new membrane materials and structures. The breakthrough happened in 1970 by the development of composite membranes, where a thin active layer is supported by another material of porous sublayer. In 1976, during the enhancement studies of these RO membranes, John Cadotte discovered a membrane type which displayed high flux and high permeability to chloride ions but high rejection to sulphate ions [5]. This membrane type was appreciated by Filmtec cooperation in 1984 [5]. Thereafter, the process, which was categorised between RO and UF, called as open RO, loose RO or tight UF, was given the name nanofiltration. Later on, the development of polypiperazineamide NF membranes by interfacial polymerisation technique accelerated the commercialization of NF membranes with different variations by the companies such as Toray, Nitto, Osmonics. Table 1 gives a general overview of the historical development of NF membranes.

Table 1: A general overview of historical development of nanofiltration membranes

Membrane	**Person / Manufacturer**	**Year**
porous CA membranes (integrally asymmetric)	Reid, Breton, Loeb-Sourirajan	1959
CA NF membranes (integrally asymmetric)	Loeb-Sourirajan, Cohen	1970
composite RO membranes	Rozelle, Cadotte, Riley	1970
composite NF membranes	Rozelle, Cadotte	1976
polypiperazineamide NF membranes (99 % $MgSO_4$, < 60 % NaCl rejection)	Cadotte, Steuck, Petersen	1981
fully aromatic cross-linked polyamide NF membranes	Filmtec Co.	1985
polyethyleneimine NF membranes	Linder, Aviv, Perry, Katraro	1988
acid/base stable NF membranes	Linder, Perry, Aviv	1988
chlorine resistant NF membranes	McCray, Petersen	1989
NF membranes modified from RO membranes by acid, base, oxidant treatment	Strantz, Brehm, Cadotte	1989
solvent resistant NF membranes	Black, Shavit Perry, Yacubowicz, Linder	1990

Note: Information in table was extracted from Chapter 2 in [5]

The classification of NF between UF and RO membranes is a consequence of its separation range and pressures applied in its processes. NF membranes retain molecules with molar masses between 200 to 1000 g/mol in a pressure range from 3 to 50 bar. An interesting aspect of NF membranes is the fact that so many parameters can appear when one tries to model and characterise the selectivities of such membranes [5]. Unlike the other membrane types, charge is an unique property for NF membranes. Consequently, apart from steric, electrical effects can be decisive for the separation behaviour. Recently, in addition to the membrane morphological and charge characters, solute properties such as polarity, hydrophobicity and shape have been addressed in terms of their contributions to the separation performance. Although the interactions of various parameters offer many advantages in diverse applications, there are some hindrances in design of new NF processes and improvement of existing ones. These are mostly associated with its complex transport phenomenon. The membrane charge and its dependence on several factors (concentration, salt type, pH), accompanied by the effects of operating parameters give rise to a more complicated transport phenomena than the ones encountered in other membrane processes. Furthermore, the numerical complexity of the physical models is augmenting by the increasing number of components as well as their valences. Consequently, compared to RO, modelling of NF performance is much more complex [6].

Up to now, physical models of NF have been applied to the model solutions of organics as well as binary and ternary ion systems. However, it has been pointed out that there is a need for the applications of existing theoretical and experimental methods to the separations of real industrial streams [7]. At this point, experiments regarding real process streams are of paramount importance, since simple model solutions of less components can be misleading or insufficient to describe the separation performance of NF for the concerning process stream. Therefore, recently, the focus is given to the understanding of NF performance for the multicomponent systems as well as the application of mass transfer models to such systems.

NF has various application areas in diverse industrial fields, particularly for the separation of salts and small molecules due to its selective removal for ions and removal of organic matter above 200 g/mol molar mass. The market developed in many industries in the last 25 years and enlarges incessantly, especially in the chemical and pharmaceutical industries since 1990. This growth is attributed particularly to the increasing variety and stability of membranes and the realisation of NF advantages in terms of energy savings, costs and waste reductions along with the increased product qualities. Correspondingly, the research studies ascended as well. Based on the database from Web of Science, the number of publications in the fields of UF, RO and NF are presented in Figure 1.

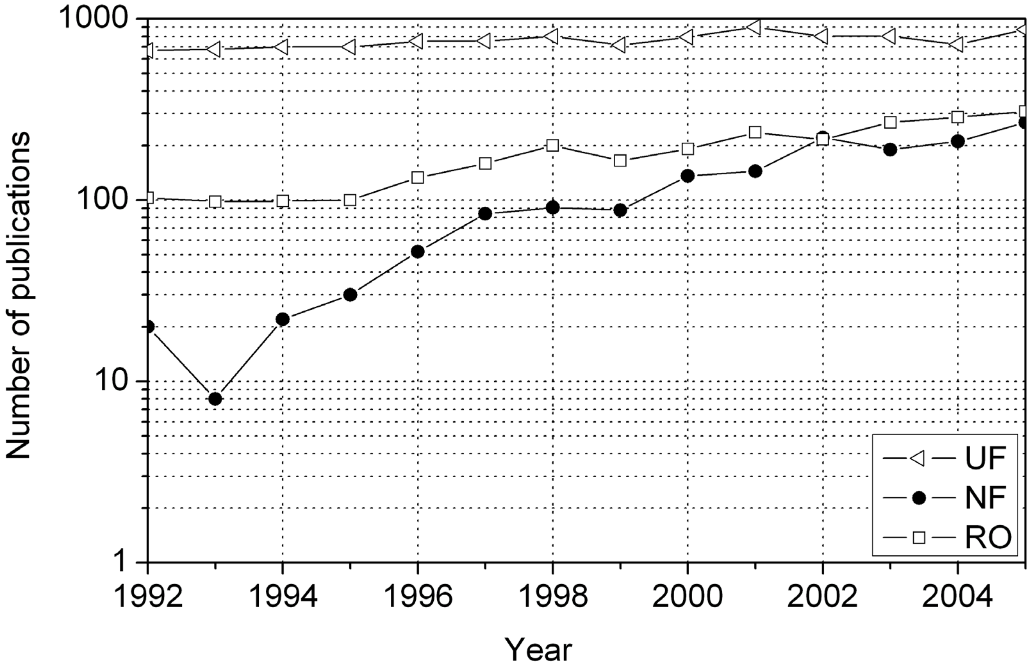

Figure 1: Number of publications of UF, NF and RO from 1992 to 2005 obtained from the Web of Science database [8] (modified from [5])

Figure 1 depicts the increasing research studies in nanofiltration field. In association with the developments in NF technology, there is an increasing need for process design and optimisation tools. However, missing of such tools and the specific behaviour of NF membranes to the regarded process streams give a high priority to the time intensive experiments. At present, for the design of NF processes, a number of experiments have to be performed. Consequently, such program tools can decrease time and costs invested in experimental studies. Accordingly, current research studies focus on the development of reliability of existing models and the generalisation of them for the industrial applications.

2. OBJECTIVES OF THE RESEARCH WORK

At present, membrane development, its characterisation and transport phenomena as well as system design studies are the main research areas of membrane technology [9]. Having considered the problematic introduced in NF field and general research areas in NF technology, this thesis work focuses on the characterisation of NF membranes and the investigations of their mass transport phenomenon through experimental and modelling studies.

In particular, this work aims at contributing to the understanding of NF performance for a wide spectrum of feed streams in consistent with its wide variety of applications. Hereby, NF separation behaviour for aqueous single salt solutions and their mixtures having combinations of mono- and divalent ions as well as aqueous solutions of uncharged components should be investigated. NF pre-treatment of seawater has been recognised in process intensification of the seawater desalination process. Consequently, research studies are still ongoing. Therefore, experimental investigations of NF seawater pre-treatment are to be conducted in order to determine the convenience of the considered NF membranes for this process. In this regard, a special attention is to be given to the salts abundant in seawater in the experiments of model salt solutions and their mixtures. To summarise, a systematic experimental program should be established covering simple to complex feed streams, finally seawater.

Another main goal is to describe and predict the NF membrane performance for the aqueous salt solutions and their mixtures up to seawater by means of a practical tool. Here, the practical tool addresses to a program, which allows straightforward modifications for the regarded feed stream. For this purpose, at first a suitable mass transport model based on the transport-mechanistic physical models, which are the most appropriate ones for NF, should be built up. Subsequently, a program in a suitable code should be developed, which:

- has a flexible model set up adoptable for multicomponent systems straightforwardly. Up to now, extending NF models for a feed stream with increasing number of components demanded considerable changes in the program code, which is almost equal to writing a new code.
- does not require writing a program code for the numerical integration of differential equations, a usual method in NF modelling, so that computational demand in terms of programming complexity decreases.
- necessitates limited number of experiments for the determination of membrane properties.
- serves as a membrane charge characterisation tool.

- enables the investigation of relations between membrane and operating parameters to membrane performance.
- should be a tool for the identification and understanding of transport mechanisms inside membranes. So far, many models ignored some transport mechanisms inside membrane for simplification. At this point, the program should enable to analyse the limits of such an assumption.
- predicts membrane performance. The limits of the program should be tested for the above mentioned feed streams.

Describing the transport phenomenon through NF membranes using physical models requires the knowledge of membrane characteristics, solute properties and operating conditions. Among them, data of membrane properties entails a characterisation study. Consequently, both of the themes, namely mass transport modelling and membrane characterisation are interconnected. In addition, membrane characterisation has of paramount importance in understanding of membrane separation performance. Therefore, it should be considered in detail in this work. Membrane charge effect on separation performance and its dependency on several factors are critical. In order to understand NF performance, an understanding of membrane charge behaviour is indispensable. In this respect, filtration experiments for various salts, at different concentrations and pH values, which are the most important parameters affecting membrane charge, are to be conducted. Another method for membrane charge investigations is electrokinetic measurements, which determine surface charge of a membrane. This method is to be applied for the investigations of the charge characters of the membranes. Membrane charges determined from the electrokinetic measurements should be compared quantitatively with the ones calculated from the simulations. Moreover, membrane charge character should be compared qualitatively with the ones asserted from the filtration experiments. In addition to membrane charge, various other parameters were given attention in terms of their contributions to the separation performance such as solute properties, solution pH and membrane characteristics (pore size, hydrophobicity, surface roughness). In order to study the steric effects as well as to determine the membrane pore sizes, which is a model parameter, experiments with solutions of uncharged components are of importance so that electrical effects can be excluded. Surface analysis using various methods should be executed to characterise the membrane morphologies and hydrophilic characters. Consequently, through comprehensive experiments and membrane characterisation studies, the relations of membrane performance to membrane characteristics, to operating conditions and to the medium properties and types are aimed to be investigated in detail.

3. STATE OF THE ART

This chapter will provide the imperative background information to fulfil the aims of this thesis work in association with the current state of NF technology.

It starts with introducing the commercially available NF membranes in market, their structures along with the most widely applied manufacturing methods. Afterwards, their current applications and the potential application fields in future will be acquainted. In this section, a number of publications regarding examples of some industrial applications and the ones under development will be presented. Herewith, the motivations to apply NF in industry with the associated NF characteristics will be apparent. In industry, the filtration tests of NF membranes for the related application purposes are inevitable since they show highly different performances in slightly different systems. In addition, there are no standard tests, which enable the comparison of membranes from different manufacturers. Furthermore, such tests are also essential in scientific researches to understand the separation behaviour of membranes and to meet the improvements for a better process and / or a better membrane. Therefore, the importance and the methods of filtration experiments as well as general characterisation methods will be highlighted. These will be pursued by the inherent NF characteristic, namely membrane charge. In this section, charge effects and other rejection mechanisms responsible for the retention of various components will be investigated. This will be followed by their mass transfer mechanisms inside membrane. Finally, the modelling of NF mass transport phenomenon is of concern. Herewith, different modelling approaches will be presented and compared in company of discussions regarding their relevancy to NF. In addition, some important publications contributing to NF mass transport modelling will be underscored.

3.1. Nanofiltration membranes and spiral wound module

Membrane manufacture and material type play an important role in the selective character of a membrane. In addition, membrane structure is another significant parameter for the regarding application in respect of chemical as well as the mechanical stabilities. Two structural categories can be given: symmetric and asymmetric membranes. The latter one is the mostly applied structure in the commercially available membranes and consists of two subgroups: integrally skinned asymmetric membranes and composite membranes.

Integrally skinned asymmetric membranes are produced by phase inversion technique, which is a controlled transformation of a polymer solution from a liquid into a solid state [5]. First, a homogenous polymer solution is cast on a film to a thickness between 0.2 to 0.5 mm then the volatile solvent part is evaporated, which leads to an enrichment of polymer on the surface [10]. Thereafter, it is sent to a non-solvent bath where the solvent is exchanged by non-solvent, through which the polymer is solidified. The polymer concentration in the solution, the solvent evaporation temperature and time, the type of the non-solvent and the speed of the solvent non-solvent exchange determine the structure and thus the selectivity of the membrane [5, 10].

A thin film composite (TFC) membrane consists of an ultrathin active layer on a porous support layer, e.g. polysulphone, which is further cast on a fabric such as polyester web. The separation occurs in the active layer, the thickness of which affects the permeate flow. The membrane has a good mechanical stability owing to the porous support layer, which shows a minimal resistance to the permeation and has a nonselective character. Skin and support layers of different materials in composite membranes enable a certain amount of tailoring of membrane function for specific applications [11]. Compared to CA, one of the drawbacks of composite polyamide (PA) membranes are low chlorine tolerance and high fouling (deposition of solutes on membrane surface or within its pores) tendency [11]. However, they are more stable in organic solvents than CA membranes [12] and not compacted under an applied pressure as CA would experience. The most widely used methods to produce composite membranes are dip coating and interfacial polymerisation. In dip coating, the support layer is dipped into a low concentration polymer solution. Afterwards, it is dried in an oven where solvent evaporates and a thin (up to $1\,\mu$m) active layer forms dependent on the concentration of the polymer solution [10]. Interfacial polymerisation, the currently widely applied method, produces ultrathin layers ($< 50\,$nm). In this technique, polymerisation occurs at the interface between two immiscible monomer solutions. First, support layer (for instance an UF membrane) is immersed in an aqueous hydrophilic monomer solution then dipped into a hydrophobic organic monomer. Consequently, two monomers react to form a thin layer, which is further exposed to a heat treatment for the shrinking and the cross-linking of the polymer with the support layer [10]. The advantage of this process is the possibility of varying monomer concentrations in solutions and thus adjusting the membrane selectivity. Consequently, tailoring of polymers for a particular process is a challenge for the development studies of high pH, solvent and oxidant stable membranes.

In this work, polymeric NF membranes, which are employed in almost the whole NF application spectrum, are of importance. One of the most successful TFC membranes is based on FT30 chemistry, which is an aromatic polyamide and is used in all Filmtec RO membranes and for NF 90. It has a chemically resistant and structurally strong polymer, which contains carboxylic acid and free amines at different levels. Another famous type, mixed aromatic / aliphatic PA (polypiperazineamide) was also initially developed by John Cadotte at Filmtec [5]. Meanwhile, polypiperazineamide membranes are the largest family of NF membranes [13]. Some other commercially prominent NF membranes are polysulphone, polyvinyl alcohols, perflouropolymers as well as alumina and silica [11]. Table 2 presents the characteristics of some polymeric NF membranes of technical interests. The data collected and presented in Table 2 are not enough for design purposes. However, it can be useful for salty water treatment or