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Υποβληθείσα στο
Τμήμα Χημικών Μηχανικών
tου
Πανεπιστημίου Πατρών

Υπό
ΑΝΑΣΤΑΣΟΠΟΥΛΟΥ ΙΩΑΝΝΗ

Για την απόκτηση του τίτλου του
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Υπό

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Membrane Bioreactors (MBRs) are well established preferably in industrial wastewater treatment and were introduced aiming at the coupling of membrane separation properties simultaneously with a biochemical reaction. The solid-liquid separation that is conventionally carried out in gravity-based clarifier is replaced by membrane filtration in a MBR system thus combining the strength of biological treatment processes and efficiency of membrane filtration. MBRs have been implemented across a number of industrial sectors such as the food and beverage sector, chemical, pharmaceutical and cosmetics, textile industry as well as in laundries, and have seen extensive take-up of this technology. However, the commonly employed MBRs combined to nanofiltration membrane systems have a high operating efficiency with respect to cost and quality for treatment of wastewater containing high biodegradable organic compounds.

The successful fusion of nanotechnology and membrane technology has been stated to lead to efficient next generation separation systems. A novel technology with regards to MBR and membrane systems for efficient wastewater treatment is proposed for the development of a new class of functional low fouling membranes showing enhanced properties such as high water flux and high rejection of organic matter with low molecular weight, by the subsequent inclusion of carbon nanotubes (CNTs) into porous polymeric membranes. The hollow CNT structure provides frictionless transport of water molecules, a feature that makes them suitable for the development of high flux separation systems. The type and quality of CNTs, the filling/host/substrate materials, the processing, and the fabrication methods used for the synthesis of CNT-membranes are the main factors influencing their performances.

Different approaches concerning the fabrication of CNT-membranes were studied in the context of the present thesis. The study of the experimental parameters influencing the efficient incorporation of CNTs in the thin selective layer of the ultra-filtration membrane with pore diameters of ~40 nm in order to transform it to a nano-filtration one with pores to be defined exclusively by the hollow CNT-internal
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diameters, aiming at the rejection of a variety of organic pollutants of industrial wastewaters was the main target of the thesis. Additionally, the immersion precipitation phase separation method was studied and employed for the preparation of porous membranes of tailored morphological features. Mixed matrix membranes prepared by the subsequent mixing of CNTs during the preparation processes were investigated as well, while, the incorporation of vertically aligned CNTs, grown on silicon substrates, to polymer matrix was also examined for the preparation of a CNT-membrane.

A basic principle of the CNT-membranes is the efficient binding of CNTs in the membranes to eliminate probable health risk associated with chances of product water getting contaminated with CNTs. Provided that health issues are important concerns to be addressed, the potent release of CNTs into water was investigated by the use of Surface Enhanced Raman Scattering (SERS) technique on the detection and quantification of multi-walled CNTs functionalized with pyridine moieties. In addition, given that extremely small amounts of substances can be detected and further quantified via SERS, the method applied on the investigation of the dye molecules Methylene blue and Remazol Brilliant Blue R, potent wastewater effluents.
Περίληψη

Οι βιοαντιδραστήρες μεμβρανών (Membrane Bioreactors: MBRs) αποτελούν μια εδραιωμένη τεχνολογία στην επεξεργασία βιομηχανικών αποβλήτων και εισήχθησαν στοχεύοντας στη σύζευξη των ιδιοτήτων διαχωρισμού των μεμβρανών ταυτόχρονα με την πραγματοποίηση βιοχημικών αντιδράσεων. Ο συμβατικός διαχωρισμός μεταξύ στερεού-υγρού σε λύματα που συμβατικά διεξάγεται με διεργασίες διαύγασης βασισμένες στη βαρύτητα, αντικαθίσταται από το διαχωρισμό με χρήση μεμβρανών σε ένα σύστημα MBR, συνδυάζοντας έτσι την αποδοτικότητα της βιολογικής επεξεργασίας με την αποτελεσματικότητα του διαχωρισμού με χρήση μεμβρανών. Η τεχνολογία MBR εφαρμόζεται σε διάφορους βιομηχανικούς τομείς, όπως στον τομέα των τροφίμων και ποτών, χημικών, φαρμακευτικών, καλλυντικών, καθώς και στη βιομηχανία κλωστοϋφαντουργίας. Ωστόσο, οι συμβατικοί MBRs όταν συνοδεύονται με συστήματα μεμβρανών νανο-διήθησης, παρουσιάζουν χαμηλή απόδοση σε συνάρτηση με το κόστος και την ποιότητα του επεξεργασμένου νερού που παράγεται από λύματα που περιέχουν υψηλά βιοποικιλομόρφιμες οργανικές ουσίες.

Η επιτυχής συνδυασμός της νανοτεχνολογίας με την τεχνολογία μεμβρανών αναμένεται να οδηγήσει σε καινοτόμα συστήματα διαχωρισμού. Αναφορικά με την τεχνολογία MBR με χρήση μεμβρανών για την αποτελεσματική επεξεργασία λυμάτων, έχει προταθεί η ανάπτυξη νέας κατηγορίας λειτουργικών μεμβρανών χαμηλής ρύπανσης που θα παρουσιάζουν ενισχυμένες ιδιότητες, όπως η υψηλή διαπερατότητα του νερού και ταυτόχρονα υψηλό ποσοστό απόρριψης οργανικών ενώσεων χαμηλών μοριακών βάρων, με την επακόλουθη ενσωμάτωση νανοσωλήνων άνθρακα (N.A) στο ενεργό πορώδες πολυμερικό μεμβράνη. Τα λεία, χημικώς αδρανή, υδροφόβη γραφικά τοιχώματα των N.A σε συνδυασμό με τις μικρές εσωτερικές διαμέτρους τους, της τάξης της νανο-κλίμακας, μέσω των οποίων λαμβάνουν χώρα φαινόμενα διάχυσης, αναμένεται να παράσχουν ταυτία ροή του νερού και ταυτόχρονα υψηλή εκλεκτικότητα στη διαπερατότητα μορίων με βάση το μεγεθός τους, χαρακτηριστικά που τους καθιστά κατάλληλους για την ανάπτυξη αποδοτικών συστημάτων διαχωρισμού. Το είδος και η ποιότητα των N.A, τα υλικά πλήρωσης/υποστρώματα υποδοχής τους, η επεξεργασία καθώς και οι μέθοδοι παρασκευής που
θα χρησιμοποιηθούν για τη σύνθεση μεμβρανών με Ν.Α, είναι οι κύριοι παράγοντες που θα καθορίσουν τις επιδόσεις τους.

Στο πλαίσιο της παρούσας διατριβής μελετήθηκαν διαφορετικές προσεγγίσεις για την παρασκευή μεμβρανών με χρήση Ν.Α. Η μελέτη των πειραματικών παραμέτρων που καθορίζουν την αποτελεσματική ενσωμάτωση των Ν.Α στη λεπτή εκλεκτική στιβάδα μεμβρανών υπερδιήθησης ώστε να μετατραπούν σε μεμβράνες νανο-διήθησης, με τις εσωτερικές διαμέτρους των Ν.Α να αποτελούν αποκλειστικά το ενεργό εκλεκτικό πορώδες των μεμβρανών, στοχεύοντας στην δυνατότητα απόρριψης μιας ποικιλίας οργανικών ρύπων παρόντων σε βιομηχανικά απόβλητα, ήταν ο κύριος στόχος της διατριβής. Επιπρόσθετα, η μέθοδος διαχωρισμού φάσεων μελετήθηκε και χρησιμοποιήθηκε για την παρασκευή πορωδών μεμβρανών με καθορισμένα μορφολογικά χαρακτηριστικά. Επιπλέον, μελετήθηκε τον έλεγχο της αποτελεσματικότητας της διαδικασίας ενσωμάτωσης των Ν.Α, με την επακόλουθη ανάμιξη Ν.Α κατά τις διεργασίες παρασκευής των μεμβρανών, ενώ εξετάστηκε και τον έλεγχο της ενσωμάτωσης Ν.Α, που έχουν αναπτυχθεί κάθετα σε υποστρώματα πυριτίου, σε πολυμερική μήτρα για την παρασκευή μεμβράνης από Ν.Α.

Βασική προϋπόθεση για τη χρήση μιας μεμβράνης με Ν.Α είναι η ισχυρή πρόσδεση των Ν.Α στους πόρους της μεμβράνης ώστε να αποκλειστεί οποιαδήποτε πιθανότητα αποδέσμευσής τους και επιμόλυνσης του παραγόμενου νερού. Με στόχο τον έλεγχο της αποτελεσματικότητας της διαδικασίας ενσωμάτωσης των Ν.Α στους πόρους των πολυμερικών μεμβρανών, επιστρατεύτηκε η τεχνική της Επιφανειακής Ενίσχυσης της Σκέδασης Raman (Surface Enhanced Raman Scattering:SERS) στην ανίχνευση και ποσοτικοποίηση Ν.Α τροποποιημένων με ομάδες πυριδίνης σε υδατικά διαλύματα. Επιπλέον, δεδομένου ότι εξαιρετικά χαμηλές συγκεντρώσεις χημικών ουσιών σε υδατικά διαλύματα είναι δυνατό να ανιχνευτούν και να ποσοτικοποιηθούν με τη χρήση αυτής της δυναμικής τεχνικής, πραγματοποιήθηκαν μετρήσεις SERS σε υδατικά διαλύματα εξαιρετικά χαμηλών συγκεντρώσεων της οργανικής ένωσης Methylene Blue, εν δυνάμει ρύπου σε απόβλητα βιομηχανικών κλωστοϋφαντουργικών. Επίσης, πραγματοποιήθηκαν μετρήσεις SERS σε υδατικά διαλύματα της οργανικής ένωσης Remazol Brilliant Blue R με τη χρήση διαφορετικών παραγόντων συσσωμάτωσης.
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Introduction

1.1 GENERAL INTRODUCTION - WATER SCARCITY

Water is the substance more necessary to our existence than any other. In its purest form, it's odorless, nearly colorless and tasteless. Uniquely, it appears in nature in all three common states of matter, as a solid (ice), a liquid and a gas (water vapor). It's in our bodies, the food we eat and the beverages we drink. We use it to clean ourselves, our clothes, our dishes, our cars and everything else around us. We can travel on it or jump in it to cool off on hot summer days. Many of the products that we use every day contain it or were manufactured using it. All forms of life need it, and if they don't get enough of it, they die. Political disputes have centered on it. In some places, it's treasured and incredibly difficult to get. In others, it is incredibly easy to get and then squandered.¹

Water covers about 70% of the earth, for a total of approximately 1,386 billion km³. Although over two-thirds of the earth is covered in water, 97% of it, is salt water that ocean holds. The remaining 3% is freshwater found in glaciers and ice, below the ground, or in rivers and lakes (Fig. 1.1). Of the 3% of the water that is not in the ocean, about 69% is locked up in glaciers and icecaps. The 90% of that frozen water is in Antarctica, and about 9% covers Greenland. Of the remaining fresh water, 30% of it is groundwater, captured below our feet. About 0.3% is found in rivers and lakes.
This means that of the world’s small supply of this precious resource, less than 1% is available for human consumption (Fig. 1.2). Consequently, the demand for freshwater is growing twice as fast as the global population.

Figure 1.1 - Broad breakdown of Earth’s water.

However, freshwater is not evenly distributed throughout the world. More than half of the world’s water supply is contained in just nine countries: the United States, Canada, Colombia, Brazil, the Democratic Republic of Congo, Russia, India, China and Indonesia. Urban areas, obviously, have a greater need for water beyond the basics for drinking and sanitation but overpopulation in undeveloped countries means that many people don’t even get the basics.

Figure 1.2 - Detailed distribution of the water on Earth. (Note: Numbers are rounded, so percent summations may not add to 100).
Outrageous exploitation of our finite fresh water resources has already impacted both eco-systems and global water reserves that highly depend on rainfall and geological hydrodynamics to regenerate. Entire parts of the world are drawing down their water reserves because of excessive extraction of the ground resources or collection from the rivers. Freshwater is vital for our societies either for irrigation in agriculture, cooling, cleaning or as a reactive media in industry and of course for health purposes.5

The United Nations estimates that human consumption of water increased six fold in the 20th century, while the population only tripled. As if freshwater isn’t scarce enough, much of it is wasted due to aging infrastructure. Worldwide, governments and industry alike increasingly recognize that improving the water infrastructure will be critical to solving the global water crisis.6 But not all countries can afford the infrastructure necessary to clean and transport it.

For example, most people in China’s cities suffer from water shortages since most of China’s available water is polluted while, countries in the Middle East use the least amount of water per person because there are so few natural sources of freshwater.

Figure 1.3 - The reality of global water infrastructure: Percentage of population with access to safe drinking water. (Percentage of population with a supply of at least 20 liters of safe drinking water per day within 1 km from their place or residence). (Data derived from United Nations Development Programme, Human development index 3008).
Conclusively, more than a billion people, about 17 percent of the world’s population, don’t have access to clean water. There are several governmental and nongovernmental organizations, including UNICEF and Water Aid, working to help poor communities in Asia and Africa obtain sustainable supplies of drinking water and sanitation facilities.\(^7\)

But also European countries already partially suffer from insufficient clean water supply. Particularly, southern countries like Portugal, Spain, Malta, southern parts of Italy, Greece and Cyprus will be affected the most due to increasing temperature and dryness caused by climate changes. **The low quantity of freshwater in these countries for industrial, agricultural and municipal usage has to be well preserved by efficient, sustainable and cost-effective technologies.** Water contaminated from industry and agriculture with heavy metal ions, pesticides, organic compounds, endocrine disruptive compounds, nutrients (phosphates, nitrates, nitrites) has to be efficiently treated to protect human intoxication. Furthermore, incidental sludge of industrial wastewater treatment facilities is commonly highly contaminated with toxic compounds.

**Figure 1.4** - Changes in the global water market during the period 2007-2025. *(Data derived from Global Water Intelligence 2007 [Global Water Market 2008]*)

As water is such fundamental part of life, water business came to be administered by governments in various countries around the world as it is essential to ensure a safe and stable supply of water to all people.
Thereafter, the need of advanced technologies for water treatment results huge. Efficient wastewater treatment and recycling of the industrial, municipal and agriculture wastewater may at least reduce the overall exploitation of the remaining freshwater. Membrane Bioreactor (MBR) technology is regarded as a key element of advanced wastewater reclamation and reuse schemes, and can considerably contribute to sustainable water management. MBRs are used for wastewater treatment and reuse in municipal, agricultural and a variety of industrial sectors in Europe and Middle East and North Africa countries.

![Figure 1.5 - Water and wastewater treatment: the industrial and municipal market (2013). (Data derived from Global Water Market 2014).](image)

### 1.2 MEMBRANE BIOREACTOR TECHNOLOGY ON WASTEWATER TREATMENT

With respect to wastewater treatment and subsequently to filtration of organic compounds, Membrane Bioreactors are well established preferably in industrial wastewater treatment. MBRs were introduced aiming at the coupling of membrane separation properties simultaneously with a biochemical reaction. The solid-liquid separation that is conventionally carried out in gravity-based clarifier is replaced by membrane filtration in a MBR system thus combining the strength of biological treatment processes and efficiency of membrane filtration. The additional step of a separation process
within the reaction process was placed in order to remove an endoprodut and thus shift the reaction equilibrium in the direction of the product side. In a nutshell, the biological unit is responsible for the biodegradation of the waste compounds and the membrane module for the physical separation of the treated water from the mixed liquor.

Polymeric materials are extensively used within the MBR systems as active membranes and this is justified since there is a high availability of different chemistries combined to low costs compared to inorganic, ceramic or metallic materials. The pore diameters of the commonly used microfiltration (MF) or ultrafiltration (UF) membranes, is in the range between 0.01 to 0.1 μm, so that particulates and bacteria can be kept out of permeate, and the membrane system replaces the traditional gravity sedimentation unit (clarifier) in the biological sludge process.

MBRs have been implemented across a number of industrial sectors such as the food and beverage sector, chemical, pharmaceutical and cosmetics, textile industry as well as in laundries, and have seen extensive take-up of this technology. By 2006, around 100 municipal full-scale plants (>500 p.e.*) and around 300 industrial large scale plants were in operation in Europe. Now, MBRs have been set up in over 200 countries and global market growth rates of up to 15% are regularly reported in various market analyses (BCC 2008, Srivivasan 2007, Markets and Markets 2013). The market value for the membrane equipment portion of MBR facilities was estimated at $0.75 billion in 2011, with around 40% of the revenue going to the Asia Pacific region. Confidence in the process still appears to be increasing as the number and size of the reference installations grows further, with a number of plants over 100 million liters per day (MLD) in capacity now having being installed. The total installed capacity of MBRs in 2017 is expected to exceed 12,000 MLD.

*Population equivalent or unit per capita loading, (PE), in waste-water treatment is the number expressing the ratio of the sum of the pollution load produced during 24 hours by industrial facilities and services to the individual pollution load in household sewage produced by one person in the same time. For practical calculations, it is assumed that one unit equals to 54 grams of BOD per 24 hours.
1.2.1 Bottlenecks of conventional MBRs

MBRs are increasingly becoming the technology of choice for water and wastewater treatment applications where high quality treated water is required, or where space is limited. However, MBR technology is not always the best wastewater treatment solution. For a conventional MBR system, which is commonly combined with a MF or an UF membrane, several technical barriers exist which reduce the overall robustness mainly related to membrane fouling.\(^{12,13}\)

Concerning MBR-microfiltration/ultrafiltration systems, besides fouling effects, due to their large molecular-weight cut-off (MWCO)*, they do not display a barrier effect to low-molecular weight organic micropollutants. However, such micropollutants which are produced world-wide on a 100,000 ton scale have generally become a matter of great concern in wastewater treatment.\(^{14,15}\) There are different categories of micropollutants such as endocrine disrupting compound (EDCs), pharmaceutical active compounds and pesticides. These substances exhibit an adverse health effect to humans and can be accumulated in the fatty tissue. For example, antibiotics and their metabolites can significantly increase antibiotic resistance in the population, and EDCs can disrupt the body’s normal functions. The removal efficiency of a variety of micropollutants using conventional bioreactors and MBR has been reported in many publications.\(^{16}\)

MBR can in some cases enhance the elimination of micropollutants over the conventional activated sludge process. This can be attributed to the high sludge age of the biomass and high removal due to adsorption onto the sludge flocs. However, since the large membrane pore size has not the ability to retain the low molecular weight substances, MBR cannot be regarded as an intrinsically safe treatment process. Reemtsma et al.\(^{17}\) reported no indication that MBR will improve the removal of polar poorly biodegradable organic pollutants in tannery wastewater.

* MWCO is defined as the lowest molecular weight (in Daltons) at which greater than 90% of a solute with a known molecular weight is retained by the membrane. Dextran, polyethylene glycol, and proteins of various molecular weights are commonly used to rate the MWCO of membranes.
Radjenovic et al.\textsuperscript{18} reported that the drug carbamazepine turned out to pass through conventional bioreactor and MBR. Schoeberl et al.\textsuperscript{19} reported on the basis of experimental data that the MBR is basically an effective system for treating industrial wastewater such as textile wastewater compared to the conventional aerobic biological treatment. However, colour components are still present in the MBR effluent to an extent unacceptable for direct reuse.\textsuperscript{20} Therefore, an additional post-treatment process such as nanofiltration (NF) has been recommended.\textsuperscript{19}

\textbf{Figure 1.6} – Conventional membrane bioreactor process combined to nanofiltration.

Unlike MF and UF membranes, **NF membranes** due to their smaller MWCO, have the ability to retain also low-molecular weight species. To date, NF membranes are used typically in ground and surface water to produce drinking water, for reverse osmosis pre-treatment and wastewater treatment.\textsuperscript{20} NF can reject micropollutants to a high degree (>90\%) and it is an efficient technology for decontamination and recycling of wastewater generated in many industries.\textsuperscript{21}

\textbf{Figure 1.7} – 2-step treatment process and threats of conventional MBR-NF systems.
Tang and Chen\textsuperscript{22} reported that by using NF the colourity of textile wastewater can be removed >98\% and a high quality of reuse water could be recovered. In order to improve water quality, nanofiltration is in some cases applied downstream to MBR. However, this combination has the following drawbacks:

- The subsequent combination of these two steps requires additional technologies resulting in additional costs and maintenance efforts in order to achieve high quality recycling water.
- Relatively high capital and operating cost due to required high-pressure pump. NF is energy consuming since it needs elevated pressure (around 10 bar).
- Recycling and/or treatment of toxic NF concentrate are laborious and expensive.
- The efficiency within MBR+NF depends on the composition of the under treatment water. Substances creating stress for bacteria reduce the organic compound filtering ability. The building up of a filter cake at the MBR and/or NF/RO membranes furthermore reduces the overall performance of the system.\textsuperscript{23}
- Last but not least, the high concentration of salts may decrease the biodegradation of the sludge resulting in toxic disposal.

With increased tendency to fouling, the MBR filtration performance inevitably decreases with filtration time. Membrane fouling is the most serious problem affecting system performance as it leads to a significant increase in hydraulic resistance, resulting in a decline of permeates flux. Typical flux rates range around 20 L/m\textsuperscript{2} hour. Also, an increase of transmembrane pressure (TMP) occurs under constant flux conditions.

As an overall result, the commonly employed MBR-NF systems have a high operating efficiency with respect to cost and quality for treatment of wastewater containing high biodegradable organic compounds.

However, they are inefficient with respect to water containing a high amount of stress-inducing substances, high colourity and low biodegradable organic compounds. Thereafter, these systems can only be applied to wastewater with high biodegradable organic pollutants and can be considered as 1-for-1 only solution.
1.3 BioNexGen PROJECT APPROACH

A novel technology with regards to MBR and membrane systems for efficient wastewater treatment has been proposed by BioNexGen (Next Generation Bioreactor systems) project. The project was designed to develop a new generation of MBR-NF hybrid process in order to collect high water quality in a single step by a MBR-NF reactor. (Fig. 1.8) This reactor would be equipped with a new class of functional low fouling membranes showing enhanced properties such as high water flux and high rejection of organic matter with low molecular weight, while allowing high salt passage in order to avoid concentrating salts in the MBR.

![BioNexGen approach](image)

**Figure 1.8** – BioNexGen 1-step MBR process approach.

The accomplishment of such membranes would guarantee the incorporation of Carbon Nanotubes (CNT) in thin commercial ultrafiltration membranes. The ambitious general idea was the embedment of CNT in the pores of a commercial UF membrane, in a way that the CNT hollow cavities to substitute the pores of the UF membrane transforming it to a nanofiltration one. Tailor-made functionalized nanoparticles would eventually be added on an additional surface antimicrobial coating. An assistant schematic representation of the main experimental concept of the project is illustrated in Figure 1.9.
The selection of CNT to be employed on the modification of pristine membranes was based on their special features concerning mass transport through CNT hollow cavities and they are discussed in details in the 3rd chapter of this thesis.

Eventually, the significant advances expected of the new MBR-NF approach are summarized as:

- Highly robust process of wastewater without the necessity of performing additional antifouling or cleaning and/or replacement steps of the membranes, resulting in an increase of operational time of 20-30-% and decreased operating costs of 15-20%.
- Chemically and physically tailoring of the new membranes would result in **highly fouling resistant** properties of the MBR-NF reactor.
- Specifically functionalized membrane pores would allow a **high-flux** at low air requirement and thus a high performance of this new type of MBR.
- **Less stress for bacteria** would furthermore increase the bio-degradation capabilities of the new MBR technology.
- **No need for cost-intensive pressure pumps** and other equipment, resulting in lower energy consumption and lower operating cost.
- **Easy to operate and user-friendly** due to the standardized and modular properties of the new membranes.
Figure 1.10 – Schematic 1-step process treatment of BioNexGen MBR-NF approach.

In Table 1.1 a comparison between the performance parameters of a conventional MBR system and of the ones expected for the MBR-BioNexGen approach, is presented. The long term aim of these new membranes would be their employment in MBR systems for separation processes of industrial (textile, cosmetic and olive mill) wastewaters containing organic compounds - micro-pollutants of low molecular weight from ~200 to 1000 Daltons (Da).

Table 1.1 - The expected performance of the new MBR-NF versus the conventional MBR system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Current average value</th>
<th>Expected MBR-NF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>15-20 L/m²·h</td>
<td>25 L/m²·h</td>
</tr>
<tr>
<td>Specific air requirement</td>
<td>0.3-0.9 Nm³/m²·h</td>
<td>0.2 Nm³/m²·h</td>
</tr>
<tr>
<td>Overall COD removal rate</td>
<td>90-97 %</td>
<td>&gt;98 %</td>
</tr>
<tr>
<td>Safety for low-molecular weight pollutants removal</td>
<td>Not intrinsically safe due to high MWCO ≥100 kDalton</td>
<td>Intrinsically safe due to low MWCO ca. 250-300 Dalton</td>
</tr>
<tr>
<td>Maintenance cleaning</td>
<td>1 per week</td>
<td>None*</td>
</tr>
<tr>
<td>Recovery cleaning</td>
<td>1-5 per week</td>
<td>1 per week</td>
</tr>
</tbody>
</table>

*Not necessary due to antimicrobial properties of membranes.

1.4 Synergasia-MEKKA PROJECT APPROACH

A lateral approach on the development of functional novel membranes for efficient wastewater treatment processes has been proposed by the project Synergasia-MEKKA (Development of new generation polymeric
membranes with vertical aligned Carbon nanotubes for wastewater treatment and water recycling). The project targeted on the development of porous membranes by the incorporation of vertically aligned CNT in a polymeric matrix aiming at the efficient treatment of industrial organic wastewater. Further details concerning Synergasia-MEKKA project theoretical background and experimental approaches are discussed in chapters 3 and 5.

**1.5 SCOPE & OUTLINE OF THE THESIS**

The scope of this thesis that was implemented under the aforementioned projects BioNexGen and Synergasia-MEKKA covers a variety of research fields in the context of application of Carbon nanotubes in membrane science and technology. The general aim was to engineer membranes for separation processes based on Carbon Nanotubes for their potential application in Membrane Bioreactors as an alternative technology for the nano-filtration processes during industrial, municipal and agricultural wastewater treatment. The main focus of this work was the study of the parameters influencing the efficient incorporation of CNT into porous polymeric membranes, the fabrication of potently advanced composite membranes following different preparation approaches, as well as the use of advanced spectroscopic techniques as the Surface Enhanced Raman Scattering (SERS) in the efficiency control of the fabricated CNT membranes.

**Chapter 2**

This chapter constitutes an introduction to membrane technology defining the term “membrane” in terms of chemical engineering of the separation processes. Basic aspects and the classification of synthetic membranes are given. Thereafter, a description of the asymmetric porous membranes is presented as well as the classification of porous membranes and membrane processes with regards to the pore sizes and the components to be separated. Basic aspects on preparation methods of porous asymmetric membranes are discussed focusing on the diffusion-induced phase-separation process.
Chapter 3

This section, entitled “From carbon to nanotubes...to carbon nanotube membranes”, consists of an overview of the element Carbon and carbon materials encompassing carbon allotrope formations, giving main emphasis to carbon nanotubes from historical details of their first synthesis and observation, the forms they appear in, their synthesis techniques, their properties and applications, to their recent employment in membranes for water purification and desalination. A comprehensive review is presented concerning the different approaches scientists have followed, to exploit the mass transport properties of CNT’ hollow cavities in the fabrication of advanced separation filters. The CNT special features as well as the reasons CNT are potent to consist the ideal solution on water purification technologies are presented. Special pretreatments and functionalization of CNT needed in order to be applied on membrane technology are discussed, while all the concerns and barriers leaving CNT-membranes in a lab-scale level until today are presented.

Chapter 4

In the context of BioNexGen project, all the parameters addressed for the transform of a commercial ultra-filtration polymeric membrane to a nano-filtration one by the subsequent embedment of CNTs in the thin selective layer bearing pores in the scale of nanometers are described. The characterization and treatment of both the under study membrane, and the CNTs used for the CNT-infiltration studies are presented as well. Representative efforts on the embedment of CNTs in the membrane pores using filtration methods and barriers had to be transcended are described in detail. Experimental conditions and protocols extracted for the efficient incorporation of appropriate CNTs in the thin selective layer of the polymeric membrane are discussed and conclusions over this effort are presented.

Chapter 5

In the present chapter the fabrication of tailor-made polymeric ultra-filtration membranes and the subsequent incorporation of CNTs by filtration methods are presented. The morphological characterization and the performance in terms of pure water permeability and
determination of molecular weight cut-off of the modified membranes are shown. Further treatments for the filling of empty spaces between CNTs and their stabilization in the membrane pores are presented. Different approaches concerning CNT-membranes are studied as well. Polymeric solutions mixed with dispersed CNTs for the preparation of mixed matrix CNT-membranes are used and their morphological features as well as their performance in terms of pure water flux and rejection capacity with regards to industrial wastewaters in the context of Synergasia-MEKKA project are presented. In addition, the use of a polymeric matrix to serve as host for the incorporation of vertically aligned CNTs and the subsequent fabrication of a CNT-membrane in the same context is presented.

Chapter 6

The basic principles of Raman Scattering are presented in this chapter. The classical and quantum descriptions of the Raman scattering are given and an introduction to Surface Enhanced Raman Scattering (SERS) phenomenon is presented. The factors contributing to the SERS effect are described as well as factors influencing the SERS enhancement are presented. Additionally, the preparation of metallic substrates, silver colloids, needed for the stimulation of SERS effect is presented and further treatment as aggregation by the use of salts are discussed.

Chapter 7

In this chapter the implementation of SERS for the efficiency control of CNT-infiltrated membranes is presented. SERS used a powerful tool to detect the potential presence of CNTs in the permeates after the CNT-embedment into the membrane pores. Functionalized MWCNTs with pyridine moieties were used for the indirect investigation of CNTs in aqueous suspensions that finally led to direct detection and quantification of CNTs in the aqueous suspensions.

Chapter 8

The use of SERS technique on the detection and quantification of dye molecules, apparent effluents in wastewaters of textile industries is
described. The dye molecule Methylene Blue was qualified using SERS in aqueous solutions at extremely low concentration level pointing out the efficiency of SERS in the quantification of organic molecules of low molecular weight in aqueous solutions at concentration level that other conventional techniques cannot respond to. Additionally, the use of different aggregation agents for silver colloids on the study of the Remazol Brilliant Blue R dye molecule with SERS is presented and observations on the aggregating agents’ effect on SERS signals are given.

Chapter 9

In this chapter, the conclusions of the studies presented in the present thesis are gathered, and aspects and ideas for potential future plans and studies are referred.

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11 www.thembrsite.com
Chapter 1

**Introduction**


Chapter 2  Basic aspects on polymeric membranes

Introduction to membrane technology

The concept of a membrane first discovered in the 18th century by Nollet who discovered that a pig’s bladder passes preferentially ethanol when it was brought in contact on one side with a water-ethanol mixture and on the other side with pure water. Nowadays, “membrane” is defined as a selective barrier that allows mass transport under the influence of a driving force (e.g. concentration, pressure). A characteristic property of a membrane is it’s permselectivity, which is determined by differences in the transport rates of various components in the membrane matrix. The permeability of a membrane is a measure of the rate at which a given component is transported through the membrane under specific conditions of concentration, temperature, pressure and/or electric field. The transport rate of a component through a membrane is determined by the structure of the membrane, by the size of the permeating component, by the chemical nature and the electrical charge of the membrane material and permeating components, and by the driving force, i.e. concentration, pressure or electrical potential gradient cross the membrane.

In separation processes technology, where membranes are used extensively, the influent of a membrane is known as “feed-stream/solution”, what passes through the membrane is known as “permeate”, and finally the volume containing the retained constituents is the “retentate” or “concentrate”. Generally, membranes can be classified into synthetic and biological membranes. The
selectivity capacity of a membrane depends on its pore diameters. Thus, they are further classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis membranes (RO).\textsuperscript{1,2,3}

\section*{2.1 BASIC ASPECTS ON SYNTHETIC MEMBRANES}

The commonly used materials for the fabrication of synthetic membranes include polymers, ceramics, glass, metals or liquids. And as the variety of the used materials is large, so is the variety of the physical structures they form. Hence, they are further classified into symmetric, where the structure is uniform over the entire cross section of the membrane, or asymmetric, where the structure varies over the cross section of the membrane. Regarding their conformation, they are encountered as flat sheets, tubular, or hollow fibers. The schematic drawing of \textbf{Figure 2.1} illustrates the materials, morphology and configuration of relevant synthetic membranes.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure21.png}
\caption{Schematic drawing illustrating the materials, morphology and configuration of synthetic membranes.}
\end{figure}
2.1.1 Asymmetric porous membranes

The asymmetric membranes not only exhibit variations concerning their structure, but also on transport properties over their cross area. They commonly consist of a “skin layer” of thickness ranging from 0.1 to 1 μm formed on a wide-porous substructure of thickness from 100 to 200 μm. The pore diameters increase gradually from the top to the bottom of the membrane cross section by a factor 10-1000. The actual selective barrier of this membrane type is what is called “skin layer” which in all respects determines the separation properties of the membrane and depends as much on the material made of, as on the skin-layer-pore size. The thickness of the skin layer determines the flux properties while the porous sublayer serves only as a support having hardly any effect on the membrane separation properties.

**Figure 2.2** – Schematic structure formation of typical asymmetric membranes.

Given the incomparable properties of the asymmetric membranes with regards to high fluxes and good mechanical stability, they are largely employed in pressure-driven membrane processes such as reverse osmosis, ultrafiltration, and vapor or gas separation. In these processes, the separation of the components is accomplished by a filtering mechanism with the determining parameters to be the pore diameters and the particle sizes. Accordingly, the macromolecular size of the species to be separated plays an important role in determining the pore size of the membrane to be utilized and the related membrane process. Porous membranes with average pore diameters larger than 50 nm are classified as macroporous; those with average pore diameters in the intermediate range between 2 and 50 nm are classified as mesoporous; and membranes with average pore
diameters between 0.1 and 2 nm are classified as microporous. Dense membranes have no individual permanent pores, but the separation occurs through fluctuating free volumes. In Figure 2.3 is illustrated the classification of membranes and membrane processes related to their separation capacity.

*Figure 2.3* – Schematic representation of the classification of membranes and membrane processes with regards to the pore sizes and the under separation components.

**2.2 PREPARATION OF POLYMERIC POROUS ASYMMETRIC MEMBRANES**

The mechanical properties of a membrane are determined primarily by the proper choice of the base material, namely the polymer. The molecular weight, chain flexibility and chain interaction of the selected polymer are factors influencing the chemical and thermal stability, adsorption capacity and wettabillity of the fabricated membranes. However, stability and processability are two contrasting concepts and as the stability of a polymer increases, it generally becomes more difficult to process.
A common and widely applied technique used for the preparation of asymmetric porous membranes from polymers, mobilizes the phase inversion process, which leads to gradient structure membrane morphology, consisted of a skin layer and a wide-porous support structure made of the same material. This technique is based on the inversion of homogeneous liquid mixtures into heterogeneous solid phases. These membranes were first developed by Loeb and Sourirajan\textsuperscript{5} in 1962 using cellulose acetate, for membranes to be used in water demineralization.

2.2.1 The phase inversion technique

Soon after the first observation of the phase inversion phenomenon in the preparation of cellulose acetate membranes, it became apparent that it is feasible to fabricate asymmetric membranes with skin-type formation, from almost any polymer that is soluble at a certain temperature in an appropriate solvent or solvent mixture and can be precipitated as a continuous solid phase by either changing the temperature of the composition or the composition of the system by the following general procedures:\textsuperscript{4,6,7}

- cooling of a homogeneous polymer solution, which separates at a certain temperature in two phases;
- evaporation of a volatile solvent from a homogeneous polymer solution with two or more solvents of different dissolution capacity; and
- addition of a nonsolvent or nonsolvent mixture to a homogeneous polymer solution.

All the above procedures result in the formation of a two-phase system. The liquid phase forming the membrane pores and the solid phase that constitutes the membrane structure. The only thermodynamic presumption for all the three membrane preparation procedures is that the system has a miscibility gap over a defined concentration and temperature range. When the temperature change is the causing factor of a phase separation, it is called temperature induced phase-separation. This method is based on the decreasing quality of the solvent when temperature decreases. After the separation process, the solvent is removed by extraction, evaporation or freeze-drying. In the second case, during the solvent evaporation the polymer solubility decreases, resulting in phase separation. When
the separation causing factor of phase separation is the addition of a nonsolvent into a homogeneous polymer solution the phenomenon is known as diffusion-induced phase-separation or immersion precipitation phase-separation and is based on the exchange of polymer solvent for nonsolvent.\textsuperscript{8,4} The combination of these basic processes is largely used for the fabrication of tailor-made membranes and are widely implemented by membrane companies.

Table 2.1 – Polymers used for commercial membranes fabricated by phase inversion and their application on membrane processes.\textsuperscript{4}

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Membrane process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate</td>
<td>EP, MF, UF, RO</td>
</tr>
<tr>
<td>Cellulose esters (mixed)</td>
<td>MF, D</td>
</tr>
<tr>
<td>Polyaclonytril (PAN)</td>
<td>UF</td>
</tr>
<tr>
<td>Polyamide (aromatic, aliphatic)</td>
<td>MF, UF, RO, MC</td>
</tr>
<tr>
<td>Polyimide</td>
<td>UF, RO, GS</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>MF, MD, MC</td>
</tr>
<tr>
<td>Polyesersulfone</td>
<td>UF, MF, GS, D</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>UF, MF, GS, D</td>
</tr>
<tr>
<td>Sulfonated polysulfone</td>
<td>UF, RO, NF</td>
</tr>
<tr>
<td>Polvinyldene fluoride</td>
<td>UF</td>
</tr>
</tbody>
</table>

\textit{EP}: electrophoresis; \textit{MF}: microfiltration; \textit{UF}: ultrafiltration; \textit{RO}: reverse osmosis; \textit{GS}: gas separation; \textit{NF}: nanofiltration; \textit{D}: dialysis; \textit{MD}: membrane distillation; \textit{MC}: membrane contactor.

2.2.2 Diffusion-induced/immersion precipitation phase-separation process

As aforementioned, during the phase separation process, a homogeneous polymer solution is transformed into a two-phase system, \textit{i.e.}, a polymer-rich solid phase which forms the membrane structure and a polymer-poor (solvent-rich) liquid phase which forms the liquid-filled membrane pores.\textsuperscript{6} The diffusion-induced phase-separation process consists of three steps:\textsuperscript{4}

- a polymer is dissolved in an appropriate solvent to form a homogeneous polymeric solution,
- the solution is casted into a film with thickness of \(\sim 100-500\) \(\mu\)m, and
the film is immersed into a nonsolvent, typically water or an aqueous solution and precipitates.

The evaporation of the good solvent enriches the cast film in nonsolvent causing precipitation. The precipitation takes place rapidly and first at the surface of the film. Thus, the surface pores are formed rather smaller than those in the interior substructure and that phenomenon leads to asymmetric membrane formations.

Figure 2.4 – (Left) Schematic representation of the immersion precipitation phase-separation process and (Right) scanning electron microscopy micrographs of porous polymeric (PES) formations produced with the use of the method.

By varying the polymer, the solvent, the precipitant and other preparation parameters, membranes with different structures and properties are formed. Typically, in Figure 2.5 are presented different membrane structures formed by the phase separation technique.
Figure 2.5 – Scanning electron microscopy images of mainly cross sections of membranes with different structure formed by phase separation.\textsuperscript{9,10,11}

Different approaches of phase separation techniques are discussed in the literature regarding the control of different parameters that determine the form of the final structure. Zhang \textit{et al.}\textsuperscript{12} studied the influence of dope composition and casting conditions on phase separation process in the preparation of polyethersulfone (\textit{PES}) microfiltration membranes. Among other interesting results, they concluded that for PES membranes prepared from casting solutions close to phase separation, pore size and permeability are influenced by the casting conditions, such as gelation water bath temperature, exposure time to air, and thickness of the cast film. Uragami \textit{et al.}\textsuperscript{13} investigated the formation of finger-like cavities in asymmetric cellulose nitrate membranes changing the composition of the casting solvent and the evaporation period during the membrane formation process. Plentiful studies with different variations to the general procedure have been published since Loeb’s and Sourirajan’s first observation and even today the interest of membrane preparation by phase inversion is boundless. Understanding the thermodynamic and kinetic parameters governing the mechanism of phase inversion -such as the chemical potentials and diffusivities of the individual components and Gibb’s free energy of mixing of the entire system- has motivated scientists to direct towards the controlled development of tailor-made membranes with advanced properties.
2.2.3 The mechanism of the diffusion-induced/immersion precipitation phase-separation process

The three-component phase diagram of a mixture consisting of a polymer, one or more solvents, and precipitant(s) is considered to be a valuable tool in the understanding of the thermodynamic aspects regulating the phase separation mechanism. The membrane formation by phase separation goes along with kinetic parameters that are difficult to quantitatively be described. Thus, the phase diagram is a thermodynamic description of an equilibrium state. Additionally, the complexity is reduced as the immersion precipitation process can be regarded as an isothermal process. In Figure 2.6 is illustrated such a ternary phase diagram consisting of a mixture of three components, a polymer, a solvent and a nonsolvent as function of temperature.

![Phase diagram showing the formation of a microporous system by the addition of a nonsolvent to a homogeneous polymer solution in the three-component mixture exhibiting a miscibility gap at certain conditions of temperature and composition. A, casting solution; B, membrane porosity; B', polymer poor-phase; B'', polymer rich-phase.](image)

In the phase diagram, a miscibility gap is indicated over a wide range of compositions. If a nonsolvent is added to a solution consisting of polymer and solvent, the composition of which is indicated by the point A on the solvent-polymer line, and, if the solvent is removed
from the mixture at about the same rate as the nonsolvent enters, the composition of the system will change following the line A-B.

When the composition of the system reaches the miscibility gap, it will separate into two phases forming a polymer-rich phase presented by the upper boundary of the miscibility gap, which is determined by the bimodal, and a polymer-poor phase represented by the lower boundary of the miscibility gap. When the solvent is replaced completely by the nonsolvent, the mixture has reached the composition indicated by point B. Point B represents a mixture of the solid polymer-rich phase and the liquid polymer-poor phase, indicated by points B' and B", respectively.

The phase diagram predicts only under which conditions of temperature and composition a system will separate into two phases. Information concerning the pore size, the pore shape, that is finger- or sponge-like, and the pore-size distribution are determined by kinetic parameters such as diffusivities of the various components in the mixture, the viscosity of the solution, and the chemical potential gradients, which act as driving forces for the diffusion of the various components in the mixture.4,6,8

### 2.3 CLASSIFICATION OF FILTRATION MODES

Filtration modes can be divided by cross-flow filtration and dead-end filtration depending on the flow direction on membrane surface (Fig. 2.7). In cross-flow filtration, feed moves parallel to the filter medium to generate shear stress to scour the surface. Extra energy is required to generate cross-flow, but cake layer thickness can be controlled. Pseudo steady-state may exist, where scouring effect and particle deposition find a balance and cake layer hardly grows. This filtration mode is particularly effective when feed water carries high level of foulants such as suspended solids and macromolecules.
In **dead-end filtration**, no cross-flow exits and feed moves towards the filter medium. All the particles that can be filtered by filter settle on the filter surface. Since the filtration is not sustainable forever without removing accumulated solids, backwashing is performed periodically and/or filter medium is replaced. This filtration mode is particularly effective when feed water carries low level of foulants. Many surface water filtrations, pretreatment for seawater RO, and tertiary filtrations are adapting dead-end modes.

### 2.4 FLOW THROUGH MEMBRANES\(^\text{15}\)

The flow of water through MF and UF membranes follows the fundamental law for flow through porous media known as Darcy’s law:

\[
v = k_p \frac{h}{L} \tag{Eq. 2.1}\]

where,

- \(v\) = superficial fluid velocity, m/s
- \(k_p\) = hydraulic permeability coefficient, m/s
The hydraulic permeability coefficient in Darcy’s law is an empirical parameter that is used to describe the proportionality between head loss and fluid velocity and is dependent on media characteristics such as porosity and specific surface area. Although flow through membranes follows Darcy’s law, the standard equation of membrane flow is written in a substantially different form. Flow is expressed in terms of volumetric flux \( J \) rather than superficial velocity, the driving force is expressed as transmembrane pressure \( \Delta P \) rather than head loss (which are related by \( \Delta P = p_w gh_L \)), and media characteristics are expressed as a resistance coefficient (the inverse of a permeability coefficient). In addition, the membrane flow equation includes the fluid viscosity explicitly (Darcy’s law buries it in the permeability coefficient) because viscosity has a significant impact on flux and is easy to determine (via temperature). Finally, the membrane flux equation incorporates the membrane thickness into the resistance coefficient. The equation for membrane flux is:

\[
J = \frac{Q}{a} = \frac{\Delta P}{\mu \kappa_m} \tag{Eq. 2.2}
\]

where,
- \( J \) = volumetric water flux through membrane, L/m²h or m/s
- \( Q \) = flow rate, L/h
- \( a \) = membrane area, m²
- \( \Delta P \) = differential pressure across membrane, bar
- \( \mu \) = dynamic viscosity of water, kg/ms
- \( \kappa_m \) = membrane resistance coefficient, m⁻¹

The membrane resistance coefficient can be calculated from laboratory experiments so that flux through a new membrane can be determined for other pressure or temperature conditions.

Flux is normalized for pressure by calculating specific flux, which is the flux at a standard temperature divided by the transmembrane pressure:

\[
J_{sp} = \frac{J_s}{\Delta P} \tag{Eq.2.3}
\]

where,
- \( J_{sp} \) = specific flux at standard temperature, L/m²hbar
$J_s =$ flux at standard temperature (typically 20 °C), L/m²h

Ideally, it would be desirable to calculate flux from measurable parameters that describe the internal structure of MF and UF membranes, such as porosity, nominal pore diameter, specific surface area, and membrane thickness, as is done for clean-bed head loss in granular filtration. These parameters, however, are difficult to measure, and the amorphous internal structure of MF and UF membranes cannot be described mathematically with any great accuracy.

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Chapter 2
Basic aspects on polymeric membranes

14 Synder Filtration
From carbon to nanotubes...to carbon nanotube membranes

Carbon is the 15th most abundant element in the Earth's crust, and the fourth most abundant element in the universe by mass after hydrogen, helium and oxygen. It is present in all known life forms, and in the human body carbon is the 2nd most abundant element by mass (about 18.5%) after oxygen.\textsuperscript{1,2} This abundance, together with the unique diversity of organic compounds and their unusual polymer-forming ability at temperatures commonly encountered on Earth, make this element the chemical basis of all known life.

\section*{3.1 CARBON MATERIALS}

\textbf{Carbon} forms a vast number of compounds, more than any other element, with almost ten million compounds described to date,\textsuperscript{3} which in turn are a tiny fraction of such compounds that are theoretically possible under standard conditions. There are several allotropes of carbon of which the best known are graphite, diamond, and amorphous carbon. Once considered exotic, fullerenes are nowadays commonly synthesized and used in research; they include buckyballs, carbon nanotubes, carbon nanobuds and nanofibers. Several other exotic allotropes have also been discovered, such as lonsdaleite, glassy carbon and carbon nanofoam. The physical properties of carbon vary widely with the allotropic form. All carbon allotropes are solids under
normal conditions, with graphite being the most thermodynamically stable form, while under normal conditions, diamond, carbon nanotubes and graphene have the highest thermal conductivities of all known materials. They are chemically resistant and require high temperature to react even with oxygen.\textsuperscript{2} Figure 3.1 illustrates the T, P phase and “reaction” diagram over a wide range of pressures for pure carbon that guided the historical synthesis of diamond in 1960, and has continued to inspire interest in new forms of carbon, as they are discovered.\textsuperscript{4}

\textbf{Figure 3.1} - P, T phase and transition diagram for carbon. Solid lines represent equilibrium phase boundaries. A: commercial synthesis of diamond from graphite by catalysis; B: P, T threshold of very fast solid-solid transformation of graphite to diamond; C: P, T threshold of very fast transformation of diamond to graphite; D: single crystal hexagonal graphite transforms to retrievable hexagonal-type diamond; E: upper ends of shock compression/quench cycles that convert hex-type graphite particles to hexagonal-type diamond; F: upper ends of shock compression/quench cycles that convert hex-type graphite particles to cubic-type diamond; B,F,G: threshold of fast P/T cycles, however generated, that convert either type of graphite or hexagonal diamond into cubic-type diamond; H,I,J: path along which a single crystal hex-type graphite compressed in the c-direction at room temperature loses some graphitic characteristics and acquires properties consistent with a diamond-like polytype, but reverses to graphite upon release of pressure.
Although it has learned much about carbon since that time, much ignorance remains about the possible phases of carbon. From the phase diagram is found that while $sp^2$ bonded graphite is the ground state phase of carbon under ambient conditions, at higher temperatures and pressures, $sp^3$ bonded cubic diamond is stable. Other regions of the phase diagram show stability ranges for hexagonal diamond, hexagonal carbynes and liquid carbon. It is believed that a variety of novel π-electron carbon bulk phases remain to be discovered and explored.$^5$ In addition to the bulk phases featured in the carbon phase diagram, much attention has recently focused on small carbon clusters, since the discovery of fullerenes in 1985 by Kroto et al.$^6$ and of carbon nanotubes in 1991 by Iijima.$^7$ The physical reason why these nanostructures are formed is that a grapheme layer of finite size has many edge atoms with dangling bonds and these dangling bonds correspond to high energy states. Therefore, the total energy of a small number of carbon atoms (30-100) is reduced by eliminating dangling bonds, even at the expense of increasing the strain energy, thereby promoting the formation of close caged clusters such as fullerenes and carbon nanotubes.

### 3.1.1 Allotropes of Carbon

The **diamond** structure is probably the most-thoroughly investigated of all crystallographic structures. The ideal diamond structure (**Fig. 3.2**) has two distinct carbon sites and has the characteristic property that every carbon atom is surrounded by four other carbon atoms at the corners of a regular tetrahedron. The central carbon atom is bonded to those four neighbors by strong covalent $sp^3$ bonds. The nearest-neighbor carbon-carbon distance is 1.544 Å, nearly 10% larger than in graphite.$^8$
The ideal crystal structure of graphite (see Fig. 3.3) consists of layers in which the carbon atoms are arranged in an open honeycomb network containing two atoms per unit cell in each layer, labeled A and B. The stacking of the graphene layers is arranged, such that the A and A’ atoms on consecutive layers are on top of one another, but the B atoms in one plane are over the unoccupied centers of the adjacent layers, and similarly for the B’ atoms on the other plane. This gives rise to two distinct planes, which are labeled by A and B. These distinct planes are stacked in the ‘ABAB’ Bernal stacking arrangement shown in Fig. x-x, with a very small in-plane nearest-neighbor distance $a_{cc}$ of 1.421 Å, an in-plane lattice constant $a_0$ of 2.462 Å, a $c$-axis lattice constant $c_0$ of 6.708 Å, and an interplanar distance of $c_0/2 = 3.354$ Å.
**Amorphous carbon** (a-C) refers to a highly disordered network of carbon atoms that predominantly have $sp^2$ bonding, with perhaps 10% $sp^3$ bonds and almost no $sp^1$ bonds. Although a-C has no long-range order, some short-range order is present. Since the nature of the short-range order varies significantly from one preparation method to another, the properties of a-C films likewise vary according to preparation methods. Two parameters, the carbon bonding and the hydrogen content, are most influential in characterizing the short-range order, which may exist on a length scale of ~10 Å. a-C tends to form under the conditions of carbon nanotube formation in all available empty space. Heat treatment in the presence of oxygen is generally effective in removing a-C, taking advantage of the weaker carbon-carbon bonding in a-C, relative to the bonding in more ordered-forms of carbon, such as carbon nanotubes.

![Figure 3.4 - Structure of amorphous carbon.](image)

The identification of the larger carbon clusters ($n_C > 30$) with cage-like molecules, the observation of the special stability of $C_{60}$, the postulation that the 60 carbon atoms are at the vertices of a truncated icosahedrons, and the naming of these cage molecules as **fullerenes** stems from the pioneering gas phase studies of Kroto and Smalley and were awarded the Nobel Prize for their efforts in 1996. By forming closed cage clusters, dangling bonds with their high energies are eliminated, thereby lowering the total energy of the system.
On the surface of the shell, the bonding between carbon atoms is predominantly \( sp^2 \) as in graphite, but because of the curvature of the shells, some \( sp^3 \) bonding is also admixed to the carbon wave functions, thereby increasing their energies somewhat. Of all the fullerenes, icosahedral \( C_{60} \) is the most stable. The second most-common fullerene is \( C_{70} \) and last the rugby-shaped \( C_{80} \) fullerene (see Fig. 3.5). Of great significance is the fact that the average nearest-neighbor carbon-carbon distance \( (a_{c-c}) \) in fullerenes is only 1 or 2\% larger than that of graphite (1.4 Å). The elongated “cousins” of fullerenes, carbon nanotubes, were identified by Iijima Sumio\(^7\) in 1991 and are discussed further on.

**Figure 3.5** - Molecular structures of fullerenes: A) structure of \( C_{60} \), B) structure of \( C_{70} \) and C) structure of \( C_{80} \).

**Carbon fibers** represent an important class of graphite-related materials which are closely connected to carbon nanotubes, with regard to structure and properties. The as-prepared vapor-grown fibers have an “onion skin” or “tree ring” morphology and after a heat treatment to 2500 °C bear a close resemblance to carbon nanotubes. After further treatment to about 3000 °C, the outer regions of the
vapor grown carbon fibers form facets, and become more like graphite because of the strong interplanar correlations resulting from the facets. The remarkable high strength and modulus of carbon fibers are responsible for the most of the commercial interest in these fibers. Vapor-grown carbon fibers can be prepared over a wide range of diameters (~10 nm to more than 100 μm) and these fibers have central hollow cores. A distinction is made between vapor grown carbon fibers and fibers with diameters in the range 10-100 nm, which are called nanofibers, and exhibit properties intermediate between those of typical vapor grown carbon fibers, on the one hand, and multi-walled carbon nanotubes, on the other.\textsuperscript{5,8} In Figure 3.6, representative SEM and TEM images of carbon nanofibers are shown (Pyrograf III Carbon Nanofiber).\textsuperscript{11,12}

![Figure 3.6 - SEM (up) and TEM (down) images of carbon nanofibers.](image)

**Glassy carbon** is another common carbon material that is manufactured as a commercial product by slow, controlled degradation of certain polymers at temperatures typically on the order of 900 to 1000 °C. Glassy carbon refers to a family of disordered carbon materials, having a range of properties that depend somewhat
on the precursor material and significantly on the processing conditions. This material is granular, moderately hard, can be easily polished, is thermally conducting, impermeable, biocompatible, and stable at high temperatures.\(^8\) The morphology of glassy carbon is shown in Figure 3.7.\(^{13,14,15}\)

**Figure 3.7** - Glassy Carbon: (A) Stone-like sample of glassy carbon, (B) powder from spherical particles (SEM image) and (C), (D) TEM images of the commercial glassy carbon SIGRADUR\(^\text{®}\) G and SIGRADUR\(^\text{®}\) K respectively.

Carbon nanofoam is an allotrope of carbon discovered in 1997 by Andrei V. Rode and co-workers.\(^{16}\) It consists of a cluster-assembly of carbon atoms strung together in a loose three-dimensional web. Each cluster is about 6 nm wide and consists of about 4000 carbon atoms linked in graphite-like sheets that are given negative curvature by the inclusion of heptagons among the regular hexagonal pattern. The large-scale structured of carbon nanofoam is similar to that of an aerogel, but with 1% of the density of previously produced carbon aerogels. Unlike carbon aerogels, carbon nanofoam is a poor electrical conductor but unusually, has magnetic properties. Carbon nanofoam has been extensively studied under electron microscope by John...
Giapintzakis and group\textsuperscript{17} at the University of Crete and representative SEM images are shown in \textbf{Figure 3.8}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{carbon_nanofoams.jpg}
\caption{SEM images of Carbon nanofoams.}
\end{figure}

\subsection*{3.1.2 Carbon Nanotubes}

The discovery of fullerenes led to the discovery of carbon nanotubes (CNT) by Iijima in 1991.\textsuperscript{7} Whereas earlier studies had been carried out on CNT,\textsuperscript{18,19,20,21} their significance was not widely appreciated until the connection was made between fullerenes and CNT both experimentally and theoretically. One can conceptualize carbon nanotubes as cylinders appropriately rolled from a graphene sheet, capped at both ends by hemispheres of fullerenes, of nanometer size diameter. Since nanotubes can be rolled from a graphene sheet in many ways, there are many possible orientations of the hexagons on the nanotubes, even though the basic shape of the carbon nanotube wall is a cylinder.\textsuperscript{5,8} Different structures of CNT are shown in \textbf{Figure 3.9}.\textsuperscript{22,23} Carbon nanotubes were observed in the carbon soot of graphite electrodes during an arc discharge, by using a current of 100 amps, that was intended to produce fullerenes. Their name is derived from their long, hollow structure, and they have been constructed with length to diameter ratio (aspect ratio) of up to 132.000.000:1,\textsuperscript{24} significantly larger than for any other material with diameters of nanometers scale.
These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of material science and technology. In the following paragraphs, historical details about carbon nanotube synthesis, carbon nanotube types, their properties and their applications are described more extensively.

3.1.2.1 Historical Introduction

The beginning of widespread CNT research in the early 1990s was preceded in the 1980s by the first industrial synthesis of what are now known as multi-wall carbon nanotubes and documented observations of hollow carbon nanofibers as early as the 1950s.

Figure 3.9 - Graphics showing types of carbon nanotubes.
Very small diameter (less than 10 nm) carbon filaments were prepared in the 1970s and 1980s through the synthesis of vapor grown carbon fibers by the decomposition of hydrocarbons at high temperatures in the presence of transition metal catalyst particles of <10 nm diameter. However, no detailed systematic studies of such very thin filaments were reported in those early years, and it was not until the observation of carbon nanotubes in 1991 by Iijima of the NEC Laboratory in Tsukuba, Japan (see Fig. 3.10), using high resolution transmission electron microscopy that the carbon nanotube field was seriously launched. Independently, and at about the same time (1992), Russian scientists also reported the discovery of carbon nanotubes and nanotube bundles, but generally having a much smaller length to diameter ratio.

Figure 3.10 - The observation by TEM of multi-wall coaxial nanotubes with various inner and outer diameters, \(d_i\) and \(d_o\), and numbers of cylindrical shells \(N\) reported by Iijima in 1991: (a) \(N=5\), \(d_o=6.7\) nm, (b) \(N=2\), \(d_o=5.5\) nm, and (c) \(N=7\), \(d_i=2.3\) nm, \(d_o=6.5\) nm.
Whereas the initial Iijima’s experimental observation was for Multi-Wall Carbon Nanotubes (MWCNT), it was less than two years before Single-Wall Carbon Nanotubes (SWCNT) were discovered experimentally by Iijima and his group and by Bethune and coworkers. These findings were especially important and heralded the entry of many scientists into the field of carbon nanotubes. A major breakthrough occurred in 1996 when Smalley and coworkers at Rice University successfully synthesized bundles of aligned single wall carbon nanotubes, with a small diameter distribution, thereby making it possible to carry out many sensitive experiments relevant to 1D quantum physics, which could not previously be undertaken. Of course, actual carbon nanotubes have finite length, contain defects, and interact with other nanotubes or with the substrate and these factors often complicate their behavior.

### 3.1.2.2 Type of Carbon Nanotubes

Carbon nanotubes have many structures, differing in length, thickness, and in the type of helicity and number of layers. They typically have diameters ranging from <1nm up to 50 nm while their lengths are typically several microns, but recent advancements have made the nanotubes much longer, and measured in centimeters. Carbon nanotubes can be categorized by their structures:

**A. Single-Wall Carbon Nanotubes (SWCNT)**

Most SWCNT have a diameter of close to 1 nm, with a tube length that can be many millions of time longer. The structure of a SWCNT can be conceptualized by wrapping a one-atom-thick layer of graphite (graphene) into a seamless cylinder capped at the edges of the cylinder with structures which look like half-fullerenes. The three different structures of SWCNT, zig-zag, armchair or chiral variety, formed depending on the sheet direction about which the graphite sheet is rolled to shape a cylinder and on the appearance of a belt of carbon bonds around the nanotube diameter, are shown in Figure 3.11.
Figure 3.11 - Schematic illustrations of the structures of (A) armchair, (B) zig-zag, and (C) chiral SWCNT. Projections normal to the tube axis and perspective views along the tube axis are on the top and bottom, respectively. (D) Tunneling electron microscope image showing the helical structure of a 1.3-nm-diameter chiral SWCNT. (E) Transmission electron microscope (TEM) image of a MWCNT containing a concentrically nested array of nine SWCNT. (F) TEM micrograph showing the lateral packing of 1.4-nm-diameter SWCNT in a bundle. (G) Scanning electron microscope (SEM) image of an array of MWCNT grown as a nanotube forest.

B. Multi-Wall Carbon Nanotubes (MWCNT)

MWCNT consist of multiple rolled layers (concentric cubes) of graphene. There are two models that can be used to describe the structures of multi-wall nanotubes. In the Russian Doll model (Fig. 3.12 (a)), sheets of graphite are arranged in concentric cylinders, e.g., (8,0) SWCNT within a larger (10,0) SWCNT. This type of MWCNT is observed more commonly. In the Parchment model (Fig. 3.12 (b)), a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper. The interlayer distance in MWCNT
is close to the distance between graphene layers in graphite, approximately 3.4 Å.

**Figure 3.12** - Multi-wall carbon nanotube structure described by the models: (a) *Russian Doll* and (b) *Parchment*.

**Double-wall carbon nanotubes** (DWCNT) form a special class of nanotubes because their morphology and properties are similar to those of SWCNT but their resistance to chemicals is significantly improved. This is especially important when functionalization is required to add new properties to the carbon nanotubes.

**Figure 3.13** - Schematic illustrations of the structure of double-wall carbon nanotubes.\textsuperscript{30,31}
In the case of SWCNT, covalent functionalization would break some carbon-carbon double bonds, leaving “holes” in the structure and, thus, modifying both its mechanical and electrical properties. In the case of DWCNT, only the outer wall yields modifications.

### 3.1.2.3 Synthesis techniques of Carbon Nanotubes

Nanotube characterization and device explorations have been greatly facilitated by progress in nanotube synthesis over the years. At the same time, many aspects of basic research and practical application requirements have been driving and motivating synthetic methods for better and more homogeneous materials. Soon after the discovery of carbon nanotubes using the arc discharge technique, several other techniques have been developed for the production of nanotubes in sizable quantities including:

- **Laser ablation**
- **High pressure carbon monoxide disproportionation**
- **Chemical Vapor Deposition (CVD)**

Arc-discharge and laser ablation employ solid-state precursor to provide carbon sources needed for nanotube growth and involve carbon vaporization at high temperatures.\(^{32}\) CVD growth of CNT can occur in vacuum or at atmospheric pressure and is the dominant mode of high-volume CNT-production typically using fluidized bed reactors that enable uniform gas diffusion and heat transfer to metal nanoparticles.\(^ {33}\) While large quantities of nanotubes can be synthesized by these methods, advances in catalysis and continuous growth are making CNT more commercially viable.

### 3.1.2.4 Properties of Carbon Nanotubes

Carbon nanotubes represent one of the best examples of novel nanostructures derived by bottom-up chemical synthesis approaches. They have the simplest chemical composition and atomic bonding configuration but exhibit perhaps the most extreme diversity and richness among nanomaterials in structures and structure-property relations.\(^ {34}\) They are generally regarded as the single hardest materials known. A single-wall CNT is able to withstand a pressure that amounts to 24 GPa without having any kind of deformity. They are also known for having kinetic properties that make them get
nested with each other. Moreover, their electrical properties are very unique making them extremely sensitive to charge transfer and chemical doping effects by various molecules. In addition to mechanical and electrical properties, carbon nanotubes are distinguished for their high thermal conductivity plus their exceptional optical properties. More and above that, their high aspect ratios, their inert, smooth, hydrophobic, graphitic walls and their extremely small, inner pore diameters ranging from 0.8 nm up to 50 nm, make carbon nanotubes to allow ultra-efficient transport of molecules through their hollow cavity. The fundamental aspects of CNT regarding their transport properties are discussed in the subsequent chapter.

Figure 3.14 - Schematic illustrations of molecules’ transport through carbon nanotubes.

3.1.2.5 Applications of Carbon Nanotubes

Carbon nanotubes are increasingly being studied for their potential application into a variety of technologies including drinking water treatment. Since their first discovery and the subsequent establishment of the method for large-scale synthesis, the production and use of CNT in industrial and consumer products has increased dramatically due to their aforementioned superb electrical, mechanical, thermal, and chemical properties. Worldwide commercial interest in CNT is reflected in a production capacity that presently exceeds several thousand tons per year. Currently, bulk
CNT powders are incorporated in diverse commercial products ranging from rechargeable batteries, automotive parts, and sporting goods to boat hulls and water filters. Advances in CNT synthesis, purification, and chemical modification are enabling integration of CNT in thin-film electronics and large-area coatings. Although not yet providing compelling mechanical strength or electrical or thermal conductivities for many applications, CNT yarns and sheets already have promising performance for applications including super-capacitors, actuators, and lightweight electromagnetic shields.\textsuperscript{39}

**Figure 3.15** - Trends in CNT research and commercialization. (A) Journal publications and issued worldwide patents per year, along with estimated annual production capacity. (B to E) Selected CNT-related products: composite bicycle frame, antifouling coatings, printed electronics and electrostatic discharge shielding.\textsuperscript{39,40}

More analytically, in composite materials, CNT are met in the automotive industry where conductive CNT plastics have enabled electrostatic-assisted painting of mirror housings as well as fuel lines and filters that dissipate electrostatic charge. They are also used for load-bearing applications, where CNT powders are mixed with polymers or precursor resins to increase stiffness, strength and toughness.\textsuperscript{41} Such composites are used to enhance sporting goods,
including tennis racquets, baseball bats, and bicycle frames. Additionally, CNT resins are also used to enhance fiber composites.\textsuperscript{41,42} Recent examples include strong, lightweight turbine blades and hulls for maritime security that are made by using carbon fiber composite with CNT-enhanced resin. In coatings and films, leveraging CNT dispersion, functionalization, and large-area deposition techniques CNT are emerging as a multifunctional coating material. For example, MWCNT-containing paints reduce biofouling of ship-hulls by discouraging attachment of algae and barnacles.\textsuperscript{43} In microelectronics, CNT are attractive for transistors because of their low electron scattering and their bandgap, which depends on diameter and chiral angle.\textsuperscript{44,45} In energy storage and environment industry, CNT are widely used in lithium ion batteries for notebook computers and mobile phones, marking a major commercial success.\textsuperscript{46,47} Also, for fuel cells, the use of CNT as catalyst support can potentially reduce Pt usage by 60\% compared with carbon black.\textsuperscript{48} In biotechnology, ongoing interest in CNT as components of biosensors and medical devices is motivated by the dimensional and chemical compatibility of CNT with biomolecules, such as DNA and proteins. An upcoming application domain of CNT is water purification.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{carbon_nanotube_products.png}
\caption{Images of commercialized and under research carbon nanotube-products. (a) Body of car made of carbon nanotube composites, (b) carbon nanotube technology to baseball bat and other sporting equipment,}
\end{figure}
(c) carbon nanotube artificial muscles, (d) carbon nanotube-reinforced polyurethane for lighter and more durable wind turbine blades, (e) advanced marine coatings are formulated with carbon nanotubes giving them very high abrasion resistance, (f) touchscreens containing carbon nanotubes, (g) fibers created with carbon nanotubes and polyacrylonitrile, (h) highly breathable membranes with pores made of a few nanometer-wide vertically aligned carbon nanotubes.\cite{49,50,51,52,53,37}

Here, tangled CNT sheets can provide mechanically and electrochemically robust networks with controlled nano-scale porosity. These have been used to electrochemically oxidize organic contaminants,\cite{54} bacteria and viruses.\cite{55} Portable filters containing CNT meshes have been commercialized for purification of contaminated drinking water. Moreover, membranes using aligned encapsulated CNT with open ends permit flow through the interior of the CNT, enabling unprecedented low flow resistance for both gases and liquids.\cite{56} This enhanced permeability may enable lower energy cost for water desalination by reverse osmosis in comparison to commercial polycarbonate membranes. However, very-small-diameter SWCNT are needed to reject salt at seawater concentrations.\cite{57,39}

### 3.2 CARBON NANOTUBE-MEMBRANES ON WATER PURIFICATION AND DESALINATION

In the present subsection, an effort has been made to review the recent developments in the utilization of CNT in the field of membrane technology. It includes notable efforts to demonstrate the possibility of CNT membranes to be widely employed in water purification and desalination processes. Moreover, membrane fabrication techniques, functionalization and influencing factors are presented as well, while the major barriers and future challenges for the commercialization of CNT based membrane technologies are mentioned.

#### 3.2.1 Need of novel membrane technology

The recorded increase in mean annual temperature has provoked climate change and is already affecting many ecosystems. Among the most pronounced effects of increased temperature is the variation in physical systems, leading to melting of ice masses around the world,
the rise of the sea level, soil, and freshwater submergence and increasing evaporation. These natural incidences are collectively making the fresh and sea water saltier and the availability of existing fresh water rapidly dwindling.

In order to address the enormous need of pure water, various water treatment technologies have been proposed and applied at experimental and field levels. These technologies are commonly fall into primary (screening, filtration, centrifugation, separation, sedimentation, coagulation and flocculation); secondary (aerobic and anaerobic treatments); and tertiary (distillation, crystallization, evaporation, solvent extraction, oxidation, precipitation, ion exchange, reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), adsorption, electrolysis and electrodialysis) level of water treatment technologies. Nevertheless, the major part of these technologies is not efficient in fixing water pollutants effectively. Most of the current treating methods are energy and operationally demanding and thus, they are unaffordable at a commercial scale. The commonly used adsorption techniques are accessible and uncomplicated but cannot be used in water desalination. In this regard, membrane technologies have got some attention because of their alluring intrinsic features. Membranes do not need chemical additives, thermal inputs and spent media regeneration making them more popular over other water treatment technologies.

Literally, the onset of membrane technologies has delivered boundless facilities and favorable circumstances to purify water even at level of ions. Membrane filtration allows the transport of water solvent/dispersant while at the same time rejects solutes, gases, fluids and various particles present in the polluted under treatment water. Applicable membrane separation processes such as RO, NF, UF, MF, distillation, dialysis and electrodialysis are presently available and among them, RO, NF, UF and MF are pressure driven membrane processes well established preferably in industrial wastewater treatment. RO process is used both for the desalination of sea and brackish water and around 19% of the world’s desalination plants have successfully installed the RO membrane. However, like most of the other membrane treatment processes, RO is combined to high-pressure systems and is resulted to a subsequent huge energy consumption.

Additionally, several other technical barriers exist which reduce the overall robustness of these separation systems that have significantly
limited their popularity at commercial interest. The membrane separation efficiency depends on the composition of the water; substances creating stress for bacteria reduce the membrane filtering ability. The building-up of a filter cake at the RO/NF membranes causes fouling and pore blocking and furthermore reduces the overall performance of the systems. Last but not least, the high concentration of salts may decrease the biodegradation of the sludge resulting in toxic disposal. Besides, membrane technologies are less robust and incapable of self-cleaning function, necessitating the chemical treatments for cleaning and recycling. As an overall result, pressure-driven membrane systems have high operation efficiency with respect to cost, maintenance and quality for waste water containing high biodegradable organic pollutants, but are inefficient with respect to water containing a large amount of stress-inducing substances, high colourity and low biodegradable organic compounds.

These drawbacks have compelled scientists to develop new generation membranes such as carbon nanotube membranes (CNT) for cost-effective water purification and desalination technologies with high treatment efficiency and high quality treated water under low maintenance efforts.

### 3.2.2 ...Why Carbon Nanotubes?

Giving emphasis in the use of CNT in the membrane technology, it is manifested that well-aligned CNT can serve as competent pores in membranes for water desalination and decontamination applications. The hollow CNT structure provides frictionless transport of water molecules, a feature that makes them suitable for the development of high flux separation systems. The channels of proper pore diameter-CNT can constitute mass/volume barriers, rejecting even salt ions allowing water transport through the nanotube hollows.

In addition to CNT-diameter synthesis control, modification of CNT cavities in order to selectively reject ions is also feasible. Thus, CNT membranes can be used as 'gate keepers' for size controlled separation of multiple pollutants. Besides, they show antifouling and self-cleaning properties and may be reusable. Both SWCNT and MWCNT have been used for water desalination studies. The CNT employment in advanced membrane technologies, since they provide.
low energy solution for efficient water treatment and reuse, proves intriguing and challenging.

### 3.2.3 Water transport through Carbon Nanotubes

Transport of all molecules, including charged molecules through nanochannels, is affected by the molecular size with respect to the lateral channel dimensions, and also by considerations of molecular entropy. Molecules can be excluded from channels by ion exclusion, by steric hindrance or because of the cost in internal entropy. On the basis of these three factors, nanochannels work as molecular sieves, much like membranes. Effects that happen at the channel walls become increasingly important when decreasing channel height. Typical examples of these effects are the occurrence of electrical double layers, slip and specific adsorption effects.

**Liquid slip**

Whereas no slip represents a situation where the liquid in the first molecular layer is stagnant and all other molecules are sheared past the first molecular layer, the first molecular layer does move in slip flow, though with strong friction with the wall. The lower this friction with the wall—achieved, for example, by employing very hydrophobic walls—the less force is needed for a given flow velocity. Therefore, slip is very important in nanofluidics since it drastically reduces the required pressure in pressure-driven flows.

![Figure 3.17](image)

**Figure 3.17** - Three cases of slip flow past a stationary surface. The slip length $b$ is indicated. $^{68}$
In **Figure 3.17**, the consequences of slip for the velocity of the liquid are clearly shown. The case on the right is particularly informative, because it represents a situation where liquid does not experience any friction with the wall and could theoretically be accelerated to the speed of light. Parameters that are known to influence slip in nanochannels are surface roughness and hydrophobicity. The slip length is the additional length from the wall at which the tangent to the fluid velocity at the wall is extrapolated to reach zero relative tangential velocity between fluid and solid. Generally, the slip length is increased for increasing hydrophobicity and decreasing surface roughness when the channel walls are hydrophilic. There is, however, convincing evidence that surface roughness in the case of hydrophobic channels leads to greater slip lengths (several tens of microns as compared to around 20 nm for smooth hydrophobic channels) because of air trapping in surface inhomogeneities.

The flow rates of water in CNTs depend strongly on the slip length. Numerous experimental and simulation studies have been carried out in order to find the transport properties of water through CNTs. The flow enhancement results differ by 1–5 orders of magnitude compared to the classical no-slip flow predictions. The slip length $L_s$ and flow enhancement $E$ for Hagen-Poiseuille flow are defined as follows:

$$u_s = u(R) = L_s \left( \frac{\partial u(r)}{\partial r} \right)_{r=R}$$  \hspace{1cm} (Eq. 3.1)

$$E = \frac{Q_{\text{slip}}}{Q_{\text{no-slip}}} = \left( 1 + \frac{8L_s}{D} \right)$$  \hspace{1cm} (Eq. 3.2)

where $u_s$ is the slip velocity (fluid velocity at the wall), $Q_{\text{slip}}$ is the observed flow rate, $Q_{\text{no-slip}}$ is the expected flow rate using the no-slip boundary condition, and $D$ is the diameter of the tube. For a given fluid-solid combination the slip length is a useful property, which is commonly quoted in the nanofluidics literature. Above a certain channel width/tube diameter the slip length is independent of the channel size. Using Eq. 3.2 one can estimate the flow enhancement given the slip length.

Studies on CNTs have provided evidence for the flow of water through CNTs. Many studies have reported a higher than expected flow rate, when compared to the predictions of classical Hagen-Poiseuille (HP) equation, for water flowing through CNT. Hummer *et al.* had done molecular dynamics computations to study the water conduction
through a CNT and they pointed out that the inherent smoothness of the CNT, the tight hydrogen bonding, and the lower chemical potential were responsible for the pulse like transmission of water through the nanotube. Molecular dynamics simulations performed by Joseph and Aluru\textsuperscript{71} have claimed that this enhancement in flow may be due to the existence of a hydrogen bond depleted area near the tube wall.\textsuperscript{72}

Majumder \textit{et al.} \textsuperscript{73} observed the frictionless movement of water molecules with high velocities from 9.5 to 43.0 cm s\textsuperscript{-1}/bar through a 7 nm diameter CNT pore studying the water passage through membranes consisting of an array of aligned CNT. They have claimed that the flow rates are four to five orders of magnitude faster than those of conventional fluid flow of between 0.00015 and 0.00057 cm s\textsuperscript{-1}/bar.

Molecular simulation dynamics have shown that the water conductance of the (7, 7) and (8, 8) tubes are roughly double and quadruple than that of the (6, 6) tube respectively, given that the permeability of a single water chain forming in a tube (5 ,5) is a little under half of the one from a tube (6, 6), due to the fact that water chains only form across the narrower pore half of the time.\textsuperscript{57} Accordingly, it is concluded that CNT type and structure play role of critical importance in water transport and permeability through CNT.

### 3.2.4 Type and fabrication of Carbon Nanotube-membranes

The successful fusion of nanotechnology and membrane technology has been stated to lead to efficient next generation separation systems. The type and quality of CNT, the filling/host/substrate materials, the processing, and the fabrication methods used for the synthesis of CNT-membranes are the main factors influencing their performances. Currently, three types of CNT-membranes are available:

- Membranes made by arrays of vertically aligned CNT (\textit{VA-CNT-membranes}),
- Mixed matrix CNT-membranes (\textit{MM-CNT-membranes}), and
- Membranes with CNT infiltrated through their porosity (\textit{CNT-infiltrated-membranes}).

Illustrations showing the three types of CNT-membranes are depicted in \textbf{Figure 3.18}. Further discussion on the fabrication of the
aforementioned CNT-membranes is stated in the following subsections.

**Figure 3.18** – Schematic representation of different type CNT-membranes. *(Up)* Membrane made by arrays of vertically aligned CNT and *(down)* an asymmetric membrane mixed with CNTs.
3.2.4.1 Vertically aligned-CNT-membranes (VA-CNT-membranes)

The VA-CNT-membranes are synthesized by arranging perpendicular CNT with supportive filler contents between the tubes. These membranes are high molecular sieves with intercalated filler matrix such as polymer between them. The fillers may be also epoxy, silicon nitride and others with no water permeability. The VA-CNT membrane was first introduced by Hinds et al. in 2004 with polystyrene as filling material between CNT. The fabrication procedure was simple but the pore sizes were irregular. The membrane could not retain Ru(NH$_3$)$_6^{3+}$ ions initially, following H$_2$O plasma and HCl treatments, respectively. However, functionalization of CNT core with negatively charged carboxylate groups bounded the positively charged Ru(NH$_3$)$_6^{3+}$ ions. Biotin and streptavidin attachment onto the functionalized CNT membranes reduced ion transport by a factor 5.5–15. Such functionalized membranes worked as ‘gate keeper’-controlled chemical separators, demonstrating the ability to gate molecular transport through CNT cores for potential applications in chemical separations and sensing.

Holt et al. in 2006, introduced micro-electromechanical method for synthesizing VA-CNT-membranes with stimulated nano-fluidic functions. The growth of a dense, vertically aligned array of DWCNT- of sub-2-nm nanotube pore diameter on the surface of a silicon chip by catalytic chemical vapor deposition, was followed by conformal encapsulation of the nanotubes by a hard, low-pressure chemical vapor deposited silicon nitride (Si$_3$N$_4$) matrix. The Si$_3$N$_4$ was used as filler between the nanotube spaces in order to inhibit water flow through the nanotube gaps, and create stress to stimulate water flow through the tubes. The excess Si$_3$N$_4$ was removed from both sides of the membrane by ion milling, and the ends of the nanotubes were opened up by reactive ion etching. The membranes remained impermeable to the tested gases and liquids until the very last etching step. That was an evidence for the fabrication of crack-free and void-free membranes. Similar procedure was also followed for the construction of MWCNT-membrane in a preceding work in 2004 by Holt’s group. A thorough description of the VA-CNT membrane fabrication process is illustrated in Figure 3.19. Finally, they observed increased (>3 folds) over other no-slip water flux, and hydrodynamic flow, and enhanced ion selectivity compared to MWCNT-membranes. The membrane transported Ru$^{2+}$(bipyrr)$_3$ species.
with sizes up to 1.3 nm but blocked 2 nm Au particles, suggesting that their pore sizes were between 1.3 and 2 nm. The performances of those membranes succeeded promising results such as high selectivity to multiple variants, high water fluxing and low energy consumption.

The key findings of the aforementioned works pointed out that the design of the CNT-pore sizes to match with the target molecules allow the molecular sieving effects to improve the membrane selectivity. This advancement was predicted to directly benefit the field of chemical separations and water purification processes.

Figure 3.19 - Process flow for the fabrication of VA-CNT-membrane.\textsuperscript{75}

More recently, Baek et al.\textsuperscript{76} in 2014, fabricated VA-CNT-membranes from Fe catalyst using water-assisted thermal chemical vapor deposition onto a silicon (Si) wafer. After nanotube growth, the
synthesized VA-CNTs were incorporated into epoxy resin for filling up the vacant areas. The performance of the fabricated membranes was evaluated in terms of various solvents' flux and diverse nanoparticles’ rejection compared to commercial UF membranes with similar pore size. The VA-CNT-membrane appeared to have a water flux approximately three times higher than the UF membrane and water transport approximately 70,000 times faster than conventional no-slip flow, while showing similar rejection rate to the UF membrane.

3.2.4.2 Mixed matrix-CNT-membranes (MM-CNT-membranes)

The unique properties of CNT have spurred a great deal of interest in their use as nanofillers. Their introduction in polymer matrices represents a new promising direction for the development of composite materials. For separation purpose, most of the recent studies are mainly focused on the preparation of randomly dispersed and distributed CNT in polymer composites. In the major part of these studies, the nanocomposite membranes were prepared through physical solution mixing of CNT in the polymer dope, followed by the phase inversion technique to remove the solvent and allow the formation of the membrane. This fabrication approach poses a significant disadvantage since the randomly dispersed CNT in the polymer matrix mostly hinder the passage of fluid molecules through CNT tube channels. It’s worth noting that, in the case of CNT mixed with a polymer matrix, CNT mainly act as interlayer spacers to form gap abundant channels increasing the free volume of the composite. Therefore, high flux and permeability can only be realized when CNT are set as fast diffusion channels for the transport of fluid molecules. 77, 78

Nevertheless, a MM-CNT-membrane is composed of polymeric blend or other composite materials with CNT (Fig. 3.18). Such membranes can be easily fabricated with reduced cost and was introduced by Zimmerman et al. 79 to overcome the disadvantages of polymeric membranes for gas purification. Generally, this type of membrane has significantly strengthened the water purification ability of the existing membranes in many terms. MM-CNT-membranes could be a cheap solution to overcome certain hurdles of current conventional separation technologies, namely, the membrane fouling and pollutant precipitation. More and above that, irregular pore size, deleterious
micro pollutants, influent water quality and pH variations decrease membrane capacities. Additionally, fouling creates defects in membrane pores causing pore blocking and complicating membrane regeneration.

In this context, many studies have revealed the benefits of the use of MM-CNT-membranes in water purification. Choi et al.\textsuperscript{80} have used MM-CNT-membranes to improve filtration capacity of UF membranes. It was observed enhanced water permeability, solutes retention and mechanical robustness of the membrane.\textsuperscript{59} A holistic description of MM-CNT-membrane fabrication is described in the experimental section (Chapter 5).

### 3.2.4.3 Membranes with infiltrated CNT (Infiltrated-CNT-membranes)

Yet, the third approach of a CNT-membrane refers to infiltrated-CNT-membranes. Such a membrane is fabricated by the incorporation of CNT into a porous polymer matrix using filtration methods. Analytically, a polymeric porous membrane, usually micro-filtration, is used as the main body of the CNT-membrane, and by filtering a very well dispersed CNT-suspension in organic or aquatic dispersant, using low vacuum during the infiltration process, CNT are embodied in the pores of the membrane active surface (selective layer). The incorporation of CNT alters the internal diameters of the polymeric pores which are substituted by those of the CNT, either by SW, DW, or MWCNT. Kim et al.,\textsuperscript{81} have used polytetrafluoroethylene (PTFE) micro-filtration membranes with pore size 0.2 \( \mu m \) as substrates and have studied the filtration of SWCNT dispersed in THF. The membranes were developed for practical gas separation applications and exhibited high gas flux transport (Fig. 3.20).
In the same context, Madaeni et al.,\textsuperscript{82} have studied the embedment of MWCNT of outer diameters 10-30 nm in polyvilylidene fluoride (PVDF) micro-filtration membrane with pore size 0.22 μm by means of filtering and subsequently a polydimethylsiloxane (PDMS) coating was applied. The scope of that study was to prepare a superhydrophobic nano-filtration membrane getting as precursor material a micro-filtration membrane (Figure 3.21). The results revealed that the flux recovery ratio for membrane coated with 5 wt.% PDMS was enhanced, showing that the fabricated superhydrophobic NF membrane possessed superior antibiofouling property.
The main observations regarding generally to CNT-membrane studies are summarized in Table 3.1.

Figure 3.21 - Fabrication process of superhydrophobic nano-filtration membrane, infiltrating MWCNT through PVDF micro-filtration membrane.\textsuperscript{82}
Table 3.1 - Main observations of CNT-membrane studies.\textsuperscript{35}

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Substrate/Filler/Host matrix</th>
<th>Main observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>VA-CNT</td>
<td>Polystyrene</td>
<td>Have potentiality in chemical separations and sensing.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Modest interaction of ion with the CNT tips and the core is secured.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Removed heavy metals and hydrocarbons.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Filtered E. coli and poliovirus (\textasciitilde 25 nm).</td>
</tr>
<tr>
<td>VA-CNT</td>
<td>SiN\textsubscript{4}</td>
<td>Water flux rate was 2.4 \times 10^{-4} mol/m²/s.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bamboo shaped CNTs can be used in separation and chemical sensing.</td>
</tr>
<tr>
<td>VA-CNT</td>
<td>Si\textsubscript{3}N\textsubscript{4}</td>
<td>Water flow exceeded \textasciitilde 3 orders.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pores (\textasciitilde 2 nm) enhanced ion selectivity and water permeability.</td>
</tr>
<tr>
<td>VA-CNT</td>
<td>Epoxy resin</td>
<td>Nanotube filter separated diesel and water layers.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cleaned oil spill.</td>
</tr>
<tr>
<td>VA-CNT</td>
<td>Polyethyleneimine</td>
<td>Increased water permeability.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Degraded recalcitrant contaminants upon functionalization.</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polysulfonate</td>
<td>Increased hydrophilicity.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Increased water permeability, up to 2 wt.%.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Decreased solute rejection, up to 2 wt.%.</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polysulfonate</td>
<td>Decreased permeability and increased rejection at 4 wt.%.</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polyvinylidene fluoride</td>
<td>Eliminated E. coli cells (\textasciitilde 2 \mu m) through size exclusion.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inactivated 80% of the bacteria within 20 min contact time.</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polyamide-Polysulfone</td>
<td>Removed viruses with great extent.</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polyethersulfone</td>
<td>Increased water permeability.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Enhanced bacterial cytotoxicity (60%/h).</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Poly(methyl methacrylate)</td>
<td>Increased water flux (62%) with improved selectivity and sensitivity.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Retained Na\textsubscript{2}SO\textsubscript{4} (99%).</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polyvinyl-N-carbazole</td>
<td>Cytoxic for Gram-positive and Gram-negative bacteria (\textasciitilde 80%-90%).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Removed virus (\textasciitilde 2.5 logs).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cost-effective method.</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polysulfone</td>
<td>Increased fouling resistance.</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polysulfone</td>
<td>Increased water flux (60% to 100%).</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polysulfone</td>
<td>Retained solutes and resistant to protein fouling.</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polysulfone</td>
<td>Enhanced thermal stability.</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polysulfone</td>
<td>Increased heavy metals rejection.</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polyethersulfone</td>
<td>Increased water fluxing without aggressive chemical cleaning.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Excellent antifouling properties rendered membranes suitable for recycling use.</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polysulfone</td>
<td>Increased water flux (160%).</td>
</tr>
<tr>
<td>MM-CNT</td>
<td>Polyvinylidene fluoride</td>
<td>Reduced fouling tendency.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Improved self-cleaning ability.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Retained salts (R (Na\textsubscript{2}SO\textsubscript{4}) &gt; R (MgSO\textsubscript{4}) &gt; R (NaCl)).</td>
</tr>
<tr>
<td>CNT-infiltrated</td>
<td>Polytetrafluoroethylene</td>
<td>High gas flux transport.</td>
</tr>
<tr>
<td>CNT-infiltrated</td>
<td>Polyvinylidene fluoride</td>
<td>Enhanced flux recovery ration.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Superior anti-biofouling properties.</td>
</tr>
</tbody>
</table>

3.2.5 Functionalization of Carbon Nanotubes for CNT-membranes

Depending on the purpose a CNT membrane is intended for, often the functionalization of CNT constitutes a precondition especially for membranes applied on water purification technologies. Pristine CNT

\textsuperscript{35}
usually aggregate resulting in significant decrease of water flux and pollutant rejection capacities of the CNT-membranes. Generally, CNT appear contaminated with metal catalysts, impurities and physical heterogeneities. Additionally, CNT are capped into hemisphere like fullerene type curvature during synthesis and purification. These capped CNT get unzipped into open tips after special treatment and may be oxidized into specific functional groups to trap selective pollutants as already mentioned. Different CNT-functionalization treatments can result in positive (−NH₃⁺), negative (−COO⁻, sulfonic acids) and hydrophobic (aromatic rings) groups on CNT surfaces. These special chemical groups may lead to CNT-membranes with selectivity for particular pollutant retention and increased water flux through the nanotube hole.

Commonly, functionalized CNT-membranes show good water permeability, mechanical and thermal stability, fouling resistance, pollutant degradation and self-cleaning properties.

CNT can also be decorated with various nanoparticles such as Cu, Ag, Au, Pt, Pd, TiO₂, polymers, and biomolecules (pollutant degradative enzymes, DNA and proteins) which have attractive membrane properties and thus broadened applications in water purification.

### 3.2.6 Quality-control factors of CNT-membranes

CNT-membranes constitute a novel “excellent” membrane technology, but several factors are hindering their commercialization. High-density CNT-membranes with uniform pore distribution may determine the future of the membranes.

In the case of all CNT-membrane types, modification of CNT-exterior surfaces can improve the trapping of filling materials into CNT interstitial spaces; attachment of functional groups via acidic, basic, and oxidizing agent creates binding sites also for multiple filling materials. Additionally, functionalization increases miscibility in the dope solution during fabrication of MM-CNT-membranes.

For optimum water purification in water treatment, pore size and CNT diameter are fundamental factors of crucial importance. Molecular modeling of VA-CNT-membranes has demonstrated that salt rejection capacity significantly decreases, increasing pore diameter (0.32 < 0.49 < 0.59 < 0.75 nm pore rejects 100% ≥ 100% ≥95% ≥58% salt,
respectively.\textsuperscript{57,88} Typical RO and NF membranes have pore diameters 0.6–0.8 and >1 nm, respectively. Thus, a CNT-membrane, in order to occupy the position of a RO membrane, should consist of CNT of ~0.6 nm in diameter.\textsuperscript{89} The density, pore architectures and thickness of CNT drastically affect membrane morphology, water permeability and retention capacity of the CNT-membranes. The membrane thickness and water permeability inversely relate with each other.\textsuperscript{90} Increasing membrane thickness decreases water flux and selectivity and \textit{vice versa}. Peer observation is necessary to grow aligned CNT by a suitable membrane synthesis process. CNT-tip opening and making filler impermeable are rate limiting steps in developing defects-free CNT-membranes in etching process during the fabrication process of VA-CNT and CNT-infiltrated-membranes. Corrosive etching treatment further damages the tubes, producing rough CNT-surfaces. Therefore, it is necessary to optimize all sensitive parameters to fabricate an ideal CNT-membrane for water purification or desalination.\textsuperscript{35}

### 3.2.7 From lab-scale to large-scale potential of CNT-membranes

\textbf{Figure 3.22} illustrates the fractionation capacity of RO, NF, UF and MF membranes. It is easily observable that the nano-porous cavities of CNT-membranes are suitable for rejecting micro-pollutants and ions in liquid phase. The hydrophobic hollow structures encourage frictionless movement of water molecules without the need of any energy-driven force to push water molecules through hollow tubes. The cytotoxic effects of CNT membranes decrease biofouling and increase membrane life by killing and removing pathogens.

Fabrication process of CNT-membranes and functionalization of CNT are factors influencing the selective rejection of particular pollutant from water mixture.\textsuperscript{85,87} The dense porous architectures of RO and NF membranes require pressure to force the water molecules to pass through them. UF and MF membranes consume less energy but retain only suspended particles. The hydrophobic hollow tubes of CNT provide strong invitation to polar water molecules.
The nano-scale pore-diameters reject salts and retain ions. More and above that, CNT membranes can be made highly reusable, less complex, durable, scalable, and eco-friendly without the need of complicated chemical transformation.\textsuperscript{35}

3.2.8 Barriers and challenges for a step forward of CNT-membranes

Provided some critical issues are effectively addressed, the CNT-membranes have chance to state as head in membrane technology for water purification. Existing barriers hinder their commercialization, namely, the complicated methods for the synthesis of CNT with uniform pore size and distribution\textsuperscript{92} at extremely narrow orifices. Only
SWCNT and DWCNT grown on epoxy or mixed composite matrices can administer in efficient water purification for the moment. However, both SWCNT and DWCNT are expensive and hence the large-scale and sustainable synthesis of such membranes is not cost-friendly. The use of MWCNT in CNT-membranes is a significantly cheap solution but such type of membranes that could be used in place of ultrafiltration with pore sizes of 2–50 nm.\textsuperscript{85}

Although each membrane technology has its own merits and demerits, the CNT-membranes have been evolved as an ideal water purification technology. It has displayed revolutionary performances and has the potential to be commercially viable in near future. The commercial availability of the CNT-membranes must meet certain criteria such as water permeability, desalination capacity, solute selectivity, robustness, antifouling properties, energy savings, material costs, scalability and compatibility with industrial settings.

Another important barrier associated to CNT-functionalization is the adding of appropriate functional groups at CNT tips. The closed tip-ends of CNT must get opened by appropriate chemical treatments for functional water transport. Selective oxidizing agents could be used to open CNT closed-tips followed by adding hydrophilic functionalities which have shown increased affinity for water entering into the tube and eventually enhanced ion selectivity. The affinity between functional groups and water molecules may promote the temporarily pause of water molecules around the functionalized regions. Thus, the functionalization is a rate limiting step which must be carefully optimized to tune the CNT-membrane permeability to water molecules and solutes. Other minor hurdles are associated with the presence of impurities in pristine CNT, like carbonaceous, contaminated metal catalysts, ash and amorphous carbon which should be eliminated prior to use in membrane fabrication.

Most of the water permeability and salt rejection tests of CNT-membranes have been evaluated through computational modeling rather than experimental evidences. The experimental proof of the \textit{in-silico} approaches is of critical importance to evaluate CNT membrane performance at the viable scale.

Last but not least, ecosafety and health issues are important concerns to be resolved. A basic principle of the CNT incorporated membranes is the efficient binding of CNT in these membranes to eliminate probable health risk associated with chances of product water getting
contaminated with CNT. Although there is least chance of CNT to escape from carefully-fabricated CNT-membranes, any abnormalities may cause the release of CNT into water and ultimately in the environment.\textsuperscript{35} Powerful techniques have to be developed for the control of any CNT release bound in the CNT-membranes.

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37 Lawrence Livermore National Laboratory – www.llnl.gov
Chapter 3

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63 International Desalination Association (IDA), Desalination in 2008 global marker snapshot, 21st GWI/International Desalination Association Worldwide Desalting Plant Inventory 2008
Chapter 3

Introduction to Carbon Nanotube Membranes


www.alting.fr

4.1 INTRODUCTION

The concept of BioNexGen project was the fabrication of a new class of functional membranes with enhanced properties regarding permeability, selectivity and fouling resistance -as mentioned in detail in the introductory chapter- by the subsequent embedment of hollow CNTs in the thin selective layer of commercial UF polymeric membranes, in a manner that hollow CNT-cavities constitute exclusively the pores, namely the selective barriers, of the active separation layer; this is characteristically depicted in Figure 4.1. In this effort to fulfil the BioNexGen project concept many research groups - project partners have contributed and in different ways, i.e. theoretical aspects and computational modeling, commercial membrane supply, production and functionalization of appropriate CNTs, toxicological studies of CNTs, preparation of antimicrobial coatings, preparation of hydrophilic coatings.
Figure 4.1 – Schematic representation of the BioNexGen project concept. A suspension of dispersed CNTs is filtered through an UF membrane with pore diameters ~40 nm. CNTs are encapsulated in the pores of the thin selective layer of the membrane and finally, an antimicrobial coating is applied stabilizing CNTs.

The scope of our contribution in the project plan as well as the basic part of the present thesis was to study the experimental parameters influencing the efficient binding of CNTs in the thin selective layer of the ultra-filtration membrane with pore diameters of ~40 nm in order to transform/render it to a nano-filtration one with pores to be defined exclusively by the hollow CNT-internal diameters (Fig. 4.2), with selectivity ranging over ~200–1000 Da aiming at the rejection of a variety of organic pollutants of industrial wastewaters, presented in Table 4.1. In this effort, Microdyn-Nadir GmbH – project partner was assistant supplying the commercial UF membranes. Furthermore, in the present thesis, additional efforts on the preparation of CNT-membranes were carried out and they are discussed later on.
Figure 4.2 – Schematic representation of the main target of our contribution to BioNexGen project concept. A dispersed bulk of CNTs is filtered through an UF membrane with pore diameters ~40 nm so that CNTs to be encapsulated in the pores of the thin selective layer of the membrane.

Table 4.1 – Organic compounds to be rejected from CNT-membranes of industrial wastewaters.

<table>
<thead>
<tr>
<th>Cosmetics industry</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Octylphenol ethoxylate</td>
<td>600Da</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>300Da</td>
</tr>
<tr>
<td>Triclosan</td>
<td>290Da</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Olive oil industry</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanilic acid</td>
<td>168Da</td>
</tr>
<tr>
<td>Tyrosol</td>
<td>138Da</td>
</tr>
<tr>
<td>p-Coumaric acid</td>
<td>164Da</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Textile industry</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive Black 5</td>
<td>991Da</td>
</tr>
<tr>
<td>Remazol Brilliant Blue R</td>
<td>630Da</td>
</tr>
<tr>
<td>Acid Red 4</td>
<td>380Da</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>320Da</td>
</tr>
<tr>
<td>EDTA</td>
<td>300Da</td>
</tr>
</tbody>
</table>
4.2 MATERIALS & CHARACTERIZATION

4.2.1 Commercial polymeric membranes

The commercial polymeric membrane to be modified was supplied by Microdyn-Nadir GmbH. It was a hydrophilic, flat-sheet ultra-filtration membrane, made of polyethersulfone (PES), manufactured by the phase separation process, on a non-woven polyethylene terephthalate (PET) substrate for enhanced mechanical strength. The polymers usually used for membranes in MBR application are hydrophobic, which makes these membranes susceptible to fouling in the bioreactor liquors they are filtering. This normally necessitates either modification of the base polymers or further modification of the membranes to produce a hydrophilic surface.\(^1\)\(^2\) To receive an initially hydrophilic membrane, hydrophilic additives can be added to the polymer solution, or the base polymer can be modified. An example for the modification is sulphonation of polysulfone. The other possibility to get a more hydrophilic surface is the additional modification by such techniques as chemical oxidation, organic chemical reaction, plasma treatment or grafting methods.\(^1\)\(^3\) These techniques feature the possibility to functionalize the membrane surface to meet the requirements for special applications, but they always imply an additional manufacturing step that increases the manufacturing costs.

The membrane porous structure was conserved with the pores filled up with glycerine; as such, in order to treat the membrane, the glycerine was rinsed, however, with caution just because the membrane should not be dried. Therefore, a certain process consisting of the following steps was being followed for the rinsing of glycerin, in order to possess an opened-pore functional membrane:

- Submersion of the membrane in 2-propanol solution 25% v/v for 1 h.
- Rinsing and sinking of the membrane in triply distilled water overnight.
- Final rinsing with 3D water.

A schematic representation and an image of the commercial PES membrane are given in Figure 4.3.
The selective layer exposed to the feed solution of the commercial PES membrane bore pores of average ~40 nm and in terms of rejection is characterized by a nominal MWCO* of 150 kDa* (*see chapter 1). The membrane is coded as “UP150” indicating the process of separation is produced for, by U:ultrafiltration, the material made of, by P:polyethersulfone, and the MWCO, by 150 in kDa. In Figure 4.4, the specifications of the membrane derived from Microdyn-Nadir product catalogue are illustrated.
Figure 4.4 – Specifications of UP150 membrane (Tables derived from Microdyn-Nadir product catalogue).

4.2.1.1 Characterization of the commercial PES membrane

For the understanding of the membrane structure, Scanning Electron Microscopy (SEM) was utilized and micrographs of the membrane surface and cross-section were collected. In order not to destroy the structure of the membrane for the cross-section imaging, cryogenic cuts of the samples were carried out sinking small specimens of membranes in liquid N\textsubscript{2} and carefully breaking the samples trying to avoid any eventual traumas. Representative SEM micrographs of the surface and the whole cross-section of UP150 membrane are shown in Figure 4.5.
Figure 4.5 – SEM micrographs of the surfaces of UP150 membrane: (a) pristine PES surface (before glycerin withdrawal), (b) PES active surface after glycerin rinsing allowing the observation of external pores and pore distribution, (c) total cross area of PES membrane including the substrate PET layer allowing the determination of the different layers’ thickness, (d) cross-section of membrane part indicating the selective PES layer (“skin layer”) and the finger-type membrane support structure, (e) & (f) cross-section and surface respectively, of non-woven PET (substrate) allowing the observation of the broad network upon which PES layer is casted.

The examination with SEM of the commercial PES membrane resulted in information-rich images regarding the membrane structure and morphology as described in the figure 4.5 caption. In a nutshell, the
membrane structure is characterized by the gradual increase of the pores from the “skin layer” of around 40 nm to a broad PES support and an even largely broadened PET network. This “finger-type” structure seemed to favor the extrusion of CNTs from the bottom of the membrane (i.e. the PET substrate) directly to the “skin layer” targeting at the encapsulation of CNTs in the narrow pores of the UF membrane that was the challenging main concept.

Therefore, Raman spectroscopy was implemented for the identification of the materials the membrane consisted of. The theoretical aspects of Raman spectroscopy are described in Chapter 6 of the present thesis. For the collection of backscattering Raman spectra, samples were excited with the 441.6 nm line of an air-cooled HeCd laser (Kimmon Electric Co.), and were collected by the UV-Vis Labram HR-800 spectrograph (J.Y-Horiba). The excitation laser power on the samples was 1.8 mW.

Raman spectra from the PES and PET surfaces were collected and are presented in Figure 4.6. The intense Raman bands of PES at 1145 and 1595 cm\(^{-1}\) are characteristic of the symmetric stretching vibration of \(\text{O=S=O}\) and of the para-di-substituted aromatic ring, respectively. The band at 3070 cm\(^{-1}\) is attributed to the aromatic C-H stretching and conclusively the whole spectrum features are typical of PES material.\(^4\)

![Figure 4.6 - Raman spectra from UP150 membrane. Raman spectra were collected both from PES selective layer and PET substrate.](image)

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Correspondingly, in the spectrum of the PET surface four main bands are observed at 1281, 1616, 1720 and 3080 cm$^{-1}$. The band at 1281 cm$^{-1}$ is attributed to the stretching vibration of C-O of the ester bond and the band at 1720 cm$^{-1}$ to the C=O stretching. Finally, the bands at 1616 and 3080 cm$^{-1}$ certify the existence of the benzene ring in the chemical structure of the sample. Table 4.2 corresponds to the tentatively Raman band assignment of the main observed frequencies.

<table>
<thead>
<tr>
<th>Characteristic wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES:</td>
<td></td>
</tr>
<tr>
<td>1145 vs</td>
<td>O=S=O sym. stretch</td>
</tr>
<tr>
<td>1595 s</td>
<td>Benzene ring</td>
</tr>
<tr>
<td>3070 m</td>
<td>Aromatic C-H stretch</td>
</tr>
<tr>
<td>PET:</td>
<td></td>
</tr>
<tr>
<td>1281 m</td>
<td>-(C=O)-O-C as. stretch</td>
</tr>
<tr>
<td>1616 vs</td>
<td>Benzene ring</td>
</tr>
<tr>
<td>1720 s</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>3080 m</td>
<td>Aromatic C-H stretch</td>
</tr>
</tbody>
</table>

Abbreviations: vs=very strong, s=strong, m=medium

### 4.2.2 Carbon Nanotubes

A variety of carbon nanotubes, SW-CNTs, DW-CNTs, Thin-MW-CNTs and MW-CNTs, with different features concerning the diameters, the length and the existence or/not of chemical functionalities, were utilized in the study aiming at the efficient binding of CNTs into the pores of the commercial PES membrane. The major amount of the CNTs used, were supplied by Nanothinx S.A. – project partner, while pristine SW- and DW-CNTs were purchased from Cheap Tubes Inc. CNTs supplied by Nanothinx S.A. were prepared by the catalyzed chemical vapor deposition (CCVD) method under pressure equal to 1 atm and temperature at 600-900 °C. The carbon sources were either hydrocarbons or alcohols while the catalysts constituting the determinant parameters of the dimensions of the external and internal CNT-diameters are IP protected by patent.

### 4.2.2.1 Characterization of CNTs

Furthermore, laser Raman spectroscopy was implemented for the characterization of the CNTs. For the collection of backscattering
Raman spectra, bulk CNTs in powdered form were excited with the 441.6 nm line of an air-cooled HeCd laser (Kimmon Electric Co.), and were collected by the UV-Vis Labram HR-800 spectrograph (J.Y-Horiba). The excitation laser power on the samples was 1.8 mW. **Figure 4.7** illustrates the Raman spectrum of SW-CNTs of high purity (>98%).

![Raman Spectrum of SW-CNTs](image)

**Figure 4.7** – Typical Raman spectrum of SW-CNTs of high purity.

The Raman band at 1340 cm\(^{-1}\) corresponds to the D band (diamond) indicating the existence of either amorphous carbon or disorders in the carbon nanotube structure and is an evidence for the existence of functionalities on the graphitic surface.\(^6\),\(^7\) The G band (graphite) at 1593 cm\(^{-1}\) is attributed to tangential elastic movement of C-C bond among the nearest neighbors along the nanotube axis (G\(^+\), longitudinal optic vibrational mode). Depending on the quality of the carbon nanotube, a shoulder at 1543 cm\(^{-1}\) assigned to the tangential vibration of carbon atoms perpendicular to the nanotube diameter, is present.\(^8\) The G band is an evidence for the crystallinity of the nanotube grid and it is independent of the CNT diameter. Finally, the band at 2640 cm\(^{-1}\), G\(^'\), corresponds to the second order harmonic of D.\(^9\)

SW-CNTs show also Raman bands at the region of low frequencies attributed to radial breathing modes (RBM) of the molecules and they give indirect information for the CNT-diameter.\(^10\) In the spectrum of
Figure 4.7, the band at 270 cm$^{-1}$ verifies the homogeneity of the sample concerning the CNT-diameters. Theoretical studies have predicted that the RBM band frequencies are associated to the CNT-diameters and this correlation may be expressed by:

$$\omega_r = A/d \quad (Eq. \ 4.1)$$

where, \(\omega_r\) is the Raman frequency the RBM bands appear in cm$^{-1}$, \(A\) is a constant dependent of the excitation line used for the spectrum collection and fluctuates in the range over 218-248 cm$^{-1}$ and \(d\) is the isolated SW-CNT diameter in nm.$^{11}$

Concerning the spectrum of Figure 4.7, the use of Equation 4.1 for the RBM at 270 cm$^{-1}$, results in CNT-diameter of 0.92 nm. Given that the equation is predicted for an isolated SW-CNT and bulk SW-CNTs are encountered in arrays and the existence of interactions is present, the equation predicts an increase of the final result of ~7% for CNTs with $0.7<d<1.5$ nm.

Figure 4.8 illustrates both Raman spectra of SW- and MW-CNTs used for the study. For the SW CNTs, the Raman bands are typical of SW-CNTs as described earlier. Concerning the spectrum of SW-CNTs, the RBM bands appear at 168, 187 and 245 cm$^{-1}$ that means that the CNT diameters are equivalent to 1.48, 1.33 and 1.01 respectively, as arouse by using the Equation 4.1.

![Raman spectra of SW-CNTs and MW-CNTs](image)

Figure 4.8 – Raman spectra of SW-CNTs and MW-CNTs. The RBM bands of the SW-CNTs appeared at 168, 187, and 245 cm$^{-1}$. 
The ratio of the Raman relative intensities, $I_D/I_G$, determines the crystallinity quality of the nanotubes. The lower the value, the less the defects on the nanotube grid and consequently the higher the crystallinity, resulting in CNTs of better quality.

Therefore, Raman spectra were collected for the characterization of all types of CNTs utilized for the membrane modification. In Figure 4.9 Raman spectra of Thin MW-CNTs with different functionalities are presented. The functionalization of the CNTs with hydroxyl-groups (-OH) and/or carboxyl-groups (-COOH) was done in order the CNT hydrophobicity to be decreased and no degradation of the quality of the tubes was observed as indicated from the following $I_D/I_G$ values presented in Table 4.3.

![Figure 4.9](image)

**Figure 4.9** – Raman spectra of Thin MW-CNTs with different or no functionalities used for the membrane modification.

**Table 4.3** – The CNT types used in the study, their Raman bands and the ratio $I_D/I_G$.

<table>
<thead>
<tr>
<th>CNT type</th>
<th>Raman bands cm$^{-1}$, D - G</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin MWCNTs</td>
<td>1346 – 1575</td>
<td>0.980</td>
</tr>
<tr>
<td>Thin MWCNT-OH</td>
<td>1345 - 1575</td>
<td>0.994</td>
</tr>
<tr>
<td>Thin MWCNT-COOH</td>
<td>1345 - 1575</td>
<td>0.997</td>
</tr>
<tr>
<td>Thin MWCNT-OH-COOH</td>
<td>1350 - 1580</td>
<td>0.991</td>
</tr>
</tbody>
</table>
4.2.2.2 Length-decrease of CNTs

Pristine carbon nanotubes generally appear in bundles of long arrays with closed cupped ends that despite their exceptional intrinsic features make it difficult to employ at their best in a variety of applications. In order to limit this condition, CNTs may be cut to decrease their length and the closed ends to get opened that is obligatory in many cases. Two main methods have been developed for the CNT-cutting: the chemical modification by the use of acids and the mechanical modification by the use of tip sonication.

Since for the present study, the length of the nanotubes should be diminished and the cupped ends to be opened in order to fulfil the main target concerning their embedment in the thin selective layer of the polymeric membrane, both of the modification methods were employed. Thin MW-CNTs (purity 94%, length: ≥10 μm, external (ex.) diameter: 6-15 nm) and MW-CNTs (purity 97%, length≥10 μm, ex. diameter: 15-35 nm) were used for this study. SEM was employed for the characterization of the initial and the final length.

The mechanical modification was accomplished by the use of tip sonicator (UP400S Hielscher Co.) operating at 400 Watt, 24 kHz. In liquid, the rapid vibration of the tip causes cavitation, the formation and violent collapse of microscopic bubbles. The collapse of thousands of cavitation bubbles releases tremendous energy in the cavitation field. Objects and surfaces within the cavitation field are “processed”. By increasing the amplitude setting, cavitation intensity within the sample is also increased.

Aqueous suspensions of CNTs of concentration 10 μg/mL were prepared and tip-sonication was employed performing at 35% of the device amplitude for 5 different time periods: 2 min, 15 min, 30 min, 1h and 2 h. Thereafter, the suspensions were collected and filtered for the collection of dry CNTs. The CNTs were spin-coated on a mica substrate and were examined through SEM imaging. The results regarding the final length of the mechanically-treated CNTs are summarized in Table 4.4. SEM micrographs of the samples before and after being suffered both mechanical and chemical treatments are presented in Figure 4.10.
Table 4.4 – Time of mechanical treatment process CNTs underwent by the use of the tip sonication for CNTs cutting and the resulting lengths.

<table>
<thead>
<tr>
<th>Time of treatment process</th>
<th>Resulting lengths of Thin MW/MW-CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2min</td>
<td>≥10 μm</td>
</tr>
<tr>
<td>15min</td>
<td>800 nm - 2 μm</td>
</tr>
<tr>
<td>30min</td>
<td>450 nm - 1 μm</td>
</tr>
<tr>
<td>1h</td>
<td>350 - 900 nm</td>
</tr>
<tr>
<td>2h</td>
<td>350 - 700 nm</td>
</tr>
</tbody>
</table>

The chemical treatment of the CNTs was carried out by the use of acids. Particularly, 2 mg of Thin MW-CNTs in powdered form were added in a beaker containing 8 mL of acid mixture H$_2$SO$_4$/HNO$_3$ in the ratio 3:1 and was placed into sonication water bath operating at 35-40 °C for 6 h. The resulting suspension was diluted by water and CNTs were filtrated and rinsed with NaOH solution 10mM, and finally collected. SEM micrographs were collected indicating that the chemical treatment process led to CNT-length ~320 nm near the values that mechanical treatment leads to (average ~500 nm).
Figure 4.10 – SEM micrographs of: (a) Thin MW-CNTs before treatment, (b) MW-CNTs before treatment (other magnification), (c) Thin MW-CNTs after mechanical treatment for 2 h, and (d) Thin MW-CNTs after chemical treatment.

4.2.2.3 Functionalization-CNT dispersion

CNTs are characteristic of small diameter with high aspect ratio and thus possessing large surface area. Even chemically or mechanically-treated, CNTs appear in heavily entangled bundles resulting in inherent difficulties in dispersion in polymer matrices, in organic solvents and in aqueous solutions. To resolve those problems, it has been directed towards developing methods to modify surface properties of CNTs. These approaches can be divided into chemical (covalent) and physical (non-covalent) functionalization as interactions between active materials and CNTs. Both chemical and physical functionalizations were employed to enhance the dispersion of CNTs for the sake of the CNT-embedment studies in polymer matrixes with different approaches discussed in the present thesis.

Chemical functionalization is based on the covalent bond of functional groups onto carbon form of CNTs. It can be performed at
the end caps of nanotubes which tend to be composed of highly reactive, as compared with the side walls. The sidewall themselves contain defect sites such as pentagon-heptagon pairs called Stone-Walls defects, $sp^3$-hybridized defects, and vacancies in the nanotube lattice (Figure 4.11). Direct covalent functionalization is associated with a change of hybridization from $sp^2$ to $sp^3$ and a simultaneous loss of $p$-conjugation system on graphene layer. This process can be made by reaction with some molecules of a high chemical reactivity.

![Figure 4.11 – Covalent functionalization of CNTs on defect sites.](image)

Another method is **defect functionalization of CNTs**, this method was the one employed for the CNT-functionalization with -OH and –COOH groups of the CNTs used in the present study. The surface intrinsic defects are supplemented by oxidative damage to the nanotube framework by strong acids which leave holes functionalized with oxygenated functional groups. In particular, treatment of CNTs with strong acid such as HNO$_3$, H$_2$SO$_4$ or a mixture of them, tends to open these tubes and to subsequently generate hydrophilic oxygenated functional groups that exhibit a higher affinity with water molecules.

The CNTs are functionalized **non-covalently** by aromatic compounds, polymers, and surfactants, employing $\pi-\pi$ stacking or hydrophobic interactions for the most part. In these approaches, the non-covalent modifications of CNTs can do much to preserve their desired properties, while improving their solubility quite remarkably. Aromatic molecules, such as pyrene, porphyrin, and their derivatives, can and do interact with the sidewalls of CNTs by means of $\pi-\pi$ stacking interactions, thus opening up the way for the non-covalent
functionalization of CNTs. Polymers, especially conjugated polymers, have been shown to serve as excellent wrapping materials for the non-covalent functionalization of CNTs as a result of $\pi-\pi$ stacking and of van der Waals interactions between the conjugated polymer chains containing aromatic rings and the surfaces of CNTs.\textsuperscript{19}

In addition, surfactants were used to functionalize CNTs. The physical adsorption of surfactant on the CNT-surface, lower the surface tension of CNTs that effectively prevent their aggregation. Furthermore, the surfactant-treated CNTs overcome the van der Waals attraction by electrostatic/steric repulsive forces. Sodium dodecyl sulfate (SDS) is an anionic surfactant with the formula $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$. It consists of a 12-carbon tail attached to a sulfate group giving it amphiphilic properties and was extensively used for the dispersion of CNTs in the ratio 1:1 (SDS:Thin MW/MW-CNTs) or 1.5:1 (SDS:SW-CNTs), in the aqueous media prepared. Another surfactant employed was the poloxamer 407 which is a non-ionic surfactant. It is a triblock copolymer consisting of a central hydrophobic block of polypropylene glycol (propylene glycol block: 56 repeat units) flanked by two hydrophilic block of polyethylene glycol (total PEG blocks: 101 repeat units). Poloxamer 407: CNTs ratio was the same as the SDS:CNTs.

However, even functionalized CNTs did not show the “excellent” dispersion demanded in many cases in aqueous mediums. This is due to hindrances discussed in the following subchapters.

**4.3 INFILTRATION OF CNTs THROUGH COMMERCIAL PES MEMBRANES**

The membrane cross-area structure and morphology as examined by SEM seemed to favor the extrusion of CNTs from the wide porosity of the PET substrate towards the edges of the “finger-type” membrane channels until their final encapsulation/protrusion at/from PES selective layer’s-40-nm-pores using filtration methods. The PES membrane was placed in a dead-end filtration apparatus in a manner that the PET substrate to be exposed to the feed stream so that CNTs to enter the membrane porosity from the wide network of the membrane in order to encapsulate to the narrow-pore PES surface area. The process was followed by the simultaneous use of the tip sonicator (see 4.2.2.2) operating in the CNT-suspension (feed solution), an additional process within the filtration process,
contributing to the alignment and the impulse of CNTs towards the membrane pores. Round-shaped specimens 4.7 cm in diameter cut from the flat sheet membrane were appropriate to match the cylinder funnel of the vacuum filtration apparatus (Supelco®) (300 mL volume); this allowed an active membrane surface 3.5 cm in diameter to be infiltrated. The membranes were left on a rigid stainless steel sieve and the apparatus was equipped with a pressure gauge. Pressurized nitrogen gas was applied to limit the vacuum of the pump at 0.5 bar due to the limitation for the proper operation of the membrane; a note is made of the fact that the membrane supplier indicated a value of the negative pressure of <0.7 bar to be applied for the procedure. A schematic representation of the experimental setup for the CNT-infiltration process is illustrated in Figure 4.12.

![Figure 4.12](image)

**Figure 4.12** - Schematic representation of CNT infiltration process through the PES membrane followed by a diagram describing the experimental setup.
Preliminary experiments\textsuperscript{20} were carried out filtrating CNTs dispersed in ethanol (EtOH). Different types of CNTs regarding the functionalities possessed and different suspensions regarding the amount of CNTs dispersed in the EtOH media (i.e. CNT concentration) as well as different volumes of CNT dispersions were used. EtOH was selected as the dispersant, since CNTs seemed to disperse homogeneously in EtOH suspensions. SEM micrographs were collected from cross sections of the CNT-infiltrated membranes in order to investigate both the path in the cross-area of the membrane, CNTs followed during the filtration process, and any eventual deterioration effect of the membrane structure associated to the use of EtOH as dispersant and subsequently as feed solution. In Figure \textbf{4.13}, such SEM micrographs are presented.
Figure 4.13 – SEM micrographs in cross-section of PES membranes infiltrated with CNTs in EtOH of different volumes and concentration: (a) MWCNT-OH, 40 mL, 3 μg/mL, (b) MWCNT-OH, 120 mL, 3 μg/mL, (c)
MWCNT-OH, 400 mL, 12.5 μg/mL, (d) MWCNT-OH, 600 mL, 12.5 μg/mL, (e) MWCNT-OH, 40 mL, 50 μg/mL, (f) same as e., (g) Thin MWCNT-OH (SDS), 40 mL, 12.5 μg/mL, (h) as g. (The red arrows indicate the CNTs).

Examination with SEM, allowed the collection of important information concerning CNT infiltrations. Mainly, CNTs were always observed to reach the skin selective layer in the pore structure of the PES membranes but only in few cases they managed to protrude from the surface pores. Additionally, EtOH appeared to affect the membrane material provoking swelling effects, an issue discussed also in the literature by Roy et al.\textsuperscript{21} Thus, alternative approaches were performed and they are presented in the following subsection.

### 4.3.1 Infiltration of CNTs dispersed in aqueous suspensions

The previous preliminary study showed that the use of alcohols as dispersants ended to the deterioration of membrane due to swelling effects since the PES structure did not show excellent resistance to EtOH. Consequently the use of water as dispersant resulted mandatory. Thus, all the infiltration processes that followed, for the encapsulation of the CNTs into the selective layer’s pores, presupposed the preparation of CNT-aqueous-suspensions. The 200 mL CNT-suspensions reached homogeneity by the use of tip-sonicator for 15 min in beakers of 300mL prior to infiltration.

Additionally, a variety of parameters were addressed in order to efficiently infiltrate the CNTs through the PES membrane in terms of water permeability and retention/rejection capacity/efficiency, which are listed as:

- **Type of CNTs**: Only certain types of CNTs with respect to their diameters were appropriate for the rejection of small organic molecules of molecular weight ranging from ~200-1000 Da. The transformation of the UF membrane to a NF one preconditioned the decrease of the pores from ~40 nm to less than 2 nm (Figure 4.14). The succeeded transformation would be guaranteed exclusively by using SW-CNTs with internal diameters in the range 0.8-1.6 nm and probably DW-CNTs with 1-2 nm respectively. However, even with use of Thin MW-CNTs bearing internal
diameters ranging from 1-6.5 nm, the rejection target could be approached, whereas MW-CNTs with external diameters 15-35 nm would not even be able to penetrate the ~40-nm-pores. Thereafter, there was a broad variety of available CNTs to be employed. The type and the features of the CNTs used for the infiltration studies are presented in **Table 4.5**.

**Figure 4.14** – Schematic illustration of the rejection capacity the transformation of a UF membrane to a NF one would bring in with use of CNTs bearing appropriate internal diameters.\(^{22}\)
Table 4.5 – Type and features of CNTs tested for the infiltration study.

<table>
<thead>
<tr>
<th>Type of CNT</th>
<th>Carbon purity (％)</th>
<th>External diameter (μm)</th>
<th>Internal diameter (μm)</th>
<th>Length (μm)</th>
<th>Price (1 gram) (€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW (Cheap Tubes)</td>
<td>&gt;90</td>
<td>1-2</td>
<td>0.8-1.6</td>
<td>5-30</td>
<td>90</td>
</tr>
<tr>
<td>SW-COOH</td>
<td>&gt;90</td>
<td>1-2</td>
<td>0.8-1.6</td>
<td>5-30</td>
<td>90</td>
</tr>
<tr>
<td>DW (Cheap Tubes)</td>
<td>&gt;90</td>
<td>2-4</td>
<td>1-2</td>
<td>5-15</td>
<td>60</td>
</tr>
<tr>
<td>Thin MW (Nanothinx)</td>
<td>94</td>
<td>6-15</td>
<td>1-6.5</td>
<td>≥10</td>
<td>16</td>
</tr>
<tr>
<td>Thin MW-OH (Nanothinx)</td>
<td>94</td>
<td>6-15</td>
<td>1-6.5</td>
<td>~0.6</td>
<td>36</td>
</tr>
<tr>
<td>Thin MW-COOH (Nanothinx)</td>
<td>94</td>
<td>6-15</td>
<td>1-6.5</td>
<td>≤1</td>
<td>31</td>
</tr>
<tr>
<td>MW (Nanothinx)</td>
<td>97</td>
<td>15-35</td>
<td>3.5-12.5</td>
<td>≥10</td>
<td>14</td>
</tr>
</tbody>
</table>

(The lengths of the CNTs given in the table are before CNTs suffer tip sonication)

Membrane conformation in the filtration apparatus: as mentioned before, the membrane structure seems to favor the intrusion of CNTs from the broad formed substrate porosity to reach the pores of the skin layer. However, both the configuration aforementioned and the reverse one (i.e. the selective layer exposed to the feed during filtration) were tested to ensure the efficient CNT hooking into the membrane pores (Figure 4.15). On occasion, both the processes were performed.

Figure 4.15 – Filtration processes were performed with either the substrate to be exposed to the CNT suspension (a) or inversely, the selective layer to be exposed to the feed suspension (b).
**The volume of the feed solution (i.e. the CNT-suspension) and the concentration of the CNT-suspensions to be infiltrated through the polymeric membrane**: The capacity of the filtration cylinder determined the volume of the suspension to be infiltrated. The addition of the tip-sonicator operating during the filtration process limited the volume of the suspensions due to the preconditions required in terms of the sonicator-probe position in order to operate properly. Thus, the volume of the feed suspension determined at 250 mL allowing the permeance of 50 mL for each infiltration. With respect to the concentration of the CNT-suspensions, a broad range of concentration studied, ranging from 0.078 μg/mL to 150 μg/mL in an effort to cover the whole active surface of the membrane with CNTs.

**The position of the tip-sonicator-probe**: The distance of the sonicator-probe from the membrane surface seemed to be an important parameter to be studied for the efficient transport of CNTs from the substrate to the skin layer. The probe should both not to affect the membrane surface and at the same time to contribute positively to the CNT-diffusion through the conical-shaped membrane porosity. Thereafter, the distance of the edge of the probe to the membrane surface determined to be at 5 cm (Figure 4.11). Additionally, this distance ensured that the membrane remained unaffected after the sonication-filtration process. For any eventual effect concerning pore-dilation or membrane rip due to sonication, was examined thoroughly with the use of optical microscope and SEM. Additionally, theoretical aspects and computer modelling were performed with the 3D reconstruction of the active layer of the polymeric membrane and the motion of the CNTs as they approach the membrane were simulated by V. Burganos and E. Skouras (ICE/HT) in the context of BioNexGen. Numerical techniques developed that may identify conditions for selective deposition of the CNTs at the tip of the entrance face.

The determination of the parameters influencing the efficiency of the CNT-infiltration process was extracted though a vigorous effort to conceive the CNT-infiltration effect on the membrane by experimental observations in terms of visual and microscopic imaging. The black imprint of CNTs in the skin layer when imported from the substrate side was a clear indication that CNTs had followed the right path to reach the pores of the membrane. A representative assistant-illustration is depicted in Figure 4.16. The efficiency of the prepared
CNT-infiltrated membranes were initially tested in terms of water flux and selectivity measurements of aqueous solutions of the dye molecule Blue R (MW: 320 Da) and a model textile wastewater consisted of a mixture of Remazol Brilliant Blue R (MW: 630 Da) & Acid Red 4 (MW: 380 Da) in equal concentrations (50 μg/mL). Respective measurements are presented further on.

**Figure 4.16** – The infiltration process carried out by filtering a CNT-suspension from the support side (left) to reach the selective layer (right). The black imprint of CNTs on the side of the selective layer is clear indicating their existence to the surface pores while the substrate is empty of CNTs indicating that all CNTs were pushed towards the PES skin layer.

In **Tables 4.6, 4.7, 4.8 & 4.9** various efforts of the CNT-infiltration through the commercial membrane are summarized with respect to the membrane configuration, the number of the samples, the type of the CNTs used, the type of the surfactant for the dispersion of CNTs used, the concentration of the CNT-suspension prepared, and the amount of CNTs calculated to have covered the membrane surface per cm².

**Table 4.6** – Factors studied for the infiltration of SWCNTs from the PET substrate.

<table>
<thead>
<tr>
<th>CNT type</th>
<th>Concentration (μg/mL)</th>
<th>Surfactant</th>
<th>CNT area (μg/cm²)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW</td>
<td>0.312</td>
<td>SDS</td>
<td>1.6</td>
<td>12</td>
</tr>
</tbody>
</table>
### Table 4.7 – Factors studied for the infiltration of Thin MWCNTs from the PET substrate.

<table>
<thead>
<tr>
<th>CNT type</th>
<th>Concentration (μg/mL)</th>
<th>Surfactant</th>
<th>CNT area (μg/cm²)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin MW</td>
<td>10</td>
<td>SDS</td>
<td>52.1</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 4.8 – Factors studied for the infiltration of SWCNTs through the PES selective layer.

<table>
<thead>
<tr>
<th>CNT type</th>
<th>Concentration (μg/mL)</th>
<th>Surfactant</th>
<th>CNT area (μg/cm²)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW</td>
<td>0.312</td>
<td>SDS</td>
<td>1.6</td>
<td>11</td>
</tr>
<tr>
<td>SW</td>
<td>0.625</td>
<td>SDS</td>
<td>3.2</td>
<td>14</td>
</tr>
<tr>
<td>SW</td>
<td>1.25</td>
<td>SDS</td>
<td>6.5</td>
<td>8</td>
</tr>
<tr>
<td>SW</td>
<td>2.5</td>
<td>SDS</td>
<td>13</td>
<td>10</td>
</tr>
<tr>
<td>SW</td>
<td>5</td>
<td>SDS</td>
<td>26</td>
<td>5</td>
</tr>
<tr>
<td>SW</td>
<td>10</td>
<td>SDS</td>
<td>52.1</td>
<td>4</td>
</tr>
<tr>
<td>SW</td>
<td>100</td>
<td>SDS</td>
<td>384.6</td>
<td>5</td>
</tr>
</tbody>
</table>
Table 4.9 – Factors studied for the infiltration of Thin MWCNTs through the PES selective layer.

<table>
<thead>
<tr>
<th>CNT type</th>
<th>Concentration (μg/mL)</th>
<th>Surfactant</th>
<th>CNT area (μg/cm²)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-PGMA</td>
<td>10</td>
<td>SDS</td>
<td>52.1</td>
<td>8</td>
</tr>
<tr>
<td>Thin MW-COOH</td>
<td>0.312</td>
<td>SDS</td>
<td>1.6</td>
<td>5</td>
</tr>
<tr>
<td>Thin MW-COOH</td>
<td>50</td>
<td>SDS</td>
<td>192.3</td>
<td>4</td>
</tr>
<tr>
<td>Thin MW-COOH</td>
<td>100</td>
<td>SDS</td>
<td>384.6</td>
<td>10</td>
</tr>
<tr>
<td>Thin MW-OH</td>
<td>0.312</td>
<td>SDS</td>
<td>1.6</td>
<td>4</td>
</tr>
</tbody>
</table>

Concerning the membranes grafted with CNTs by filtration through the substrate, the parameter of the sonication-probe position as well as of the concentration of the CNT-suspensions seemed to favor the intrusion of CNTs towards the selective layer. Representative images are illustrated in Figures 4.17, 4.18 and 4.19 noting the CNTs-imprint on the PES surface when the infiltrations carried out from the substrate.
Figure 4.17 – Infiltrated membranes with SWCNT-COOH in the concentration range 0.5-10 μg/mL. The black imprint on the selective layer appears to increase gradually with the suspension-concentration increase (left) whereas the PET substrates the infiltrations carried out from remain “clear”.
Figure 4.18 – Commercial membranes grafted with either Thin MWCNT-COOH or SWCNTs from the substrate, the selective layer or both. The images show the selective surfaces in all cases.

Figure 4.19 – Commercial membranes grafted with Thin MWCNT-OH-COOH of concentration 1.25 μg/mL, from the PET substrate. (a) PES selective layer & (b) PET substrate.

Thereafter, groups of the prepared CNT-grafted-membranes were evaluated in terms of Scanning Electron Microscopy (SEM), Atomic
Force Microscopy (AFM), Raman Spectroscopy, water flux measurements and rejection tests. In the following subsection the characterization and evaluation of the membranes is presented.

### 4.3.2 Treatment of carboxyl acid-functionalized CNTs

CNTs with their high van der Waals force, surface area and high aspect ratio inevitably cause self-aggregation. In aqueous suspensions, they tend to cohere due to their high surface energy and lack of chemical affinity with the dispersing medium. Even oxidized CNTs after carboxyl-functionalization show limited dispersion stability in aqueous media for long time periods. Further treatment of oxidized CNTs may improve the dispersion of CNTs in aqueous dispersants facilitating the CNT-infiltrations through porous membranes. In this context, in order to obtain stable aqueous dispersions of CNTs for long time periods, deprotonation of Thin-MWCNT-COOH and SWCNT-COOH was carried out by treatment with an aqueous NaOH solution and their dispersion stability was examined.

For the substitution of the carboxylic acid groups (-COOH) with carboxyl anion groups (-COO$^-$), 500 mg of carboxylated CNTs were grinded in an agate mortar and diluted in 400 mL TDW, stirred and filtrated by a polycarbonate membrane (pore size: 0.4 μm). Afterwards, the CNTs were re-dispersed in 400 mL TDW and filtered again. Next, CNTs were mixed under ultrasonication with 50 mL of 10 w/v aqueous NaOH solution three times (Fig. 4.20) Filtering, washing with TDW and re-dispersion were repeated at least 5 times until the pH of the filtrate reached near 7.0.
After complete drying in oven at 90 °C, the deprotonated CNTs were placed in 20 mL of aqueous solutions in the composition 100 μg/mL and tip-sonicated for 2 min. Finally, the dispersions were left in stable position for 5 months.

The investigation of the dispersion state of CNTs in liquids is quite difficult due to its opaque blackness even at very low concentration. However, distinguishable visible change of the darkness of the CNT suspensions prepared took place only few hours later and remained similar for several months (Fig. 4.21).

Two comparative studies between Thin MWCNTs and same CNTs functionalized with carboxyl groups, and between SWCNTs and carboxyl-functionalized CNTs, by the use or not of surfactant, were carried out. The observation of the dispersions of the CNT-suspensions was evaluated by means of UV-Visible absorbance (Fig. 4.22) and zeta-potential measurements (Table 4.10) that were carried out after 5 months in order to observe the eventual long-term stability.
Figure 4.21 – Digital photographs of CNT-suspensions of pristine and modified CNTs 5 months after the treatment process. The most stable suspensions are presented in frames.

Judging from the photographs, the CNTs, either Thin MWCNTs or SWCNTs bearing carboxylic anions showed much improved stability in water due to the chemical affinity between the polar modified groups and water and the electrostatic repulsion.

Figure 4.22 – UV-Vis absorption spectra of CNT-suspensions treated and dispersed in different methods.
The UV-Vis absorption spectra indicated that the carboxylated CNTs with anion groups showed enhanced dispersion compared to the pristine or carboxyl-functionalized CNTs.

The origin of electrostatic repulsion can be found from the increased zeta potential ($\zeta$) carboxylated CNTs presented. The $\zeta$ is an important indicative of ionically stabilized colloid systems. Greater magnitude (usually $\pm 25$ mV) of the $\zeta$ endows the colloid system with an improved stability against coagulation. In Table 4.10 the values of $\zeta$ of the CNT-suspensions are presented.

**Table 4.10 – Zeta potential values for the different CNT-suspensions.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin MWCNT Poloxamer 407</td>
<td>-8.51</td>
</tr>
<tr>
<td>Thin MWCNT-COO(^{-})</td>
<td>-37.1</td>
</tr>
<tr>
<td>Thin MWCNT-COO(^{-}) Poloxamer 407</td>
<td>-28.4</td>
</tr>
<tr>
<td>Thin MWCNT-COO(^{-})</td>
<td>-41.1</td>
</tr>
<tr>
<td>Thin MWCNT-COO(^{-}) Poloxamer 407</td>
<td>-30.6</td>
</tr>
<tr>
<td>SWCNT-COO(^{-})</td>
<td>-31.7</td>
</tr>
<tr>
<td>SWCNT-COO(^{-}) Poloxamer 407</td>
<td>-25.6</td>
</tr>
<tr>
<td>SWCNT-COO(^{-})</td>
<td>-32.2</td>
</tr>
<tr>
<td>SWCNT-COO(^{-}) Poloxamer 407</td>
<td>-30.1</td>
</tr>
</tbody>
</table>

For the infiltration studies, also carboxyl-functionalized with anion groups Thin MW and SW CNTs were utilized.

### 4.3.3 Characterization of the CNT-infiltrated membranes

Zeiss SUPRA 35VP scanning electron microscope was implemented for providing visual information of the top surface and cross-sectional morphology of the CNT-infiltrated-membranes. The membrane samples were cut into small pieces and left dry. For cross-sectional images, the pieces were dipped in liquid nitrogen for 2 min, frozen and broken to two slices and kept in air for drying. The dried samples were glued on the support and gold sputtered to create electric conductivity. Representative SEM micrographs collected from the PES porous surfaces as well as from the membrane cross area are illustrated in Figures 4.23, 4.24 & 4.25.
Figure 4.23 – (a),(b) PES surface of membrane grafted with Thin-MW-COOH (conc. 5μg/mL), (c),(d),(e),(f) PES cross section of membrane grafted with Thin-MW-COOH (conc. 5μg/mL). The samples were CNT-infiltrated from the PET substrate.
Figure 4.24 – (a),(b) PES cross section of membrane grafted with Thin-MW-OH (conc. 1.25 μg/mL). The samples were CNT-infiltrated from the PET substrate.
Chapter 4  

CNT-infiltrated commercial membranes

For the membranes infiltrated through the support side, as one may notice through SEM micrographs, only few CNTs seem to protrude the surface area (Fig. 4.20) while the majority of the CNTs appeared to stack just before reaching the porous skin layer of the membrane (Figs. 4.20, 4.21). Therefore, the black imprint of CNTs on the surface of the membranes was attributed to their existence beneath the ~2 μm skin layer. In Figure 4.25, the CNTs appear to lie on the PES surface while some of them appear to have entered the membrane pores.

To elucidate the influence of CNTs addition on membrane roughness, Atomic Force Microscopy (AFM) was employed to analyze the surface morphology and roughness of the prepared membranes. The AFM measurements were carried out by Dr. Daniel Jonson at Swansea University, College of Engineering at the lab of Prof Nidal Hilal (Editor of Desalination). The membrane surfaces in few cases showed an enhancement of the Root mean square roughness (RMS roughness) of the samples that had been grafted with CNTs. In Figure 4.26 the AFM topography of the PES surfaces of an unmodified (pristine) membrane

**Figure 4.25** – (a),(b) PES surface of membrane grafted with Thin-MW-COOH (conc. 1.25 μg/mL), (c),(d) cross-sectional images from the same samples. The samples were CNT-infiltrated towards the PES selective layer.
and of a membrane infiltrated from the support side with SW CNTs are presented. In the images, the brightest areas indicate the highest point of the membrane surface and the dark regions show valleys or pores. The enhancement of the RMS roughness of ~5 nm was revealed through images, which is probably attributed to the CNT presence on the membrane surface.

**Figure 4.26** – AFM topography images: (a) Pristine Commercial UP150 membrane and (b) UP150 membrane infiltrated with SWCNTs (conc. 3 μg/mL). Down and left, RMS roughness of the pristine and the CNT-infiltrate-membrane are compared).

In addition, laser Raman spectroscopy was implemented for the characterization of the CNT-membranes. Backscattering Raman
spectra collected of bulk SWCNTs and Thin MWCNT-COOH in powdered form, of the pristine UP150 membrane and of membranes infiltrated with SWCNTs or Thin MWCNT-COOH (from the PES selective layer). In Figure 4.27, the Raman spectra are presented.

![Figure 4.27](image)

**Figure 4.27** – Raman spectra showing the existence of CNTs within the membrane structure after CNT-infiltration with SWCNTs (left) and Thin MWCNT-COOH (right).

The presence of D and G bands in the spectra of the CNT-infiltrated membranes is a clear evidence for their existence near or on the skin layer. A note is made of the fact that Raman penetration depth is of the order of 1-2 μm as much about the thickness of the selective layer.

**4.3.4 Performance of the CNT-infiltrated membranes**

Any eventual effect attributed to the infiltration of CNTs through the membranes was characterized by testing the performance of each sample of the prepared membranes in terms of pure water flux. The CNT-membranes were expected to exhibit enhanced water fluxes due to the contribution of the CNT-existence. The experiments were carried out in the dead-end filtration apparatus used for the infiltration of CNTs under 0.5 bar transmembrane pressure at room
temperature. The membrane surface area was 9.6 cm$^2$. The flux of each one membrane was measured before and after the CNT-infiltration for reasons of comparison. The tip-sonication during the CNT-filtration process had neither an effect on the surface membrane morphology nor at the flux profile of the membranes as examined by preliminary measurements. For the flux determination, the filtration funnel was filled with 200 mL of triply distilled water allowing the permeance of 100 mL water the membrane should not get dry. The time needed the 100 mL water to pass through the membrane was recorded by means of a chronometer. Thereafter, the membrane was placed in the opposite configuration and the infiltration with CNTs was carried out as described before. After the CNT-infiltration, the membrane was turned again in the opposite configuration so as the PES surface to be exposed to the feed solution and the time needed for more 50 mL of water to pass through the membranes was recorded. For the membranes infiltrated with CNTs directly through the PES selective layer, the membrane remained in the same place and the flow rate determination was carried out immediately after rinsing and cleaning with water the rest CNT suspension. Representative water flow measurements are presented in the following tables. The membrane pure water flux ($J$) was calculated by the following equation$^{24}$:

$$J = \frac{V}{A \Delta t}$$  \hspace{1cm} (Eq. 4.2)

where $V$ (L) was the volume of permeated water, $A$ (m$^2$) was the membrane area and $\Delta t$ (h) was the permeation time.

**Table 4.11** – Flow time of 100mL water through UP150 membranes before and after the CNT infiltration process with Thin MWCNT-COOH suspension concentration 0.312 μg/mL.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Flow time of pristine UP150 (sec)</th>
<th>Flow time of Thin MWCNT-COOH infiltrated UP150 (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>255</td>
<td>270</td>
</tr>
<tr>
<td>2</td>
<td>259</td>
<td>254</td>
</tr>
<tr>
<td>3</td>
<td>220</td>
<td>214</td>
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<tr>
<td>4</td>
<td>215</td>
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<tr>
<td>5</td>
<td>205</td>
<td>190</td>
</tr>
<tr>
<td>6</td>
<td>241</td>
<td>228</td>
</tr>
<tr>
<td>7</td>
<td>223</td>
<td>212</td>
</tr>
</tbody>
</table>
### Table 4.12

Flow time of 100 mL water through UP150 membranes before and after the CNT infiltration process with SWCNT suspension concentration 0.625 μg/mL.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Flow time of pristine UP150 (sec)</th>
<th>Flow time of Thin MWCNT-COOH infiltrated UP150 (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>222</td>
<td>201</td>
</tr>
<tr>
<td>2</td>
<td>203</td>
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<tr>
<td>11</td>
<td>214</td>
<td>177</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>206.1</strong></td>
<td><strong>181.6</strong></td>
</tr>
</tbody>
</table>

The above tables are representative. In many cases the CNT-membranes showed enhanced flow rate however the results were not repeatable.

Nevertheless, for those cases that the membranes exhibited an increase in the flow rate, by the use of the data from the above tables and from similar tables concerning the flow time of the water through the membranes before and after CNT-infiltration, and using Equation 4.2 the fluxes of the membranes were calculated. The type and the concentration of the CNTs used for the infiltrations of those
membranes, as well as the percentage of their flux increase are presented in Figures 4.28 & 4.29.

**Figure 4.28** – Percentage of flux increase for membranes infiltrated with CNTs from the PET side comparing to unmodified membranes.

**Figure 4.29** – Percentage of flux increase for membranes infiltrated with CNTs from the PES side comparing to unmodified membranes.
For the retention performance study of the modified membranes, aqueous solutions of 50 mL of the model foulant consisted mainly of the organic dyes Remazol Brilliant Blue R (MW: 630 Da) and Acid Red 4 (MW: 380 Da) in equal concentration (50 μg/mL) were left passing through unmodified and CNT-modified membranes in the dead-end filtration unit. The chemical composition of the model textile wastewater is presented in Table 4.13. For the collected permeates UV-Vis spectra recorded and from the absorption peaks of the dyes the concentration of the permeates were calculated. A representative diagram of the retention % is presented in Figure 4.30.

Table 4.13 – Chemical composition of the textile model foulant.

<table>
<thead>
<tr>
<th>No</th>
<th>Dyestuff</th>
<th>Concentration (μg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Remazol Brilliant Blue R</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>Acid Red 4</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>NaCl</td>
<td>2500</td>
</tr>
<tr>
<td>4</td>
<td>NaHCO₃</td>
<td>1000</td>
</tr>
<tr>
<td>5</td>
<td>Glucose</td>
<td>2000</td>
</tr>
<tr>
<td>6</td>
<td>Albatex DBC (Detergent)</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 4.30 – Retention of Remazol Brilliant Blue R - Acid Red 4 mixture of UP150 membranes infiltrated with SWCNTs of various concentration from the PES side and of the pristine membrane.
In the corresponding retention diagram, one can observe that the rejection of the dye molecules was very high. However, when additional volumes of the model foulant were left to permeate the CNT membranes, the retention was the same as that of the pristine membrane and consequently it was concluded that the initial retention was due to adsorption effects.

### 4.4 CONCLUSIONS

In the present chapter, the efforts of transforming an UF commercial membrane to a NF one were described showing representative measurements. The structure of the UP150 membrane seemed to favor the intrusion of CNTs from the substrate aiming to reach the ~40-nm-pores of the thin selective layer.

![Figure 4.31](image.png)

**Figure 4.31** – SEM micrographs of the skin layer of the commercial PES membrane. (a) As indicated, the thickness of this region was ~2 μm resulting prohibited for the CNTs extrusion the external pores of the selective layer. (b) Micrograph as (a) of high magnitude allowing the observation of the dense pore structure at the top of membrane.

However, as it is observed from the above SEM micrographs, due to the anisotropic, dense, worm/sponge like structure of the ~2 μm skin layer, the efficient CNT infiltration was impossible. Moreover, taking into consideration the length of the modified CNTs that is <1μm, it would be also not sufficient. Hence, alternative approaches were studied concerning the fabrication of CNT-membranes which are discussed in the following chapter.
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Chapter 5

Mixed matrix and Vertically-aligned CNT-membranes

5.1 INTRODUCTION

The fabrication of CNT-membranes by the subsequent embedment of CNTs in the selective layer of specific commercial UF membranes by filtration turned partially inevitable. Taking into consideration the dense sponge-like structure of the skin layer containing the active membrane pores and its thickness of ~2 μm, the extrusion of CNTs proved challenging. However, through the experimental processes, many results for the understanding of the mechanism thrusting CNTs to embody in the selective layer of an asymmetric membrane were extracted. In addition, filtration and treatment protocols of CNTs were educed and used for further studies. In the present chapter, the fabrication of asymmetric polyethersulfone membranes with tailored properties by the phase separation technique is described as well as the embedment of CNTs in the host material by two different approaches. Finally, efforts for the preparation of vertically-aligned CNT membranes are also presented.
5.2 PREPARATION OF ASYMMETRIC POLYETHERSULFONE MEMBRANES BY PHASE SEPARATION

Aiming at the preparation of PES UF membranes similar to the commercial ones, however of tailored properties with respect to skin layer-thickness, the immersion precipitation phase separation technique was studied. In this technique, as described in Chapter 2, a film of homogeneous polymeric solution is cast on a suitable surface (i.e. glass, Teflon, non-woven fabric) and immediately is immersed in a nonsolvent bath where the exchange between the solvent and the nonsolvent and the subsequent precipitation of the polymer occurs. The three-component system participated in the preparation of the membranes was as follows: polyethersulfone was used as the polymer; N-methyl-2-pyrrolidone (NMP) was selected as the solvent and 3D water as the coagulant following experimental processes described in the literature.\textsuperscript{1,2,3} Concerning the formation of the pores and the thickness of the selective layer, the polymer concentration in the casting solution was studied. A schematic representation of the immersion precipitation phase separation process is illustrated in Figure 5.1.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{immersion_phase_separation}
\caption{General schematic representation of the immersion precipitation phase separation process followed by the resulted membrane.}
\end{figure}
5.2.1 Materials

Polyethersulfone (PES) in granule form (nominal granule size: 3mm) with of medium viscosity was purchased from GoodFellow. Aromatic polysulfones are a family of polymers produced from the condensation polymerization of 4,4′-dichlorodiphenylsulfone with one or more dihydric phenols. The three most commercially important polysulfones are bisphenol A based polysulfone (PSf), 4,4′-dihydroxydiphenylsulfone-based polyethersulfone (PES) and 4,4′-dihydroxydiphenyl-based polyphenylsulfone (PPSf). They contain the subunit aryl-SO\(_2\)-aryl, the defining feature of which is the sulfone group. Polymers in this family are completely amorphous, exhibit high glass-transition temperatures (185 °C), and offer high strength and stiffness properties even at high temperatures (between 100 °C and 150 °C), making them useful for demanding engineering applications. The polymers also possess good ductility and toughness and are transparent in their natural state by virtue of their fully amorphous nature. Additional key attributes include resistance to hydrolysis by hot water/steam and excellent resistance to acids and bases. The polysulfones are fully thermoplastic, allowing fabrication by most standard methods such as injection molding, extrusion, and thermoforming.\(^4\)

NMP solvent was purchased from Sigma-Aldrich and was selected as the solvent due to its strong interaction with polymer and miscibility with water.\(^1,5\)

5.2.2 Preparation of membranes

Asymmetric PES membranes were prepared via phase inversion induced by immersion precipitation using casting solutions containing certain amounts of PES in NMP solvent. PES solutions were prepared dissolving 13g, 15g or 18g PES in 100 mL of NMP for the preparation of PES solutions of compositions 13, 15 and 18% w/v, respectively. The polymer solutions were stirred overnight under 50°C and when necessary, an ultrasonic bath was employed to help to free up air bubbles entrapped into. Thereafter, around 30 mL of each solution was poured and cast using an adjustable film applicator (Sheen, ≤300 mm film width) with 80 μm preferable thickness on a glass plate substrate. The thickness of the membranes determined at 80 μm so as the membranes to withstand the filtration and the tip-sonication
processes since they did not bare a substrate as the commercial ones. Illustrations describing the experimental process are presented in Figure 5.2.

**Figure 5.2** – Experimental process of the immersion precipitation phase separation process for the preparation of PES asymmetric membranes: (a) Image of the film applicator (for films of width ≤300 mm) on the glass substrate, (b) the polymeric solution is poured onto the glass surface and casted, (c) the polymer cast is immersed into the coagulation bath, (d) after few seconds a film starts being separated from the glass surface, (e) the film remains into the coagulation bath for 24 h and (f) a PES membrane is formed and kept wet.

The cast films were immediately immersed to a distilled water coagulation bath at 30°C for immersion precipitation without any exposure to the air and kept for 24 h. This was done in order to ensure the complete removal or evaporation of the residual solvent from the membranes. Finally, the membranes were moved to fresh water bath at room temperature and kept wet until use, exactly as done for the commercial ones described in the previous chapter. Alterations to the procedure with regards to the solvent evaporation time were also carried out and the reasons are discussed further on.
5.2.3 Morphological characterization of the PES membranes

SEM micrographs of Figure 5.3 describe the surface morphology and structure of the fabricated PES membranes of composition 13% w/v. The surface pore density appears high enough and similar to that of the commercial one.

![SEM micrographs of PES membranes](image)

**Figure 5.3** – Surface and cross-sectional SEM micrographs of PES membranes of composition 13% w/v. (a), (b) The surface morphology of the membrane. Pores were determined to range between 15-40 nm. (c), (d) Cross area of the membranes of thickness ~80 μm. The finger-type formation is
observed. (e), (f) Micrographs represent the thickness of the selective layer determined to be 60-100 nm.

The size of the pores ranged between 15-40 nm. Cross-sectional images indicate the asymmetric structure of the membranes by the formation of finger-type channels, potentially favoring the CNTs-infiltration. The thickness of the skin layer determined at 60-100 nm, fairly lower than that of the commercial membrane (~2 μm).

A representative comparison between the tailor-made PES membranes and the commercial ones, with respect to the surface morphology, the cross area and specifically of the thickness of the skin layer is depicted in Figure 5.4 by SEM micrographs of respective same magnitudes.
Figure 5.4 – Surface and cross-sectional SEM micrographs of PES tailor-made and commercial membranes. (a), (b) Comparison of the surface morphology of the membranes. Pores were determined to range between 15-40 nm for the tailor-made membranes while for the commercial ones the nominal pore size was 40 nm, usually observed to be 20-30 nm. (c), (d) Cross area of the membranes of thickness of both ~80 μm. (e), (f) The thickness of the selective layer of the tailor-made membranes was determined to be much lower than that of the commercial ones.

The features of tailor-made membranes of composition 13% w/v seemed to serve the infiltration of CNTs targeting at their embedment
through the pores of the selective layer. Thus, next, infiltrations of CNT-suspensions were followed using the protocols extracted from the previous study.

5.2.4 CNT-infiltration of tailor-made PES membranes

The determination of which PES membrane, with regards to the PES composition, were suitable for the infiltration of CNTs with subsequent covering up of the whole surface area with CNTs, revealed by CNT-infiltration experiments. Suspensions of SWCNTs or Thin MWCNTs both functionalized with -COOH groups of concentration 3 μg/mL were prepared. In order to get well-dispersed CNTs suspensions, we made use of surfactant (poloxamer 407) in the composition rate 1:1.5 (SW:surf.) or 1:1 (Thin MW:surf.), respectively with subsequent tip-sonication for 15 min in the aqueous media. The infiltrations were performed through the support side of the PES membranes. Figure 5.5 shows the process carried out step by step, from the cutting of a pure PES tailor-made membrane to the infiltration with CNTs with the subsequent operation of tip-sonicator for the alignment and the impulse of CNTs towards the membrane pores.
Figure 5.5 – Step by step procedure from the membrane cutting in proper dimensions to the infiltration of CNT-suspension through the pure PES membrane by the subsequent operation of the tip-sonicator.

For the tailor-made pure PES membranes, not baring a substrate as the commercial ones (PET substrate), the distinction of the narrow-pore sides from the wide-pore sides in order to be placed properly in the filtration apparatus for the CNT-infiltration experiments was simple. The surface of the side bearing the small-size pores, namely the selective layer, is more glowing than that of the support side due to reflection phenomena which are more intense on an anomalous surface.
In Figure 5.6 images of the PES membranes of compositions 13, 15 and 18% w/v infiltrated with SWCNT-COOH 3μg/mL are depicted showing comparatively how the polymer concentration affects the CNT-infiltration imprint and subsequently the successfulness of the process. For all cases, the other parameters of infiltration process were the same.

**Figure 5.6** – PES membranes of compositions 18, 15 and 13% w/v in the polymer solutions used for the infiltration studies.

As observed from the pictures, the higher the composition of polymer into the polymer solution for the preparation of membranes with the phase inversion technique, the more difficult CNTs to reach the selective layer. This is both due to the thicker selective layer formed increasing the polymer amount and the narrower pores developed on the surface of the selective layer. Increasing the composition of the polymer probably results in the formation of NF membranes, unsuitable for the CNT-infiltration. Decreasing the polymer amount into the polymer solution, the formation of the specific selective layer served/facilitated the infiltration of CNTs as clearly shown in the picture of **Figure 5.6**. The surface of the PES 13% w/v membrane was filled with CNTs; a note is made on the fact that the black imprint of the CNTs was even more intense from the one observed on the commercial membranes (**Fig. 5.7**). That was evidence that CNTs managed to protrude from the pores of the thin skin layer. Consequently, the selection of the polymer solution composition was made for PES 13% w/v for the fabrication of the pure PES membranes.

Regarding the CNT-infiltration process, for the optimized samples, each membrane was left to be infiltrated by three CNT-suspensions of
3 μg/mL in concentration and 100 mL in volume, with the assistance of the tip-sonicator operating at 35% in magnitude. After every single filtration process, the membrane was rotated for ~90° in order to fill up any surface region that was eventually hindered by the existence of the metallic sieve placed as membrane substrate.

**Figure 5.7** – Commercial and tailor-made PES membranes CNT-infiltrated with 3 μg/mL Thin-MW-COOH-suspension and under the same conditions from the support side. In the photographs are shown the selective layers of the membranes. (a) Commercial PES membrane; (b),(c) CNT-infiltrated commercial membrane, view from the selective layer and the substrate side, respectively; (d) Tailor-made PES membrane CNT-infiltrated from the
support layer (the white side), (e) Comparison between commercial (on the left) and tailor-made (on the right) PES membranes infiltrated by same CNT-suspensions under the same conditions from the support side.

An alteration to the solvent evaporation time from 24h to few minutes, during the phase separation process, was held in order to take advantage of the unformed structure of the polymer-rich phase that probably would facilitate the CNT-stacking and their stabilization into the pores of the selective layer impelled by the tip-sonicator. Thus, infiltration was carried out immediately after the separation of the flat-sheet membrane from the glass surface.

5.2.5 Morphological characterization of the CNT-infiltrated PES membranes

Raman spectroscopy was employed for the characterization of the CNT-membranes. Backscattering Raman spectra collected from bulk SWCNT-COOH in powdered form, from the pure PES membrane and from the selective surface of a membrane infiltrated from the finger like side with SWCNT-COOH. In Figure 5.8, the Raman spectra are presented.
Figure 5.8 – Raman spectra showing the existence of CNTs within the membrane structure after CNT-infiltration with SWCNT-COOH.

The presence of D and G bands in the spectra of the CNT-infiltrated membranes is a clear evidence for their existence near or on the skin layer. Once again, a note is made of the fact that Raman penetration depth is of the order of 1-2 μm covering the thickness of the selective layer.

Surface and cross sectional SEM micrographs confirmed the existence of the SWCNT-COOH or Thin MWCNT-COOH in the selective layer of the tailor-made PES membranes after the CNT-infiltration processes. In Figure 5.9 representative SEM images are presented.
Figure 5.9 – Surface and cross sectional micrographs of tailor-made PES membranes infiltrated with either SWCNT-COOH or Thin MWCNT-COOH suspensions 3 µg/mL; (a), (b), (c): Cross sections of PES membrane infiltrated with SWCNT-COOH; (d),(e): Surface of selective layer of membrane infiltrated with Thin MWCNT-COOH from the support layer; (f)-(k): Cross sectional images of the same membranes. (Images (j),(k) were carried out by Dr. Daniel Jonson at Swansea University, College of Engineering at the lab of Prof. Nidal Hilal).

The SEM micrographs indicated that CNTs can reach and stick out from the thin selective layer of a membrane when the thickness of the selective layer facilitates it.

5.3 PERFORMANCE OF THE NEW MEMBRANES

The performance of the new PES membranes was evaluated by permeation experiments. By the use of the same experimental setup described in the previous chapter, pure water flux and qualitative MWCO determination were carried out.
5.3.1 Pure water flux measurements

The flux profiles of PES membranes were carried out allowing the permeation of triply distilled water through the membranes for 1 h under transmembrane pressure (TMP) equal 0.5 bar. Every 10 min the quantity of permeate was weighted and recorded and the flux was calculated. In Figure 5.10 the flux profiles of pure PES tailor-made membranes, of PES membranes infiltrated with SWCNT-COOH (3 μg/mL), of similar membranes however dried after the CNT-infiltration process and finally of commercial PES membranes for reasons of comparison are depicted as a function of time. Five (X5) samples of each group of membranes were measured and the data are followed by error bars.

![Figure 5.10](image.png)

**Figure 5.10** – Pure water flux profiles of various types of PES membranes.

Even the dried CNT-infiltrated membrane was functional and the flux determined to be close to that of the wet commercial membrane. Nevertheless, the commercial membranes used to lose their functionality when measured dried. In Figure 5.11 the final fluxes of the groups of membranes presented before are shown.
In conclusion, tailor-made PES membranes bearing a thin selective layer of ~100 nm showed high fluxes. However, the embedment of SWCNT-COOH in the thin selective layer of the membranes contributed to the decrease of the flux, yet/although limited. The membranes remained functional and with high fluxes, even the dried ones.

### 5.3.2 Qualitative determination of MWCO

Molecular weight cut-off of a membrane may give information about the membrane pore size. The performance of the membranes was measured in terms of solute rejection using the standard dead-end filtration apparatus and the general setup described in Chapter 4 utilized for the CNT-infiltrations. The permeation tests were conducted at 25°C and the effective membrane area was 9.6 cm². Pressurized nitrogen gas was applied to limit the vacuum of the pump at 0.5 bar. An aqueous solution of a mixture of polyethylene oxide (PEO) and
polyethylene glycol (PEG) with various molecular weights was used as feed solution in total composition 0.6% w/v. PEO 200 kDa (PN:181994), PEO 100 kDa (PN:181986), PEG 35 kDa (PN:94646), PEG 10 kDa (PN:P6667), and PEG 4 kDa (PN:81240) were purchased from Sigma Aldrich and used without further purification.

Size Exclusion Chromatography (SEC) was employed for the qualitative determination of the MWCO. The membrane permeates were characterized on a Waters 501 apparatus using a differential refractometer R401 Waters Associates and Shodex OHpak columns. Aqueous 0.1 M LiNO$_3$ solution was used as eluent at a flow rate of 1 mL/min, while the columns were calibrated using PEO standards. Aqueous solutions of each polymer 0.2% w/v were prepared and measured by SEC. The peak of each molecular weight corresponds to respective elution volume as are presented in Figure 5.12 and the chromatographs used to confirm the molecular weights conducted after the solute rejection experiments.

Figure 5.12 – Size exclusion chromatographs of the PEO and PEG of different molecular weights used for the rejection study. The chromatographs presented were used for reasons of calibration.
For the determination of the rejection properties of the CNT-infiltrated membranes, the polymeric mixture solution was left permeating through each membrane for 1 h. The permeates were collected and measured by means of SEC. The size exclusion chromatographs are presented in Figure 5.13.

Figure 5.13 – Size exclusion chromatographs of the permeates conducted by the filtration of an aquatic mixture solution of PEO and PEG of different molecular weights for the MWCO determination.

The chromatographs exhibit the rejection tendency of a commercial PES membrane, of a tailor-made pure PES membrane, of a membrane infiltrated with SWCNT-COOH (3 μg/mL) and of a similar membrane that has been dried after the CNT-infiltration. The yellow chromatograph corresponds to the feed solution. Through the chromatographs arises that the CNT-infiltrated membranes exhibit a higher tendency to reject sizes of the higher molecular weight (200 kDa and 100 kDa), while a pure PES tailor-made membrane exhibits a similar rejection behavior to that of the commercial one. The presence of CNTs in the thin selective layer of the PES membranes increased
the selectivity of the membrane, decreasing the MWCO from 150-200 kDa to ~40 kDa. However, taking into account the decreased pure water flux results the CNT-infiltrated tailor-made membranes exhibited, it was concluded that the presence of CNTs in the selective layer of the membranes did not contribute to the overall enhancement of the counterbalance between flux and selectivity.

5.4 SURFACE COATING OF CNT-INFILTRATED MEMBRANE

When preparing a CNT-membrane by the infiltration of CNT-suspensions, the presence of vacant areas or pores from CNTs on the surface of the selective layer is practically inevitable. However, even at the best case that all the surface pores are filled up with CNTs, the eventual empty spaces between CNTs and between CNTs & support/host pores may limit as much the flux performance as the retention capacity of the membrane.

In this context, an approach for the potential application of a polymeric coating aiming at the filling of empty pores and/or vacant spaces between CNTs and support pores walls and at the same time at the binding of nanotubes protruding the pores of the selective layer was studied.

A note is made of the fact that the vulnerable nature of the PES material suffers from luck of resistance to common organic solvents that many common polymers are soluble to while the deposition of a water-soluble polymeric film would prove ineffective. Therefore, the application of a common polymeric coating proved challenging.

Alginic acid is a natural linear carbohydrate polymer with a repeated formula C₆H₈O₆. Sodium alginate (NaC₆H₇O₆) is the sodium salt of alginic acid, soluble in water. In the presence of calcium chloride aqueous solution, the sodium salt is removed and replaced by calcium ions through cross-linking forming a water-insoluble gel, the calcium alginate with formula (C₁₂H₁₄CaO₁₂)ₙ (Fig. 5.14).
Doubly charged calcium ions (Ca\(^{2+}\)) can bind two different alginate strands simultaneously, thereby cross-linking and solidifying the solution. Increasing the number of calcium cross-links by raising the concentration of calcium chloride and/or lengthening the soaking time create a more solid gel.

### 5.4.1 Preparation and application of calcium alginate coating

A polymeric coating of calcium alginate was synthesized by the addition of calcium chloride solution to the dilute solution of sodium alginate by gelification method. Sodium alginate with number-averaged molecular weight 12,000-40,000 g/mol (180947) and calcium chloride (CaCl\(_2\)) (C1016) were purchased from Sigma Aldrich.

750 mg of sodium alginate was dissolved in 25 mL triply distilled water for a final composition 3% w/v and left under stirring under slightly high temperature (~40 °C) overnight. Afterwards, an ultrasonic bath was employed to help to free up air bubbles entrapped into. 10 mL of the solution was then film casted onto the surface of the CNT-infiltrated membrane and kept evaporating for 3 days in room temperature. After evaporation, a gel film onto the membrane surface.

![Figure 5.14 – Cross-linking of alginate molecules by Ca\(^{2+}\) ions forming calcium alginate.](image)
was formed and subsequently, the membrane was immersed into 50 mL aqueous solution of CaCl$_2$ 5% w/v and left overnight so that the cross-linking to occur. Finally, the membrane was rinsed with water and dried at 30°C. A water insoluble clear yellowish film was formed onto the membrane surface filling the surface pores of the selective layer and the eventual spaces between CNTs.

Cross sectional SEM micrographs allowed the observation of a thin film (<3 μm) at the top of the PES selective layer (Fig. 5.15) attributed to the calcium alginate coating.

Next step would be the withdrawal of the excess amount of the polymeric coating by means of chemical etching to the point that nanotube orifices would be present on the top of the surface. In that way, the selective pores of the CNT-membrane would be defined exclusively by the internal diameters of the carbon nanotubes.

### 5.5 MIXED MATRIX-CNT MEMBRANES

A different approach concerning the general term “CNT-membranes” is the mixed matrix-CNT membranes (MMMs) that constitute
nanocomposites in which the polymer matrix serves as host for CNTs, prepared by blending of the substances. In that case, CNTs serve as nano-fillers contributing to the formation of the membrane porosity during the membrane synthesis and are not expected to function as transport means. Therefore, MMMS are expected to exhibit different properties from those of CNT-infiltrated membranes in terms of flux and selectivity. For the present study, nanocomposite membranes composed of PES and deprotonated carboxyl-functionalized Thin MWCNTs/SWCNTs were prepared. The functionalized CNTs were embedded in PES matrix during the immersion-induced phase separation method. The membrane structure and properties were characterized by SEM, FTIR and water uptake measurements while the performance of the membranes was evaluated by flux and rejection experiments.

5.5.1 Preparation of MMMs with CNTs

The asymmetric composite membranes (Thin MWCNT/SWCNT-COO-/PES) were prepared via immersion-induced phase separation method using casting solutions containing PES (15% w/v) and proper amount of functionalized with carboxyl anions Thin MW/SWCNTs in NMP solvent. Initially, 15 g PES was dissolved in 60 mL NMP solution and left under stirring overnight. Precise amounts of CNTs (0.5% w/w with respect to PES) were dispersed into 40 mL NMP to prepare a CNT suspension and the suspension was agitated in ultra-sonication bath for 1.5 h. After dispersing the CNTs in solvent, the PES solution was added in the CNT-suspension and homogenized using a magnetic stirrer for 1.5 h. Next, the mixture was placed in ultra-sonication bath to eliminate the air bubbles created in solution during stirring and to disperse CNTs into the dissolved polymer for 1 h and finally, left stirring overnight at room temperature.

Thereafter, around 30 mL of each solution was spread and cast using an adjustable film applicator with 80 μm thickness on a glass plate substrate. The thickness of the membranes determined at 80 μm (Fig. 5.16).
Figure 5.16 - Experimental process of the immersion precipitation phase separation process for the preparation of PES asymmetric membranes mixed with CNTs: (a) Image of the film applicator (for films of width ≤300 mm) on the glass substrate, (b), (c), (d), (e) the mixture polymeric solution-CNTs is poured onto the glass surface and casted, (f) the polymer cast is immersed into the coagulation bath and after few seconds a film is separated from the glass surface.

The cast films were immediately immersed to a distilled water coagulation bath at 30°C for immersion precipitation without any exposure to the air and kept for 24 h to complete the coagulation and remove the residual solvent from the membranes. Finally, the membranes were moved to fresh water bath at room temperature and kept wet until use.

Pure PES membranes were prepared as well in order the MMMs properties to be compared to, and any eventual effect educed by the mixing of CNTs in the polymer matrix to be evaluated. Figure 5.17 illustrates the digital photographs of a pure PES membrane and a MM-CNT membrane prepared by the phase inversion method.
5.5.2 Characterization and performance of the MMMs-CNTs

SEM micrographs collected from the MM-CNT membranes indicated that the pore-size distribution formed on the permselective surface of the membrane was quite narrow (~9-12 nm) (Fig. 5.18). It is reminded that the pore size distribution of pure PES membranes was 15-40 nm. It was concluded that CNTs contributed to the formation of smaller pores and high pore density on the membrane surface.
Pure water permeability tests for a number of pure PES, MM-Thin-COO\textsuperscript{-} and MM-SW-COO\textsuperscript{-} membranes were carried out to investigate any eventual effect of CNTs in the permeability properties of the membranes. In Figure 5.19 the fluxes of the membranes are presented. The measurements were carried out using a dead-end filtration system already described; TDW was left to permeate through the membranes for 1 h.
The MM-CNT membranes exhibited most of the times increased fluxes compared to the pure PES membranes. For the membranes whose fluxes are framed in circles in Figure 5.19, rejection tests were carried out in order to ensure that the increased fluxes were attributed to the different formation of the selective layer by the contribution of CNTs. A mix-solution of PEO/PEG with different molecular weights (200, 100, 35 and 10 kDa) was left to permeate the membranes and using SEC, chromatographs of permeates were recorded showing the MWCO tendency of these membranes (Fig. 5.20).
Figure 5.20 – SEC chromatographs of PEO/PEG mix solution permeates indicating the rejection tendency of pure PES and MM-Thin MWCNT-COO⁻ membranes. The chromatograph of the feed solution is also presented.

The MM-Thin MW-COO⁻ membranes exhibited an enhanced tendency of rejecting polymers of high molecular weight compared to the pure PES membrane.

In conclusion, the MM-CNT membranes not only exhibited high fluxes but also a tendency of higher rejection properties. These results directed our attention to the investigation and elucidation of the effect CNTs’ presence cause in MMMs, through a comparative study of membranes loaded with different amounts of CNTs.

5.6 COMPARATIVE STUDY OF MM-CNT MEMBRANES LOADED WITH DIFFERENT AMOUNTS OF CNTS

By using the phase inversion method, as exactly described before, MM-CNT membranes were prepared loaded with different amounts of CNTs. Precise amounts of Thin MWCNT-COO⁻ were weighted for the
preparation of final mix solutions of 0.2, 0.4, 0.6, 0.8 and 1.0% w/w and using a casting knife, membranes of thickness 80 μm were prepared (Fig. 5.21).

Figure 5.21 – MM-CNT with various CNT-contents from 0 to 1.0% w/w prepared by the immersion precipitation phase separation method.

It is worth pointing out at this stage that the localization of MWNTs in the membrane surface phase constituting the thin selective layer is energetically favorable from a thermodynamic point of view. The observed localization is thus a clear mandate to the fact that CNTs migrate to the more preferred phase during phase separation. This thermodynamically driven migration of CNTs leads to an increase in their local concentration in the specific phase, something that facilitates their network-like structure formation in the blends.  

In general, the higher polymer solution viscosity indicates that kinetically the overall diffusion between components in the phase inversion system can be suppressed because of the increase in the rheological hindrance. The overall diffusion can be inhibited kinetically by CNTs in a solution because of the increased viscosity. Thus, membranes seem to be composed of two layers. The surface appears darker while the “support” surface more white. A schematic
representation of the phase inversion of a polymeric solution mixed with CNTs is illustrated in Figure 5.22.

**Figure 5.22** – Schematic illustration of immersion precipitation phase separation process for the preparation of MMMs-CNTs and of the resulted membrane.

### 5.6.1 Membrane characterization and performance

#### 5.6.1.1 ATR-FTIR

Attenuated total reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to identify introduced functional groups onto the surface of acid treated MWCNTs. Figure 5.23 exhibits the surface ATR-FTIR spectra of the PES membrane and the MM-Thin MWCNT-COO\(^{-}\) membrane loaded with 1% w/w of CNTs.
Figure 5.23 – ATR-FTIR spectra of a pure PES and MM-Thin MWCNT-COO-1% w/w membranes.

Table 5.1 summarizes the assignments of the main IR bands of Figure 5.23. Fig. 5.23-a presents ATR-FTIR spectrum of the pure PES membrane. The bands at 1147 & 1294 cm\(^{-1}\) can be attributed to the stretching vibrations of S=O symmetric and S=O asymmetric, respectively. The peak at 1236 cm\(^{-1}\) can be assigned to the symmetric C-O-C stretching vibration. These peaks appear in the spectrum of MM-CNT membrane, as well (Fig. 5.23-b). However, the spectrum of the MM-CNT membrane is different from that of the pure membrane showing C=O bond of carboxyl groups at 1640-1685 cm\(^{-1}\) by the added functionalized MWCNTs.
Table 5.1 – Frequencies and assignments of the peaks of the ATR-FTIR spectra of Fig. 5.23.

<table>
<thead>
<tr>
<th>Peak (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1147</td>
<td>S=O symmetric stretching vibrations</td>
</tr>
<tr>
<td>1236</td>
<td>C-O-C symmetric stretching vibrations</td>
</tr>
<tr>
<td>1294</td>
<td>S=O asymmetric stretching vibrations</td>
</tr>
<tr>
<td>1640-1685</td>
<td>Conjugation of C=O with C=C bonds or Interaction between localized C=C bonds and carboxylic acids</td>
</tr>
</tbody>
</table>

5.6.1.2 Pure water flux measurements

The MM-CNT membranes were characterized by measuring the pure water flux. The experiments were carried out in a lab-scale cross-flow filtration unit (SEPA CF Cell of Sterlitech Corporation) (Fig. 5.24). The membrane surface area was 140 cm² and the pressure in the outlet was 0.5 bar.

Figure 5.24 – Lab-scale cross-flow unit of Sterlitech Corp. used for the permeation experiments.

TDW was left to permeate through pure PES and PES-CNT membranes for 1h. The fluxes of five membranes of each group were measured and the flux profiles versus time are presented in Figure 5.25.
The pure water flux measurements revealed that the order of increasing rate of water flow through the membranes according to the percentage of CNT loading is: 0.2%>0.4%>pure PES>0.6%>commercial PES>0.8%>1.0%, as presented in Figure 5.26.
Figure 5.26 – Pure water flux measurements’ results of pure PES, of PES-CNTs and the corresponding commercial membranes.

It is concluded that the pure water flux observed to increase for MM-CNT membranes loaded with small amount of CNTs (0.2, 0.4% w/w) probably due to the increased hydrophilicity the Thin-MWCNT-COO⁻ offered to the membranes. Higher amounts of CNTs, increase the viscosity of the selective layer of the PES membranes hindering the permeance of water molecules.

Flux measurements were also carried out using as feed solution industrial wastewaters which was provided by Sirca Hellas and treated by C. Paraskeva lab at the University of Patras, both partners of Synergasia MEKKA project. The foulant-solution was left to permeate the membranes for 30 min and the results are presented in Figure 5.27.
The behavior of the membranes with respect to the permeability of the industrial wastewater was similar to that exhibited for water. The above results suggest that the pore size as well as the pore density of a MM-membrane are determined largely by the CNT content. More precisely, the membranes loaded with 0.2 and 0.4% w/w CNTs exhibited enhanced permeation properties compared both to the pure PES membranes and the ones loaded with higher contents of CNTs.

### 5.6.1.3 Rejection measurements

Rejection experiments were carried out as well for the investigation of the rejection properties of the MM-CNT membranes using the treated effluent of Sirca Hellas. Using the cross-flow filtration unit, volumes of the aqueous effluent were left to filtrate through the membranes and by the Closed Reflux Colorimetric method, the Chemical Oxygen Demand (COD) of the permeates was calculated. The effluent was oxidized by potassium dichromate in 50% sulfuric acid solution at reflux temperature. Silver sulfate was used as a catalyst and mercuric...
sulfate was added to remove chloride interference. After a 2-hour heating at 150 °C at a HATCH COD reactor the samples were cooled to room temperature and using a colorimeter SMART3 of LAMOTTE the COD and consecutively the retention was measured in units mg/Lt. The results are presented in **Figure 5.28**.

![Figure 5.28](image)

**Figure 5.28** – COD results of the filtrates of the treated industrial aqueous effluent.

Using calibration curve and the data of **Figure 5.27** the percentage of the rejected compound was calculated for each membrane as presented in **Figure 5.29**.
Figure 5.29 – Rejection percentage of treated industrial effluent according to the CNT-loading of the membranes.

Combining the results of the water flow rates through the membranes with the rejection results the performance of the MM-CNT membranes is summarized in Figure 5.30.
5.6.1.4 Water uptake of the MM-CNT membranes

The water up-take is direct indicative of hydrophilicity of the membranes. In order to examine the water up-take property of the membranes, dry specimens were weighted and immersed into water for 24 h. Afterwards the membranes were taken out of the water, and the surface droplets were removed using filter paper. Then, the membranes weighted and the percent water uptake was calculated using the equation:

\[
\% \text{water uptake} = \frac{W_w - W_d}{W_d} \times 100 \quad (Eq. 5.1)
\]

where, \(W_w\) and \(W_d\) are the weight (g) of dry and wet membranes respectively. For each membrane group, 5 membranes were measured and the results are presented in Figure 5.31 followed by error bars.
Figure 5.31 – Water uptake percentage of the MM-CNT membranes according to the CNT-loading.

The MM-CNT membranes with CNT-load 1.0% w/w exhibited enhanced water uptake properties while MM-CNT loaded with 0.2% w/w CNTs exhibited the lower percentage. These results provide an evidence for the fact that the increase in carboxylic group in the membrane component increases the hydrophilic nature of the membrane.

5.7 CONCLUSIONS

The comparative study concerning the characterization and evaluation of the functionality and performance of polyethersulfone ultrafiltration membranes and mixtures with carbon nanotubes modified with carboxylic anion groups led to the following conclusions.

The blending of hydrophilic CNTs into the polymeric matrix led to an increase in the hydrophilicity of the membranes, altering the porosity
and increasing the pore density in certain cases that caused the migration of Thin-MWCNT-COO\(^{-}\) to the surface of the membranes during their synthesis by the phase separation method. The permeation properties of the membranes-mixtures were found to be influenced and enhanced by adding a small amount of Thin-MWCNT-COO\(^{-}\) in the polymer matrix with respect to the permeation rate of water and organic waste. More specifically, for the membranes with CNT-content 0.2% w/w, the water flow rate increased by 44% compared with the pure PES membranes and 220% compared with the corresponding commercial ones. Regarding the waste rejection from the membranes, it was observed that increasing the CNT-content the rejection capacity was increased with maximum rejection \(~13\%\) attributed to membranes containing Thin-MWCNT-COO\(^{-}\) 1.0% w/w over commercial or pure PES membranes ranging between 5-6%.

### 5.8 VERTICALLY ALIGNED CNT-MEMBRANES

Among various kinds of CNT-membranes, vertically aligned CNT-membranes (VA-CNT-membranes) constituted the most promising novel separation system for water purification. The VA-CNT-membranes are synthesized by arranging perpendicular CNT with supportive filler contents between the tubes. These membranes are high molecular sieves with intercalated filler matrix such as polymer between them as already referred in Chapter 3. In the context of Synergasia MEKKA project, the preparation of a VA-CNT-membrane was studied. The objective of this study was to investigate the preparation process of a CNT-membrane prepared by vertically grown CNTs and the subsequent uncapping of the CNT ends.

#### 5.8.1 Synthesis & characterization of VA-CNT

The method of MWCNT array synthesis is based on the catalytic chemical vapor deposition method of hydrocarbon sources. Polished Si wafers \(<100\>, \ Prime/CZ Virgin, Resistance 1-50 Ohm/cm, Type: P/Dopant: Boron) enriched with Fe particles, served as substrates for the deposition of the nanotubes. The experimental system (R&D unit) consisted of a vertical quartz tube with inner diameter of 15mm, heated with a resistance furnace, in a length of 22 cm. The isothermal zone of the reactor was approximately 17 cm. Temperature was controlled by a controller with two Pt/Pt-Rh thermocouples. The wafer
was placed in a flat vessel made from platinum, and it was positioned in the middle of the isothermal zone of the reactor. The vessel was coupled to a digital microbalance (CAHN D-101) with 1 μg sensitivity able to monitor the weight change of the sample with time. The experimental device was completed by mass flow controllers and flow read-out units. After stabilization of the system at the operating temperature, the gaseous feed stream was supplied to the reactor. The feed consisted of acetylene (C2H2) and helium (He) as carrier gas. The gases were supplied from regulated gas cylinders. The flow rate of the reagents was measured and controlled with mass flow controllers. The composition of the feed mixture was 2% acetylene in helium.10

The grown VA-CNTs were analyzed by SEM. Representative micrographs of the samples used for the preparation of the membranes are illustrated in Figure 5.32. The high of the CNT arrays was ~150 μm. Vertically-aligned CNTs were supplied by Nanothinx S.A.

![Figure 5.32 – SEM micrographs of VA-CNTs synthesized on a silicon substrate.](image)

### 5.8.2 Preparation of VA-CNT-membranes

Synthesized VA-CNTs stacked on the squared Si wafer (1.0 x 1.0 cm) were placed in a petri dish (diameter: 5 cm) with the Si wafer’s view at the top. 800 mg of polyvinylidene fluoride (PVDF) dissolved in 50 mL dimethylformamide (DMF) under stirring for 2 h at 75°C for the preparation of a polymeric solution 1.6% w/v. The polymeric solution was cast into the petri dish over the VA-CNTs and placed in an oven at 70°C for 48 h in order the solvent to evaporate. When the solvent evaporated, a film of thickness 100 μm was left in which the VA-CNT
specimen was enclosed. The Si wafer was carefully withdrawn by means of forceps. PVDF was used to fill up the empty spaces between CNTs and stabilize them in a group form and was selected as a resistant material commonly used in membrane technologies. A schematic representation is illustrated in Figure 5.33.

![Figure 5.33 - Schematic representation of a VA-CNT membrane preparation.](image)

In that stage, the CNTs were submerged in the PVDF matrix and eventually coated by PVDF (Fig. 5.33) first from the right SEM micrograph). The excess PVDF film covering the CNTs had to be removed by etching. For the opening of the CNT orifices Argon ion (Ar⁺) plasma etching in the presence of oxygen used by studying the parameters time, distance and irradiation volume. Seven different tests were carried out in order the optimum etching conditions to be determined. In Table 5.2, the parameters studied are presented.
Table 5.2 – Conditions under which the plasma etching experiments were carried out.

<table>
<thead>
<tr>
<th>No</th>
<th>Plasma power (Watt)</th>
<th>Argon flow (slm)</th>
<th>Oxygen flow (sccm)</th>
<th>Distance (cm)</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>5</td>
<td>0</td>
<td>2</td>
<td>10</td>
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</tr>
<tr>
<td>2</td>
<td>50</td>
<td>5</td>
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<td>1</td>
<td>10</td>
<td>~60</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>5</td>
<td>100</td>
<td>0.5</td>
<td>18</td>
<td>~70</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>5</td>
<td>100</td>
<td>0.5</td>
<td>8</td>
<td>~70</td>
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<tr>
<td>5</td>
<td>50</td>
<td>5</td>
<td>100</td>
<td>0.5</td>
<td>4</td>
<td>~70</td>
</tr>
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<td>6</td>
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<td>5</td>
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<td>1</td>
<td>5</td>
<td>~60</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>5</td>
<td>100</td>
<td>1.5</td>
<td>6</td>
<td>~50</td>
</tr>
</tbody>
</table>

SEM micrographs were collected from the surfaces of the plasma-treated samples under the conditions described in Table 5.2 (Fig. 5.34).

Figure 5.34 – SEM micrographs of plasma-treated VA-CNTs embedded in PVDF matrix. (a) Treated sample under Ar⁺ flow from distance 1 cm. (b), (c) Samples under Ar⁺ and O₂ flow from distance 1 and 0.5 cm, respectively.

The parameters shaded in orange in Table 5.2 observed to be optimum for the removal of the excess PVDF and the CNT appearance on the membrane surface as presented in Figure 5.35.
Figure 5.35 – SEM micrograph of sample treated under Ar⁺ flow for 10 min from distance 2 cm. In the inset, the SEM micrograph of VA-CNTs before being submerged into the PVDF solution is presented. The scale of both SEM micrographs are normalized.

The optimum conditions with respect to the excess of PVDF removal were observed to be the treatment from 2 cm without O₂ flow. From SEM micrographs it is concluded that the preparation of a VA-CNT membrane under carefully controlled conditions may lead to functional membranes. However, due to the complexity of the method, plasma etching on large-scale samples is difficult. The plasma treatments were carried out by prof. E. Amanatides at the Chemical Engineering Department of University of Patras. Basic principles of plasma etching are presented in Appendix II.

REFERENCES

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6

Introduction to Raman Spectroscopy and Surface-Enhanced Raman Scattering

6.1 THE DISCOVERY OF THE RAMAN EFFECT AND THE SUBSEQUENT SURFACE-ENHANCED RAMAN SCATTERING PHENOMENON.1,2

What is called today “Raman scattering” is an effect discovered by Chandrasekhara Venkata Raman in 1921.3 It is interesting to note that the phenomenon had been predicted theoretically by Smekal4; it was observed by C.V. Raman and K.S. Krishnan in India and almost simultaneously by G. Landesberg and L. Mandelstan5 in Russia. Raman himself observed the effect with very rudimentary optical tools (essentially color filters) by using the sun as a light source and his eyes as detector. The discovery won him the Nobel prize in physics in 1930 for his work on the scattering of light and for the discovery of the effect named after him. Briefly, following interaction with an excitation present in several organic liquids, he observed that scattered photons had a higher energy than the incoming ones, what we call today ‘anti-Stokes Raman scattering’. This up-conversion process in energy, an inelastic scattering process, convinced Raman that he was in the presence of a new optical scattering phenomenon that called it “A new type of secondary radiation” in his original report, and this is what now is called the “Raman effect” or “Raman scattering”.

About fifty years after the observation of the Raman effect, the “Surface-Enhanced Raman Scattering” (SERS) phenomenon started getting discussed. In a nutshell, the SERS effect is about amplifying
Raman signals by several orders of magnitude, and this amplification of the signals in SERS comes mainly through electromagnetic interactions of light with metals, which produces large amplifications of the laser field through excitations generally known as plasmon resonances. To profit from these, the molecules must typically be adsorbed on the metal surface, or at least be very close to it (typically ≈10 nm maximum). It was in 1974 that Fleishmann et al. reported the Raman spectrum of a monolayer of pyridine adsorbed on a silver electrode surface.\(^6\) In 1977, Jeanmaire and Van Duyne,\(^7\) and Albrecht and Creighton\(^8\) noted that the scattering intensity from the adsorbed species was \(10^5\)-\(10^6\) times stronger than that of non-adsorbed species. Thus, SERS research had begun.

### 6.2 RAMAN SCATTERING\(^2,9,10,11,12\)

Laser Raman spectroscopy deals with the measurement of radiation scattered from a solid, liquid or gaseous sample. Although any light source can be used, the low intensity of Raman scattered radiation generally requires the use of laser radiation as the excitation source and in this way the use of Raman spectroscopy has increased significantly since the development of high powered continuous wave gas ion lasers in the late 60’s.

The Raman effect can be described as the inelastic scattering of light by matter. When a photon of visible light, too low in energy to excite an electronic transition, interacts with a molecule it can be scattered in one of three ways. It can be elastically scattered and thus retain its incident energy (Rayleigh scattering) or it can be inelastically scattered by either giving energy up to, or by removing energy from, the molecule. Photons undergoing inelastic loss of energy give rise to Stokes scattering while photons undergoing inelastic gain of energy give rise to anti-Stokes scattering (Fig. 6.1).

Electromagnetic radiation exhibits the properties of both particles and wave, thus Raman scattering can also be described in two ways: the classical interpretation is based on the wave theory and the quantum interpretation is based on electromagnetic radiation as energetic particles.


6.2.1 Classical description of Raman scattering

The classical interpretation of light scattering assumes that the molecule is a vibrating dipole. When a molecule is placed in an electric field, the electrons are displaced relative to its nuclei thus developing an electric dipole moment. The induced dipole moment is proportional to the field:

$$\mu = \alpha E$$  \hspace{1cm} (Eq. 6.1)

Where $\alpha$ is the polarizability of the molecule and describes the ease with which molecular orbitals are deformed by the presence of an external electric field. $E$ is the electric field and can be expressed as:

$$E = E_0 \cos(2\pi v_0 t)$$  \hspace{1cm} (Eq. 6.2)

Where $E_0$ is the intensity amplitude of the electric component, $v_0$ is the wave frequency and $t$ is time. Substituting Eq. 6.2 into Eq.6.1:

$$\mu = aE_0 \cos(2\pi v_0 t)$$  \hspace{1cm} (Eq. 6.3)

That value varies in accordance with the wave frequency and the molecule becomes the source of radiation of that frequency. Like this we obtain the Rayleigh scattering, which would be the only possible form of scattering if the molecule did not have its own internal vibrations. In the course of vibration, the molecule may change its size and shape, and thus its polarizability (the shape of the polarizability ellipsoid). If the polarizability changes during the vibration every component of the polarizability tensor $\alpha_{ij}$ will be given as:

$$\alpha_{ij} = (a_{ij})_0 + \left(\frac{\partial a_{ij}}{\partial Q}\right)_0 Q$$  \hspace{1cm} (Eq. 6.4)

where $\left(\frac{\partial a_{ij}}{\partial Q}\right)_0$ is the change of component $\alpha_{ij}$ in the course of the given vibration, characterized by the normal coordinate $Q$, describing the displacement of all nuclei of the atoms in the molecule during vibration about their equilibrium positions, and $(a_{ij})_0$ is the value of $a_{ij}$ at the equilibrium position of the nuclei.

The normal coordinate varies periodically along the axis of vibration at time $t$: 

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\[ Q_v = A_v \cos(2\pi vt) \]  
\((\text{Eq. 6.5})\)

being \(A_v\) the amplitude of the given normal vibration of the molecule. Writing the polarizability tensor in the form of matrix:
\[
(a_{ij}) = \alpha \quad (\text{where } i,j = x, y, z)
\]
and substituting equation (6.5) into (6.4) yields:
\[
\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q_v}\right)_0 A_v \cos(2\pi vt) \]  
\((\text{Eq. 6.6})\)

Considering equation (6.3) we can rewrite the expression describing the value of the moment induced in a molecule with a vibration of frequency \(v\), by an electromagnetic wave of frequency \(v_0\):
\[
\mu = \alpha_0 E_0 \cos(2\pi v_0 t) + \left(\frac{\partial \alpha}{\partial Q_v}\right)_0 A_v E_0 \cos(2\pi v_0 t) \cos(2\pi vt) \]  
\((\text{Eq. 6.7})\)

Having in mind that \(\cos(a \cos \beta = \frac{1}{2} \cos(a - \beta) + \frac{1}{2} \cos(a + \beta)\) finally we obtain:
\[
\mu = \alpha_0 E_0 \cos(2\pi v_0 t) + \frac{1}{2} \left(\frac{\partial \alpha}{\partial Q_v}\right)_0 A_v E_0 \left\{ \cos[2\pi(v_0 - v)t] + \cos[2\pi(v_0 + v)t] \right\} \]  
\((\text{Eq. 6.8})\)

The vibrating molecule can therefore be the source of scattered radiation of three different frequencies: The first term, frequency \(v_0\) unchanged with respect to the incident one, describes the Rayleigh scattering; the second term, frequency \((v_0 - v)\), describes the Stokes; and the third term, frequency \((v_0 + v)\), describes the Raman anti-Stokes scattering.

In addition equation Eq. 6.8 shows that for Raman scattering to occur \(\left(\frac{\partial \alpha}{\partial Q_v}\right)_0 \neq 0\), that is, the polarizability of the molecule must change during a vibration if that vibration is to be Raman active.

### 6.2.2 Quantum description of Raman scattering

Energy particles are generally known as quanta, and in the case of
electromagnetic radiation also as photons. The quantum theory approach to Raman scattering recognizes that the vibrational energy of a molecule is quantized according to Planck relationship:

\[ E_v = h\nu \]  

(Eq. 6.9)

Where \( \nu \) is the frequency and \( h \) is the Planck constant.

Interaction of photon with a molecule can yield three phenomena:

1. Absorption takes place if the photon energy corresponds to the difference between two stationary energy levels of the molecule.
2. Emission occurs from the excited molecule; the energy of the photon emitted also corresponds to the difference between two stationary energy levels of the molecule.
3. Scattering occurs as interaction of the photon and molecule when the photon energy does not correspond to the difference between any of two stationary energy levels of the molecule. This is an “immediate” effect, within about \( 10^{-14} \) s.

Scattering is a two-photon process, which cannot be experimentally separated into two single-photon steps of absorption and emission. **Figure 6.1** shows the scattering mechanism when identical molecules are irradiated with monochromatic light. The Rayleigh scattering arises from transitions, which start and finish at the same vibrational energy level. Stokes Raman scattering arises from transitions, which start at the ground state vibrational level and finish at a consecutive higher vibrational energy level, whereas anti-Stokes Raman scattering involves a transition from a higher to a lower vibrational level. The absolute differences between the frequency of the incident photon and both inelastically scattered photons are the same and equal to the molecular vibration frequency.
Figure 6.1 - Diagram of scattering during illumination of the sample with monochromatic light (v: vibrational levels).

At room temperature most molecular vibrations are in ground state and thus the Raman Stokes scattering results as the more intense,

\[ \frac{\text{Population excited}}{\text{Population ground}} = e^{\frac{\Delta E}{kT}}. \]

Moreover, the intensity of the Rayleigh line is $10^3$-$10^4$ times greater than that of the accompanying Raman bands.

### 6.2.3 Polarizability

As we have already seen, $\alpha$ is the polarizability of the molecule and describes the ease with which molecular orbital are deformed by the presence of an external electric field, $E$. The polarizability is a tensor and as such has components in each of the x, y, z directions of the Cartesian coordinate system.

\[
\alpha = \begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix} \quad (Eq. 6.10)
\]

Changes in any $a_{ij}$ results in Raman activity. The polarizability tensor is symmetrical, $a_{ij} = a_{ji}$. The properties of every tensor change
according to the coordinate system selected, however, there are two values that are independent of the coordinates. These values are known as invariants of the system and are:

the mean value,

\[
\bar{a} = \frac{1}{3}(a_{xx} + a_{yy} + a_{zz}) \quad (Eq. \ 6.11)
\]

and the anisotropy,

\[
\gamma^2 = \frac{1}{2}\left[(a_{xx} - a_{yy})^2 + (a_{yy} - a_{zz})^2 + (a_{zz} - a_{xx})^2 + 6(a_{xy}^2 + a_{xz}^2 + a_{yz}^2)\right] (Eq. \ 6.12)
\]

The diagonal values of the polarizability tensor, \(a_{xx}, \ a_{yy}, \ a_{zz}\) are the semi axis of the polarizability ellipsoid; if the molecule is isotropic then the polarizability ellipsoid becomes a sphere. The anisotropy \(\gamma^2\) gives the deviation of the polarizability ellipsoid from spherical symmetry. When anisotropy is equal to zero, we have spherical symmetry and only the diagonal components of the tensor are non-zero.

### 6.2.4 Resonance Raman scattering

Resonance Raman scattering occurs when the sample is irradiated with an exciting line whose energy corresponds to that of the electronic transition of a particular chromophoric group in a molecule. Under these conditions, the intensities of Raman bands originating in this chromophore are selectively enhanced by a factor of \(10^3\) to \(10^5\). This selectivity is important not only for identifying vibrations of this particular chromophore in a complex spectrum, but also for locating its electronic transitions in an absorption spectrum.

Theoretically, the intensity of a Raman band observed at \(\nu_0 - \nu_{mn}\) is given by:

\[
I_{mn} = const \cdot I_0(\nu_0 - \nu_{nm})^4 \sum_{p\sigma} |(\alpha_{p\sigma})_{mn}|^2 \quad (Eq. \ 6.13)
\]

Here, \(m\) and \(n\) denote the initial and final states, respectively, of the electronic ground state. \(I_0\) is the intensity of the incident laser beam of frequency \(\nu_0\). Finally, \((\alpha_{p\sigma})_{mn}\) represents the change in polarizability \(\alpha\), caused by the \(m \rightarrow e \rightarrow n\) transition, and \(p\) and \(\sigma\) are \(x, y\) and \(z\) components of the polarizability tensor. This term can be rewritten as:
where $v_{em}$ and $v_{en}$ are the frequencies corresponding to the energy differences between the states subscribed and $h$ is Planck’s constant. $M_{me}$, etc. are the electric transition moments, such as:

$$M_{me} = \int \Psi_m^* \mu_\sigma \Psi_e d\tau$$  \hspace{1cm} (Eq. 6.15)

Here, $\Psi_m$ and $\Psi_e$ are total wavefunctions of the m and e states, respectively, and $\mu_\sigma$ is the $\sigma$ component of the electric dipole moment. $\Gamma_e$ is the band width of the e-th state, and the $i\Gamma_e$ term is called the damping constant. In normal Raman scattering, $v_0$ is chosen so that $v_0 \ll v_{em}$. Namely, the energy of the incident beam is much smaller than that of an electronic transition. Under these conditions, the Raman intensity is proportional to $(v_0 - v_{mn})^4$. As $v_0$ approaches $v_{em}$, the denominator of the first term in the brackets of Eq.6.14 becomes very small. Hence, this term (“resonance term”) becomes so large that the intensity of the Raman band at $v_0 - v_{mn}$ increases enormously. This phenomenon is called resonance Raman scattering.

\section*{6.3 \textbf{INTRODUCTION TO SURFACE-ENHANCED RAMAN SCATTERING (SERS)}}^{1,2}

The work on pyridine on electro-chemical roughened silver electrodes by Fleischmann et al.\textsuperscript{6} in 1974 (which is considered now to be the first ever reported observation of the SERS effect) was presented and interpreted as due to an increase in the effective surface area caused by the roughening of the electrodes. In historical terms, the concept of a surface enhancement other than a resonance (Raman) effect was not envisioned as possible. The original idea of an increase in the effective surface area due to roughness was appealing for its simplicity, and was also timely at a moment when theories of “fractal effects” started to proliferate in many disciplines. The increased number of molecules resulting from the larger surface area seemed to be the most natural explanation for the observed signal enhancements.

Two independent (and almost simultaneous) papers by Jeanmaire and Van Duyne\textsuperscript{7} on one side, and Albrecht and Creighton\textsuperscript{8} on the other, provided a demonstration that the observed signal levels could not be
accounted for by an increased surface area. These papers hence suggested that a different form of enhancement acting directly on the Raman intensities of the molecules had to be invoked.

6.4 BASIC ASPECTS OF SERS\textsuperscript{1,13}

6.4.1 Enhancement factors

In normal Raman spectroscopy, the average Raman intensity of a molecule is directly proportional to the laser power density and to the Raman cross-section of the molecule. This simple fact can be generalized to SERS. In simple terms, the SERS intensity for a given vibrational mode of a given analyte should also be proportional to the laser intensity and to the normal Raman cross-section but affected by an enhancement factor.

One important aspect of SERS enhancement factors is that they should be “real” enhancement factors, i.e. they characterize the enhancement obtained with respect to what would be obtained under non-SERS conditions for the same molecule.

The \textbf{electromagnetic enhancement factor} is thought to be the main contribution. It is due to the coupling of the incident and Raman electromagnetic fields with the SERS substrate and it can usually be separated into two multiplicative enhancement factors, one for the incident field, and one for the re-emitted (Raman) field, as will be justified later. The electromagnetic enhancement relies on the large local field enhancements that occur close to metallic surfaces when localized surface plasmon resonances are excited. To profit from these, the molecule must then be in close proximity to the surface (typically within \(\sim10\) nm from the surface, at most). In most implementations, the molecule is actually directly adsorbed on the surface, either through physisorption or chemisorption (i.e. through the formation of a chemical bond with the metal).

Another multiplicative contribution to the SERS enhancement is the so-called \textbf{chemical enhancement factor}. Its existence and its contribution is, in any case, believed to be much smaller than the electromagnetic effect. The chemical enhancement factor is sometimes viewed as a modification of the electronic polarizability of the probe,
which can induce resonant-Raman scattering (and therefore enhanced signals) at wavelengths where the non-adsorbed molecules would not be resonant. The most widely accepted explanation for this is the so-called charge-transfer mechanism. This requires the molecule to be chemically adsorbed on the surface.

### 6.4.2 Electromagnetic enhancement factor

SERS enhancements are usually explained as an electromagnetic effect. Generally, the noble metals used as SERS substrates show intrinsic optical properties necessary to stimulate the SERS effect. Metals such as gold (Au), silver (Ag), copper (Cu), or aluminum (Al), have long been known to have different optical properties from standard dielectrics. They, for example, reflect light very efficiently in the visible, making them good materials for mirrors of various types. These particular optical properties, along with many other physical properties (such as heat or electrical conductivity) all have the same physical origin, the presence of free conduction electrons.

The free electrons of a metal move in a background of fixed positive ions (the vibrations of ions, or phonons, are ignored here in a first approximation), which ensures overall neutrality. This forms, by definition, a plasma and can be called a free-electron plasma, or solid-state plasma. The optical response of this free-electron plasma will govern all the optical properties of metals, at least in the visible part of the spectrum where its characteristic resonant energies reside.

To model the optical response of a free-electron plasma, one needs to determine the constitutive equations relating the currents and charges in the plasma to the electromagnetic fields. This is a very difficult undertaking in general because of many possible complications, including: the interaction of electrons with the underlying periodic structure of ions, the electron-electron correlations and the fermionic nature of electrons, the interaction of electrons with impurities and phonons, and the possible presence of surfaces. This response can be described briefly by the Drude model. This model describes the optical response of an electron in an atom or molecule, bound with a restoring force characterized by a resonant frequency $\omega_0$. The conduction electrons in a metal are not bound and can therefore, in a first approximation, be described by the Lorentz model, without restoring force (i.e. $\omega_0=0$). Moreover, because the free electrons are
distributed uniformly and randomly throughout the metal, their contributions to the total optical susceptibility are simply the sum of their individual polarizabilities, without any local field correction. The Drude relative dielectric function of a metal can then be obtained by taking $\omega_0 = 0$ in the Lorentz model:

$$\varepsilon(\omega) = 1 - \frac{ne^2}{m\varepsilon_\infty} \frac{1}{\omega^2 + i\gamma_0\omega}$$  \hspace{1cm} (Eq. 6.16)$$

where $n$ (m$^{-3}$) is the number of free electrons per unit volume and $m$ (kg) their mass. The damping term, $\gamma_0$ (rad s$^{-1}$), here corresponds to the collision rate of free electrons with the crystal or impurities. The optical response of the positive ions in the crystal has so far been ignored. In a first approximation these contribute to a constant background real dielectric function $\varepsilon_\infty \geq 1$. This affects the optical response of the crystal and the dynamics of the free electrons. This can easily be incorporated in the Drude model and leads to a slightly modified expression for $\varepsilon(\omega)$, namely:

$$\varepsilon(\omega) = \varepsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma_0\omega}\right)$$  \hspace{1cm} (Eq. 6.17)$$

where we have defined $\omega_p$ (rad s$^{-1}$) as

$$\omega_p = \sqrt{\frac{ne^2}{m\varepsilon_\infty \varepsilon_\infty}}$$  \hspace{1cm} (Eq. 6.18)$$

In the absence of an external perturbation, the charge density of a plasma is uniform and zero. It can be shown that $\omega_p$ is the natural oscillation frequency of the free-electron-plasma charge density and it is therefore called the plasma frequency. One can also define the corresponding wavelength $\lambda_p = 2\pi c/\omega_p$. Taking the real and imaginary parts of the previous expression, we have:

$$R(\varepsilon(\omega)) = \varepsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2 + \gamma_0^2}\right)$$  \hspace{1cm} (Eq. 6.19)$$

and
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\[
\text{Im}(\varepsilon(\omega)) = -\frac{\varepsilon_\infty \omega_p^2 \gamma_0}{\omega(\omega^2 + \gamma_0^2)} \quad (\text{Eq. 6.20})
\]

Keeping in mind that \( \gamma_0 \) is small compared to \( \omega \), we see that for a plasma described by a Drude model, the plasma frequency can be obtained from the condition \( \text{Re}(\varepsilon(\omega_p))=0 \). We also see that in the region where \( \omega < \omega_p \) (wavelength longer than \( \lambda_p \)), we have \( \text{Re}(\varepsilon(\omega))<0 \). Moreover, if \( \omega \) is not too small, the absorption, characterized by \( \text{Im}(\varepsilon(\omega)) \), is also small in this region. It is these two conditions, \( \text{Re}(\varepsilon(\omega))<0 \) and small \( \text{Im}(\varepsilon(\omega)) \), that make possible a whole range of interesting optical effects, including plasmon resonances.

A comparison of the optical properties (real and imaginary parts of the dielectric function) of various metals is given in Figure 6.2. The monotonous decay of \( \text{Re}(\varepsilon) \) from small values in the UV to negative values in the visible, and very negative values in the infrared, is common to all metals and is in fact predicted by the Drude model (for typical plasma frequencies in the UV). This is one of the most important characteristics of metals, as far as optical properties are concerned, and it is a consequence of the optical response of the free (conduction) electrons, as explained by the Drude model.

![Figure 6.2](image1.png)

**Figure 6.2** - Overview of the optical properties of a selection of metals in the (extended) visible range. The real *(top)* and imaginary *(bottom)* parts of \( \varepsilon \) are
plotted against wavelength on the left. Also shown (top-right) is the predicted approximate quality factor Q of localized surface plasmon resonances for a metal/air nano-particle, as defined in Eq. 6.22. The shaded area is the area of interest to many SERS applications.

The negativity of the real part of $\varepsilon(\omega)$ at visible wavelengths is also the origin of many of the known optical properties of metals, including plasmon-related effects. To understand this in simple terms, let us consider briefly the problem of a small metallic sphere interacting with an electromagnetic field (in a laser beam). The simplest treatment of this problem is to consider a sphere much smaller than the wavelength of the incident beam and solve the problem within the electrostatic approximation. It is then equivalent to the electrostatic problem of a sphere, in a medium of relative dielectric constant $\varepsilon_M$, and in a uniform external electric field. The (complex) electric field inside the sphere can then be shown to be constant and proportional to the incident field $E_0$:

$$E_m = \frac{3\varepsilon_M}{\varepsilon(\omega) + 2\varepsilon_M} E_0 \quad \text{(Eq. 6.21)}$$

The important part in this expression is the denominator. If it were close to zero (a condition which can be achieved if $\varepsilon(\omega) \approx -2\varepsilon_M$ then the fraction would be very large (infinite for perfect equality). This is not possible for standard dielectrics, for which $\varepsilon$ is typically between 1 and ~10. But for metals, this condition can be approximately met if the absorption is small ($\text{Im}(\varepsilon(\omega)) \approx 0$) at a wavelength where $\text{Re}(\varepsilon(\omega)) \approx -2\varepsilon_M$. The optical response (absorption and scattering) at this particular frequency (or wavelength) is then very large, i.e. this is the signature of a resonance. The strength and width of the resonance is characterized by a quality factor Q defined as:

$$Q = \frac{\omega}{2(\varepsilon'(\omega))} \quad \text{(Eq. 6.22)}$$

where $\varepsilon' = \text{Re}(\varepsilon)$ and $\varepsilon'' = \text{Im}(\varepsilon)$. In simple terms, Q is large when $\text{Im}(\varepsilon)$ is small. Q is also plotted in Figure 6.2 for various metals.

From these qualitative arguments one can consider that a metal is good for plasmonics if:
Re(\(\epsilon\)) is negative in the wavelength range of interest (typically the visible and near infrared).

Im(\(\epsilon\)) is small (or equivalently Q is large) in the range of interest. Typically, Q must be larger than \(\sim 2\), preferably larger than \(\sim 10\).

From the examples of Figure 6.2, this rules out a number of metals, such as aluminum, palladium, platinum, etc. The latter two present too much absorption, while aluminum would only be suitable for applications in the UV.

Among the other metals shown in Figure 6.2, silver is the most promising one and is widely used for SERS. Gold and copper are also suitable, but only at longer wavelengths (typically more than \(\sim 600\) nm). At such wavelengths, the optical absorption of gold in fact becomes comparable to that of silver. Finally, lithium also exhibits suitable properties across the whole visible range, as silver, and even better in the UV but has not been used much. Lithium reacts easily in water and does not occur freely in nature due to its chemical activity; it is therefore not very easy to be used as a plasmon supporting material. Gold is certainly the most promising in these categories, and should therefore be the material of choice for applications beyond \(\sim 600\) nm (in the red and near IR). Silver, whose absorption is the smallest especially below \(\sim 600\) nm, can be used for large field enhancement applications (such as single-molecule detection). These two metals are by far the most widely used metals in SERS applications.

### 6.4.3 Chemical enhancement factor\(^{1,14,15,16}\)

The chemical enhancement is contributed from the chemisorption interaction, the photon-driven charge transfer between adsorbate and substrate and the coupling effect between the electron-hole pair and adsorbed molecules. Figure 6.3 represents schematically the charge transfer mechanism which involves the process of photon-driven charge transfer between the analyte and the metal.
Figure 6.3 - Schematic representation of a charge-transfer mechanism in the SERS cross-section, appearing as a “resonant contribution” to the measured intensity. The laser energy can be directly in resonance with an electronic transition of the molecule-metal complex (case (a)), or can profit from an indirect coupling (charge transfer) through the metal ((b) + (c)).

This situation can occur when the difference between the Fermi level of the metal and the HOMO or LUMO energies is matched by the laser. A photo-driven charge-transfer mechanism between the HOMO and unoccupied states above the Fermi level (or between the LUMO and occupied states slightly below the Fermi level) can be triggered. Although these process result in the relative weak enhancement, they determine the frequency shift and relative intensity of the spectral bands, which is essential for SERS characterization.

Figure 6.4 – Schematic diagrams of the electrochemical interfaces exhibiting SERS and with the coexistence of electromagnetic field and the electric field.
at the electrode potentials positive (a) or negative (b) to the potential of zero charge.$^{14}$

In general, the chemical SERS enhancement factor is considered to contribute enhancement factors of $10-10^2$.

### 6.4.4 Factors influencing the SERS enhancement

The SERS process and therefore the enhancement factor, depends on many parameters including:

- Characteristics of the laser excitation, in particular: wavelength, polarization, angle of incidence (for a planar substrate), etc.

- Detection setup, in particular: scattering configuration (e.g. backscattering geometry), solid angle for collection, polarized and/or unpolarized detection, etc.

- SERS substrate, in particular: material (usually silver or gold), geometry, orientation with respect to incident beam direction and polarization, and refractive index of the environment $n_M$. The dimensionality of the substrate (e.g. 2D planar substrate or 3D particles in solution) is also an important parameter since it requires different sample preparation procedures.

- Intrinsic properties of the analyte, in particular: Raman polarizability tensors of the modes (or intrinsic Raman cross-sections).

- Analyte adsorption properties, in particular: adsorption efficiency and analyte concentration (surface coverage), distance from the surface, adsorption orientation (fixed or random), and the possible modification of the intrinsic Raman polarizability induced by adsorption. This latter aspect is essentially the chemical contribution to SERS while, the previous one provides the background and origin of surface selection rules.
6.5 METALLIC COLLOIDS AS SERS SUBSTRATES

The SERS literature makes often reference to “SERS substrates”, which generally mean any metallic structure (or nano-structure) that produces the SERS enhancement. SERS substrates can be classified into three main classes:

- Metallic particles (usually nano-particles) in solution, such as colloidal solutions.
- “Planar” metallic structures, such as arrays of metallic nano-particles supported on a planar substrate (glass, silicon, metals, etc).
- Metallic electrodes.

Amongst the other two classes of SERS substrates, solutions of metallic colloids, predominantly made of silver (Ag) or gold (Au), represent one of the simplest and most accessible routes to SERS. The colloids exist in solution (often in water for SERS applications) only because they are stabilized by Coulombic (or sometimes steric) repulsions among particles. This normally requires the presence of a “stabilizing agent”, which coats the surface of the colloids and prevents them from aggregating. In some cases, a single chemical compound plays both the role of reducing agent and stabilizer; this is the case of sodium citrate-reduced colloids, one of the most commonly-used types in SERS reported by Lee & Meisel. Au colloids are more easily stabilized being less susceptible to oxidation than Ag colloids over a long period of time. However, Ag colloids are more commonly used for SERS experiments than Au ones because Ag particles provoke larger electromagnetic enhancements at the region ~600-650 nm.

6.5.1 Preparation of citrate-reduced silver colloids

In the context of this thesis, for the preparation of SERS substrates - citrate-reduced Ag colloids-, the Lee and Meisel procedure was followed as described by the following steps:

> Initially, 90 mg of silver nitrate (AgNO₃) were dissolved in 500 mL of distilled water (H₂O) and brought to boiling in a three-
neck flask of capacity 1 L by the use of oil bath, as shown in Figure 6.5.

While the solution reached to boiling, an aqueous solution of 10 mL of 1% w/w trisodium citrate (Na$_3$C$_6$H$_5$O$_7$) was added serving as both reducing and stabilizing agent.

After the addition of Na$_3$C$_6$H$_5$O$_7$, the solution was kept boiling for ~1 h, while refluxing the evaporating water, and then cooled down to room temperature.

**Figure 6.5** – Image of the experimental procedure followed, for the preparation of citrate-reduced colloid.

The reduction of Ag$^+$ to Ag$^0$ happens through the redox reaction which involves the oxidation of carbon bonds in the citrate-ion. This yields CO$_2$ and 2-propanol. In order to destabilize the carbon bonds, energy is added through heat. The reaction is described below:

$$3Ag^+(aq) + C_6H_5O_7^{3-}(aq) + 3H_2O(l) + 3e^\text{heat} \rightarrow 3Ag(s) + C_6H_5O(1) + 3CO_2(g) + 3OH^-(aq)$$

The initial concentration of the reagents in solution therefore: 1.04 mM of AgNO$_3$ and 0.76 mM of Na$_3$C$_6$H$_5$O$_7$. 
This procedure results in a grey-yellow solution which shows a UV-Vis absorption maximum at ~400-430 nm (depending on the details of the preparation) as shown in Figure 6.6. This optical absorption is produced by the average single-particle localized surface plasmon resonance of the particles.\textsuperscript{1} The most important characteristic that is extracted from absorption spectra is the resonance wavelength. Because SERS occurs precisely as a result of the interaction with such localized surface plasmon resonances, the largest SERS enhancement is expected when the incident laser is at a wavelength close to the resonance wavelength.

![Citrate-reduced Ag colloid](image)

**Figure 6.6** – Representative UV-Vis absorption spectrum. The main peak at ~410 nm is the contribution of the dipolar localized surface plasmon resonances.

The size of the Ag nanoparticles resulted to be ~7 nm measured by DLS. Regarding their stability over time, this kind of silver colloids might display signs of “aging” after long periods of time (**Figure 6.7**).
Citrate ions, \( \text{C}_6\text{H}_5\text{O}_7^- \) are triply negative and are a weak base whose triple acid form is citric acid \( \text{C}_6\text{H}_8\text{O}_7 \). This may be relevant in pH-dependent SERS experiments.

### 6.5.2 Aggregation of citrate-reduced silver colloids

In order to abet the SERS effect, the appropriate laser excitation line is of crucial importance to be wisely chosen. For the prepared Ag colloid, the surface plasmon resonance absorption maximum appeared at \( \sim 410 \) nm as indicated before. Figure 6.8 shows the absorption spectrum of silver colloid that is close to monodisperse. It shows the profile wavelength dependence of the absorption of light by the surface plasmon for unaggregated colloid. This is chosen as the example of a substrate because the plasmon spans a relatively narrow range of wavelengths compared to many solid-state substrates or aggregated colloid and so the effects of wavelength dependence are more critical. The scattering depends on both the absorption and emission frequencies but these are relatively close together in terms of the wavelength ranges discussed here and so they are not differentiated. For unaggregated colloids, excitation close to the peak will give the most effective results.\(^{18,19,20,21}\)
Figure 6.8 – The plasmon-resonance absorption profile of unaggregated silver colloid together with four possible choices of excitation frequency. Laser excitation (a) is ideal for SERS with unaggregated colloid. On aggregation, the plasmon resonance moves to the red and broadens so (b), (c) and (d) will give effective SERS. The absorption spectrum of two dyes, one with an absorption maximum at 400 nm (A) and the other with an absorption maximum at 700 nm (B) are shown.\(^1\)

It is possible to aggregate the colloid in a controlled manner to bring particles together. This shifts the plasmon absorption to the red and broadens it. Often, external aggregating agents such as sodium chloride (NaCl) are used to do this. Zeta-potential measurements indicate that this reduces the charge on the surface making the colloidal particles less stable and causing aggregation. The result of this is that a series of different-sized clusters are formed, each with a different absorption maximum and bandwidth. The absorption spectrum is now a sum of all these giving a much broader red-shifted spectrum compared to the unaggregated colloid. It is likely that some of these clusters will be in resonance with any excitation wavelength chosen in the visible region. In this situation, the wavelength chosen is less critical but the actual enhancement depends on the number of clusters present at the wavelength chosen. In surface-enhanced resonance Raman scattering (SERRS), the situation is somewhat more complex since both the plasmon resonance and the molecular resonance contribute. Figure 6.8 shows examples of possible choices.
of excitation frequencies for a dye that absorbs at 400nm and one that absorbs at 700 nm.21

REFERENCES

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Chapter 7  

**Surface-enhanced Raman scattering of pyridine-functionalized multi-walled carbon nanotubes**

**ABSTRACT**

Carbon nanotubes (CNTs) have attracted great attention for their potential use in many applications because of their intrinsic properties. The importance other than the impact of the application of CNT-embedded membranes in the area of water technology development is immense. In this context, the identification and quantification of CNTs in aqueous resources during relevant water purification processes can be proven of high significance. Surface-enhanced Raman scattering (SERS) potentially has the sensitivity required for trace analysis and has been previously used for CNT identification on solid substrates. A thorough study for the detection and quantification of small concentrations of multi-walled CNTs (MWCNTs) in water suspensions *via* SERS has been performed. The functionalization of MWCNTs with pyridine groups seems to favor the surface enhancement of relevant Raman signal. This study constitutes the first step for the characterization of CNTs at quite low concentration range by SERS in any water suspension. It is based on an *ex ante* functionalization of the CNTs by pyridine, demonstrating the potential of the method. The long-term aim is its general application built, however, in an *ex post* relevant functionalization of the CNTs in any aqueous solution.
7.1 INTRODUCTION

Carbon nanotubes have attracted great attention because of their exceptional electronic, optical, mechanical and chemical properties, making them attractive for many applications. In recent years, a potential application with high impact is the development of CNT-embedded polymeric membranes for water purification. Membrane bioreactors (MBRs) are an innovative technology, ideal for the treatment and rehabilitation of advanced municipal and industrial wastewater containing high biodegradable organic compounds. A new category of functional membranes for MBR technology by the embedment of CNTs into porous polymeric matrixes predisposes both improved water flow and rejection of organic compounds and inorganic salts of low molecular weight as well as greater resistance to the microorganisms deposited on the membranes. A basic principle of this new type of CNT-incorporated membranes is the efficient binding of CNTs in the membranes to minimize probable health risk associated with the toxicity of as-grown CNTs being applied in water purification applications, where there are chances of product water getting contaminated with CNTs.

Raman spectroscopy has been widely utilized as a powerful tool for characterization and molecular structure determination of a range of materials. Unfortunately, the Raman effect is inherently weak and incompetent for trace analysis. However, the Raman signal can be enhanced by many orders of magnitude for molecules in the vicinity of or even attached to noble metal nanostructures; this effect known as surface-enhanced Raman scattering, (SERS), offers challenging opportunity for studying CNTs.

Limited works dealing with SERS on CNTs have been published. Namely, Li Yan et al. have reported that the attachment of Au nanoparticles (NPs) on thiol-functionalized CNTs favored the SERS effect in relevant aqueous suspensions. While, some other studies were based on multi-walled and single-walled CNTs (MWCNTs and SWCNTs, respectively) on silver or gold solid substrates. More and above that, the quantitative evaluation by means of SERS was proven difficult, because of the lack of nano-sized noble metal structures with analytically suitable stability and reproducibility especially when using solid substrates; it is easy to understand that the surface-enhanced Raman signal is strongly correlated with the local pertinent topography. On the other hand, nano-colloidal noble metal suspensions are distinguished for optimal reproducibility. Even
in this case, inhomogeneous suspensions are formed in terms of size, shape and aggregation behaviour. To overcome this obstacle prohibiting quantitative SERS measurements, flow\textsuperscript{12} and oscillating\textsuperscript{13} cells have been mainly utilized. In the case of the present study, an oscillating cell in combination with the right angle Raman scattering geometry was used, as has been reported.\textsuperscript{13} Nevertheless, even under these favorable experimental conditions, it was not possible to collect SERS spectra from CNTs and in the specific case from MWCNTs. To this end, the introduction of SERS active pyridine moieties via MWCNT functionalization was carried out, and as a result, SERS of the graphitic surface of the nanotubes was stimulated, as well.

\section*{7.2 EXPERIMENTAL}

\subsection*{7.2.1 Preparation of silver nano-colloidal suspensions and MWCNT aqueous suspensions}

High purity MWCNTs 97%, of external diameter ranging between 15 and 35 nm and synthesized by chemical vapor deposition method, CVD, using ethylene as the carbon precursor were kindly supplied by Nanothinx S.A. (GR). The CVD method is known to produce batches that are generally free from amorphous carbon and carbon nanoparticles.\textsuperscript{14,15} Pyridine-functionalized multi-walled carbon nanotubes (MWCNT-pyr), were prepared according to a solvent free sidewall functionalization reaction that C.A. Dyke and J.M. Tour proposed\textsuperscript{16,17} This approach eliminates the need for large volumes of solvent (~ 2 L/g) which were formerly considered essential due to the insolubility of carbon nanotubes. Using a series of 4-substituted anilines and a nitrite, the aryl diazonium intermediates were generated in situ and permitted to react with the tubes (Fig. 7.1).

![Figure 7.1](image)

\textbf{Figure 7.1} - General structure of chemically modified MWCNTs with pyridine, MWCNT- pyr.\textsuperscript{17}
The pyridine content in the functionalized MWCNT samples was estimated gravimetrically as 7% w/w. MWCNT-pyr suspension (100 μg/mL) was prepared in TDW; ultrasound was applied in order to break up bundles. After sonication for 10 min with sonic tip (400W, 35%), well-dispersed nanotubes were obtained.

For the preparation of silver nano-colloidal suspensions, analytical grade silver nitrate (CAS 7761-88-8), sodium citrate tribasic dihydrate (CAS 6132-04-3) and sodium chloride (EC No. 2315983) were purchased from Sigma-Aldrich. A modified procedure of Lee and Meisel method\textsuperscript{18} based on the reduction of Ag\textsuperscript{+} to Ag\textsuperscript{0} which happens through a redox reaction involving the oxidation of carbon bonds in the citrate-ion was followed for Ag colloid preparation. This yields CO\textsubscript{2} and 2-propanol. In order to destabilize the carbon bonds, energy must be added through heat. The reaction is described in Figure 7.2.\textsuperscript{19,20} All glassware was washed with piranha solution followed by extensive rinsing with TDW prior to use.

\[ 3\text{Ag}^+(aq) + \text{C}_6\text{H}_5\text{O}_3^-\text{(aq)} + 3\text{H}_2\text{O}(l) + 3e^- \xrightarrow{\text{heat}} 3\text{Ag(s)} + \text{C}_6\text{H}_5\text{O}_2(l) + 3\text{CO}_2(g) + 3\text{H}^-\text{(aq)} \]

**Figure 7.2** - Reaction of citrate synthesized Ag-NPs.

### 7.2.2 Instrumentation

To collect the SERS spectra, samples were excited with a water-cooled Ar\textsuperscript{+} laser (Spectra physics model 2017, 5W all lines) operating at 514.5 nm. An achromatic doublet (f: 145 mm; ϕ: 35 mm) was utilized to focus the laser beam into the Pyrex test tube filled with nano-colloidal silver suspensions. The Raman spectra were excited with a laser power of 120 mW on the sample and were collected with a spectral slit width of 8 cm\textsuperscript{-1} using the T-64000 spectrometer of Jobin Yvon (ISA-Horiba group) in the single spectrograph configuration.

This spectrograph bears a rectangular entrance slit long (& horizontal) in the direction perpendicular to the lateral direction of the separation of light. Therefore, it allows the optimum right-angle collection of the collateral scattering volume of a linear-like focusing field of the excitation laser line.\textsuperscript{13} For elastic Rayleigh scattering rejection, a holographic super edge filter (LP02-514RU-25, Laser 2000 (UK) Ltd.) was used. The Raman photons were dispersed by a 600-grooves/mm (76 mm X 76 mm) 500 nm blazed holographic diffraction grating and
detected by a standard LN$_2$ cooled (at 140 K) front illuminated CCD (Spectraview-2DTM, 1024x256-1) detector. The spectrometer was calibrated using the standard 992 cm$^{-1}$ Raman band position of the ring breathing mode of benzene or/and the 801.3 cm$^{-1}$ band of cyclohexane. Reproducible and improved Raman scattering collection measurements were allowed by the use of an oscillating cell in combination with the advantage of probing nanocolloidal suspensions via right angle light scattering collection geometry. A detailed description of this configuration has been reported by Manikas et al.$^{13}$ This design permits the collection of the scattered Raman light at 90° of the excitation optics, while during oscillation the linear focusing field of the excitation line of the laser covers a quite broad volume of the cell; in this way, the spectra obtained were representative of the overall volume of the sample and due to the “shaking” a continuous mixing of the solution was occurring.

To collect the conventional Raman spectra, from the pristine MWCNTs and pyridine-functionalized MWCNTs in powder form, the T-64000 spectrometer was also utilized, however, in the micro-Raman configuration. The excitation beam was directed to the sample compartment of a properly modulated metallurgical microscope (Olympus BHSM-BH2). The microscope was used for the delivery of the excitation laser beam on the sample and the collection of the backscattered light through a beam splitter and the objective lens adapted to the aperture of the microscope. The focusing objective was a long working distance (8 mm) 50X/0.55 Olympus lens. The spectra were excited with a laser power of 6 mW on the sample.

**7.3 RESULTS AND DISCUSSION**

**Figure 7.3** depicts the UV-Vis absorption spectra of the silver colloid and the colloid activated with the aggregating agent NaCl. A note is made of the fact that in order to obtain accurate UV-Vis absorption spectra, 0.5 mL of the corresponding nanocolloidal suspensions have been diluted to 2 mL of TDW.
The violet-blue extinction band of silver colloid proves the existence of silver nanoparticles and the strong interaction of violet-blue light with surface plasmons localized in these nanoparticles. The aggregation of nanoparticles differentiates the conditions for the Raman signal enhancement. The absorbance peak changes shape when the aggregating agent (NaCl) is added to the silver colloid; after addition of the small amount of NaCl 1M (40 μL) in 1 mL of Ag nanocolloidal solution, the main absorption peak of silver colloid related to the dipole plasmon resonance is reduced and broadened to the green/red/NIR side. If further amount of anions is added, the stability of colloidal suspension is affected and after a few minutes gradual precipitation of colloid is observed.\textsuperscript{21}

### 7.3.1 Activation of silver colloid

SERS spectra were collected from Pyrex test tubes containing 1 mL of silver colloid activated by 40 μL of 1M NaCl\textsuperscript{22,23,24,25,26} and 0.5 mL of the CNT suspension under study. A primary study regarding the proper amount of NaCl to be mixed with the Ag solution in order to abet the SERS effect was preceded and based on the enhancement of the ~1025 cm\textsuperscript{-1} peak; it is concluded that about 40 μL of NaCl in each
1 mL of Ag solution rise the SERS enhancement remarkably compared to a quantity range between 20 and 120 μL as shown in Figure 7.4.

![Figure 7.4 - Effect of NaCl quantity on SERS intensity of MWCNT-pyr.](image)

For the quantification study, all SERS spectra were collected three times using the same colloid and activating agent, the same order of filling the test tube, for an almost zero waiting time before spectra collection. Each group of the final measurements was carried out the same day. In order to reveal any “interaction” and/or the “size” of MWCNT-pyr in NaCl activated silver nanocolloids, beyond the collection of relevant Raman/SERS spectra discussed later on, Dynamic Light Scattering (DLS) and X-ray Photoelectron Spectroscopy (XPS) measurements were performed and explicitly are described in Appendix I.

### 7.3.2 SERS of pyridine-functionalized MWCNTs

**Figure 7.5-a** shows the conventional Raman spectrum of MWCNTs in an aqueous suspension (100 μg/mL), and **Figure 7.5-b** an effort to
excite SERS spectrum of MWCNTs in a Ag nanocolloidal solution; both spectra were collected in the 90° configuration, over the frequency range of 1000 – 2000 cm\(^{-1}\). The backscattering Raman spectrum of pristine MWCNTs in powder form is also depicted for reference as Figure 7.5-c.

![Raman spectra](image)

**Figure 7.5** - Conventional Raman spectra: (a) suspension of MWCNTs (100μg/mL) in TDW collected in the 90° configuration, (b) MWCNT water suspension (100 μg/mL) in silver colloid aggregated by addition of NaCl (no SERS effect was detected) and (c) pristine powder MWCNTs collected in the backscattering configuration.

The latter shows the characteristic D band at 1350 cm\(^{-1}\) attributed to the presence of amorphous or/and disordered carbon and the G band at around 1575 cm\(^{-1}\) originated from in-plane tangential stretching of the carbon-carbon in graphene sheets.\(^{27,28,29}\) In the corresponding conventional Raman spectra of MWCNT suspension in TDW (Fig. 7.5-a), this pair of bands can also be identified, however, with an interference of the G band with the deformation broad band of water at ~1635 cm\(^{-1}\). When 0.5 mL of MWCNT/TDW (100 μg/mL) was added to 1 mL of silver colloid aggregated with 40 μL of NaCl, no enhancement of the signal was observed (Fig. 7.5-b). In other words, no surface enhanced Raman scattering from MWCNTs has been
excited/colllected most probably due to their poor “binding” to the silver surface.

In order to overcome this limitation, CNTs functionalized/decorated with pyridine—a strong Raman scatterer—were utilized, with the perspective of enabling the identification and even the quantification of trace amounts of this probe molecule, because its detection could be directly related to the CNTs on which it is attached. This method could provide an indirect detection of the presence of CNTs. Pyridine was selected due both to the relatively easy chemistry that lies behind relevant CNT functionalization\textsuperscript{16,17} and to its intense Raman/SERS spectra; a note is made of the fact that pyridine was also the first ligand investigated by surface-enhanced Raman scattering.\textsuperscript{5,30}

In Figure 7.6, the Raman spectra of pristine and pyridine-functionalized MWCNTs both in the powdered form, are depicted in the 500-2250 cm\textsuperscript{-1} spectral range.

![Raman spectra](image)

**Figure 7.6** - Raman spectra of (a) pristine MWCNT and (b) pyridine-functionalized MWCNT (MWCNT-pyridine), both in powdered form.

They both exhibit similar D and G features. It should be noted that pyridine moieties were attached onto MWCNTs through solvent free functionalization.\textsuperscript{16,17} It is obvious that no relative increase of the intensity of the D band has occurred after the functionalization; that
means this process does not produce additional sidewall defects, as often occurred after oxidative treatments, but the chemical modification takes place in available defect sites without necessarily creating additional ones.\textsuperscript{31}

Thereafter, in order to determine whether MWCNT-pyr stimulate surface enhanced Raman scattering, 0.5 mL of a MWCNT-pyr aqueous suspension of 100 μg/mL was added to 1 mL of silver colloid aggregated with 40 μL of NaCl, and the Raman/SERS spectrum was collected; it is shown in Figure 7.7-a.

![Figure 7.7](image)

**Figure 7.7** - (a) SERS spectrum of MWCNT-pyridine (100 μg/mL), (b) conventional Raman spectrum of MWCNT-pyridine in water suspension (100 μg/mL), (c) Raman spectrum of MWCNT suspension (100μg/mL) in Ag colloid aggregated with NaCl and (d) conventional Raman spectrum of powder MWCNT-pyridine. Spectra (a, b and c) were collected in the 90° configuration while spectrum (d) in the backscattering one.

The conventional Raman spectrum of MWCNT-pyr aqueous suspension of 100 μg/mL is also shown (Fig. 7.7-b) collected under the same conditions. By adding MWCNT-pyr aqueous suspension into Ag colloid, aggregated with NaCl, an important enhancement of the peak at \( \sim 1025 \text{ cm}^{-1} \) attributed to pyridine emerges (Fig. 7.7-a) whereas no band is observed at the normal Raman spectrum of MWCNT-pyr aqueous suspension (Fig. 7.7-b). The origin of the \( \sim 1025 \text{ cm}^{-1} \) band...
cm⁻¹ band has been already assigned to silver-pyridine-halide complexes. More and above that, beyond the SERS of pyridine, at the same time, an apparent enhancement of D and G Raman features of MWCTs occurs (Fig. 7.7-a). To elucidate the overall reasoning, the spectrum of MWCTs (pyridine free) in Ag colloid aggregated with NaCl is also plotted (Fig. 7.7-c) along with the conventional Raman spectrum of MWCT-pyr powder (in Fig. 7.7-d, 50 times magnified).

These results reveal that in pyridine-functionalized MWCTs (MWCT-pyr), spectral features of both MWCTs and pyridine are enhanced when excited after being immersed in a silver nanocolloidal suspension. This surface enhancement of the overall MWCT-pyr spectral pattern (Fig. 7.7-a) compared to the corresponding of MWCT (Fig. 7.7-c), both collected using Ag colloid aggregated with NaCl, is attributed to the π-electrons delocalization over the pyridine ring in the case of pyridine-functionalized MWCTs.

In order to verify that the SERS signal of CNT features is due to the functionalization of the pyridine on the MWCTs, in a subsequent experiment, pyridine as well as 3-aminopyridine, the precursor of pyridine functionalized MWCTs, were separately added to two MWCT dispersions in a ratio 7:100 (wt%) for a total weight of 6 mg in 60 mL TDW; afterwards, 0.5 mL of these dispersions were separately added to 1 mL of Ag colloid containing 40 μL of NaCl in order to collect the corresponding Raman/SERS spectra shown as Figures 7.8-b & 7.8-c, respectively.

![Figure 7.8](image-url)
spectrum of MWCNT + pyridine (c) Raman/SERS spectrum of MWCNT + 3-amino pyridine, (d) SERS spectrum of aqueous pyridine (e) SERS spectrum of 3amino-pyridine and (f) SERS spectrum of MWCNT-pyridine.

Similar SERS spectra were collected from “pyridine-functionalized MWCNTs” and “3-aminopyridine” silver nanocolloidal suspensions, as Figures 7.8-f & 7.8-e, respectively. For reference, the Raman and SERS spectra of a pyridine aqueous solution were also collected, as Figures 7.8-a & 7.8-d, respectively. The amounts of reagents as well as the spectroscopic parameters utilized to collect all Raman/SERS of Figure 7.8 were namely identical. It is noted once again that in “MWCNT+Pyridine” and in “MWCNT+3-amino-pyridine”, the pyridine molecule is not chemically attached to the MWCNTs. In the 1000 – 1100 cm\(^{-1}\) spectral range, shown better in the inset of Figure 7.8, all pyridine Raman/SERS spectra (Fig. 7.8-a,b,d) exhibit two main Raman peaks at 1004/1010 and 1036 cm\(^{-1}\), while all meta-substituted pyridine SERS spectra (Fig. 7.8-c,e,f) one main peak at ~1025 cm\(^{-1}\). The latter peak is usually observed in SERS spectroelectrochemical experiments performed on pyridine adsorbed on silver electrodes. It was claimed that the origin of the ~1025 cm\(^{-1}\) SERS band of pyridine is closely related to silver ion clusters like Ag\(^{2+}\) and Ag\(^{32+}\), which derive from the photoreduction of silver ions in silica colloid suspension by irradiation with green laser line at 514.5 nm.\(^{35}\) The photoreduction obtained in situ by laser irradiation for the Ag-doped silica colloid resembled the roughness procedure obtained on Ag electrode by varying the potential with the oxidation-reduction cycles. However, this is not the case in the present experiments. While Muniz-Miranda et al. irradiated the sample and spectra were obtained by 30 s steps until the peak at ~1025 cm\(^{-1}\) appeared, in the present study spectra were recorded for an almost zero waiting time. Furthermore, all Raman/SERS spectra of Figure 7.8 were sequentially collected increasing the power of the excitation line from 20 to 75, to 120 and to 230 mW on the sample and are shown in Figure 7.9.
Figure 7.9 - Laser power effect on SERS analytes: (a) SERS spectra of MWCNT-pyridine, (b) SERS spectra of aqueous pyridine (c) Raman/SERS spectra of MWCNTs + 3-amino pyridine and (d) SERS spectra of 3-amino-pyridine.

No differentiation of the spectral features shown in Figure 7.9 was observed at any laser power attempted. The other two bands centered at 1004/1010 and 1036 cm\(^{-1}\) correspond to the totally symmetric ring-breathing of the free molecule; a thorough analysis on pyridine
Raman and SERS peaks’ attribution/assignment has been already published.\textsuperscript{37}

In the 1200-1700 cm\(^{-1}\) spectral range, all spectra with the exception of the SERS spectrum of MWCNT-pyr (Fig. 7.8-f) and the Raman spectrum of the aqueous solution of pyridine (Fig. 7.8-a) resemble the spectrum of surface carbon observed by several authors\textsuperscript{37,38,36,37} when studying Raman spectra of pyridine adsorbed at a silver electrode. These SERS investigations from electrochemical systems have shown that carbon is present within the laser-illuminated zone on the silver surface; namely, the intensely scattering phase appears to be a carbon-pyridine species and not the pyridine itself; the laser induced decomposition of pyridine is the dominant source of carbon surface. Indeed, there is such a similarity for the relatively weak features in the 1200-1700 cm\(^{-1}\) region of those spectra to the spectrum of carbon; however, the Raman/SERS spectrum collected in the case of “MWCNT-pyr” in the same spectral range is more like the conventional Raman spectrum of MWCNTs than the amorphous carbon. In the SERS spectra of “MWCNT-pyr”, there is clear evidence that pyridine attached to MWCNTs enhances the Raman spectrum of the MWCNTs, while the presence of pyridine or even of 3-aminopyridine in a MWCNT suspension do not contribute to such an enhancement.

\subsection*{7.3.3 Quantification study}

The fact that both pyridine and MWCNTs are easily detected by SERS in pyridine-functionalized MWCNTs, offers the possibility to detect MWCNTs in a water solution both directly and indirectly \textit{via} the pyridine. These preliminary results gave the opportunity to go further in the study and proceed through a more severe and meticulous quantitative study.

\textbf{Figure 7.10} shows representative raw SERS spectra of MWCNT-pyr aqueous suspensions at different concentrations added to silver colloid NaCl-activated. For comparison, a spectrum of silver colloid similarly activated is also depicted on the bottom of the figure, considered as blank spectrum.
Figure 7.10 - Representative SERS spectra of MWCNT-pyridine in TDW of different concentrations from 1 to 100 μg/mL.

The concentrations of the MWCNT-pyr suspensions prepared ranged from 100 to 1 μg/mL. Because the percentage of pyridine functionalization was about 7% in weight, the concentration of pyridine in the above suspensions ranged from 7 to 0.07 μg/mL. The application of SERS measurements allowed the detection of pyridine-functionalized CNTs at all above low concentrations (Table 7.1).

Table 7.1 - Concentrations of pyridine attached to MWCNTs into the aqueous suspensions detected by SERS and the relevant concentrations of the MWCNTs used for the quantification analysis.

<table>
<thead>
<tr>
<th>A/A</th>
<th>C\text{pyridine} μg/mL</th>
<th>C\text{carbon nanotubes} μg/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₀</td>
<td>7,00</td>
<td>100,00</td>
</tr>
<tr>
<td>C₁</td>
<td>4,63</td>
<td>66,14</td>
</tr>
<tr>
<td>C₂</td>
<td>2,31</td>
<td>33,00</td>
</tr>
<tr>
<td>C₃</td>
<td>1,15</td>
<td>16,43</td>
</tr>
<tr>
<td>C₄</td>
<td>0,57</td>
<td>8,14</td>
</tr>
<tr>
<td>C₅</td>
<td>0,285</td>
<td>4,07</td>
</tr>
<tr>
<td>C₆</td>
<td>0,142</td>
<td>2,03</td>
</tr>
<tr>
<td>C₇</td>
<td>0,070</td>
<td>1,00</td>
</tr>
</tbody>
</table>
It is also readily seen in Figure 7.10 that the relative intensities of the signals are changing almost linearly with respect to the concentration, particularly at the low concentration range studied in this work.

In Figure 7.11, the baseline corrected SERS intensity of characteristic bands of pyridine and carbon nanotubes - after the addition of 0.5 mL of the pyridine functionalized carbon nanotube suspensions in 1 mL of silver colloid NaCl activated - is shown against the relevant concentration of pyridine binding to the MWCNTs in their initial dispersions in TDW. Each concentration was measured three times, and the peak intensities of each vibrational band are shown with pertinent standard deviation error bars. For both the pyridine band at ~1025 cm\(^{-1}\) and the carbon nanotubes’ D & G type bands at 1360 & 1580 cm\(^{-1}\), the Raman scattering enhancement reaches a plateau at the same pyridine-functionalized MWCNTs concentration. This indicates both the association of pyridine to the MWCNTs and their relationship in the anticipated surface enhanced Raman scattering.

![Figure 7.11](image)

**Figure 7.11** - Correlation between concentration of MWCNT-pyridine in TDW and SERS intensity of the characteristic pyridine and carbon nanotubes’ bands.

The SERS saturation is most probably due to the complete coverage of the SERS active sites of the nanocolloidal substrate; it occurs at concentrations higher than 2.3 µg/mL for pyridine and 32.8 µg/mL.
for MWCNTs, apparently obeying the estimated ~7% w/w pyridine content in the functionalized MWCNT samples. A note is made of the fact that the linearity region for the signal dependence on analyte concentration is observed from 0.07 to 2.3 μg/mL in pyridine and from 1.0 to 32.8 μg/mL in MWCNTs.

### 7.4 CONCLUSIONS

In the present study, surface-enhanced Raman spectra of pyridine-functionalized MWCNTs were collected. The identification of the pyridine moiety was proven to be directly related to the presence of the relevant functionalized carbon nanotubes. The initial intention of collecting SERS spectra of CNTs indirectly, having decorated them with a SERS active group like pyridine, led to a direct detection and also quantification of MWCNTs in aqueous suspensions even at low concentration, for instance at 1.0 μg/mL.

**Acknowledgement**

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Surface-enhanced Raman scattering analysis of Methylene Blue & Remazol Brilliant Blue R using silver colloids

ABSTRACT

The application of Surface Enhanced Raman Spectroscopy, SERS, to the quantitative analysis of organic dye molecules existent as pollutants in wastewaters has been examined by using citrate reduced silver colloid activated with NaCl. The combination of SERS and resonance Raman spectroscopy that uses proximity to a surface to increase Raman intensity, and excitation wavelength matched to the maximum absorbance of the molecule being analyzed has been probed, by choosing the adequate excitation line, and the high sensitivity of surface enhanced resonance Raman spectroscopy (SERRS) has been applied for the detection and subsequent quantification of Methylene Blue. SERRS spectra of aqueous solutions of the dye at various concentrations were collected by the use of certain collection conditions and a good correlation was observed for the dependence of the intensity of the SERRS band at 1625 cm\(^{-1}\) on dye concentration using laser excitation at 632.8 nm. Yet, in an effort to understand the way factors like excitation wavelength employed and the addition of aggregating agents influence the SERS signal, Remazol Brilliant Blue R was selected as potent water pollutant and used for SERS study.
8.1 INTRODUCTION

Laser Raman spectroscopy plays an increasing important role in nanobiotechnology and nanomaterials, environmental sciences, medicine and life science. Based on vibrational transitions, it has long been regarded as a valuable non-destructive tool for the identification of chemical and biological samples as well as the elucidation of molecular structure, showing many advantages compared to other spectroscopic techniques like UV-Vis absorption. However, the Raman signals are inherently weak and the detection of analyte at low concentration range is limited. Nevertheless, Surface Enhanced Raman scattering (SERS) - a sensitive technique manifested as an enhancement by many orders of magnitude of the intensity of Raman radiation by molecules in the immediate vicinity to nano-rough metal surfaces and nanostructured metal systems as colloid clusters of noble metals - promising in overcoming the fluorescence and low-sensitivity problems inherent in conventional Raman spectroscopy, proves intriguing applied on quantification of extremely low analyte concentration range potently existing in treated water. Contribution of the metal-molecule charge-transfer resonance at the Fermi energy or and the surface plasmon resonance in the metal nanoparticle are treated as makers of the overall effect. Additionally, optimal sensitivity may be achieved when controlled aggregation of the colloidal solution occurs. Size of the colloidal particles, pH, concentration of the analytes, scattering collection geometry as well as the excitation wavelength employed are factors the SERS signal depends on. As for any Raman measurement, electronic resonant effects play an increasing role; when the excitation wavelength matches absorption band of the molecule, electronic resonance occurs and the resulted intensity is higher by several orders of magnitude. Such a feature also occurs in SERS measurements resulting in electronic resonance (Surface Enhanced Resonance Raman Scattering).

In this context, given that extremely small amounts of substances can be detected and further quantified via SER(R)S, the method should be applied on the investigation of waste water effluents. According to the World Health Organization (WHO), the most dangerous threat for health of mankind emerging during the next years is polluted water. Water contaminated from industry and agriculture has to be efficiently treated avoiding human intoxication by a variety of substances as low biodegradable organic compounds of high colourity. With dye molecules, whose absorption bands are generally located in
the visible range, resonant effects are expected to contribute to the observed signal.

So in the present chapter, a study of applying quantitative Surface Enhanced Resonance Raman scattering (SERRS) measurements of water solutions containing nanogram levels of Methylene Blue (methylthionine chloride MW:319.85 g/mol) is described. Methylene blue is a heterocyclic aromatic dye used in the textile industry that causes severe central nervous system toxicity at plasma concentrations over 1.33 mol/L (=425.4 μg/mL).\textsuperscript{11} Additionally, SERS spectra on the anionic organic dye molecule Remazol Brilliant Blue R are presented under the investigation of the effects of different aggregating agents.

SERS measurements were based on silver nano-colloids prepared according to a modified Lee-Meisel method\textsuperscript{12} whereas the use of an “oscillating cell” combined to the right angle Raman light scattering geometry provided optimum sensitivity.\textsuperscript{1,9} Laser excitations at 632.8 and 514.5 nm were applied and information-rich spectra were collected. Partial Least-Squares (PLS) analysis was used for the quantification model analysis.

## 8.2 SERS OF METHYLENE BLUE

Attention in this study was mainly paid to the quantification of methylene blue (MB) in water solutions from high to unparalleled low concentrations. In addition, the optimum pH used for the quantitative analysis is discussed and finally, the extraction of sufficient linear correlation concentration regions for the dye under certain conditions is presented. Several groups have characterized MB using SERS. Gui-Na Xiao and Shi-Qing Man\textsuperscript{13} reported MB SERS on silver nanocups while Merlen et al.\textsuperscript{10} examined the Raman and SER(R)S spectra of MB on gold substrates; both groups have reported qualitative SERS measurements from MB using different substrates. However, topics focused on in this work have not been reported.
8.2.1 Preparation of silver nano-colloidal suspensions and Methylene Blue aqueous solutions

The following reagents were purchased as indicated and used with no further purification: methylene blue, silver nitrate, sodium citrate tribasic dihydrate, sodium chloride aqueous solution, sodium hydroxide and hydrochloric acid. Methylene blue (MB) (M9140-25G) was purchased from Sigma-Aldrich (D). The chemical structure of the active compound with IUPAC name 3,7-bis(Dimethylamino)phenazathionium chloride is shown in Figure 8.1. Analytical grade silver nitrate (>99.99%) and sodium citrate tribasic dihydrate (99.0%) for colloid preparation were purchased from Sigma-Aldrich, too.

![Chemical structure of Methylene Blue.](image)

Figure 8.1 - Chemical structure of Methylene Blue.

The colloid used to collect the SERS spectra was prepared by the chemical reduction of silver nitrate with sodium citrate according to a modified Lee and Meisel procedure described in chapter 6. All glassware was purged with aqua regia solution followed by extensive rinsing with TDW prior to use. Triply distilled water, TDW (Milli-Q), was used for colloid preparation. After preliminary UV-Vis & SERS measurements, solutions of the dye, in the concentration range 7.863 μg/mL to 214 ng/mL for the UV-Visible absorption analysis and 43 ng/mL to 14.4 pg/mL for the SERS study, were prepared in TDW. The samples have been prepared just before the collection of the spectroscopic measurements.

The optimum conditions with respect to pH were determined. SERS measurements were made by simply adding 100 μL of a 1 mol/L aqueous solution of sodium chloride to 1mL citrate-reduced silver colloid followed by 500 μL of the MB solution (34 ng/mL). A series of SERRS spectra were collected at different pH values adjusted either with sodium hydroxide or hydrochloric acid aqueous solution in order to adjust pH in SERRS experiments. Next, the quantification analysis at the chosen pH came along with SERRS spectra collected using the
same analyte, colloid and aggregating agent, prepared for three times while all the final measurements were carried out the same day.

### 8.2.2 Instrumentation

UV-Vis absorption spectra were obtained with a double beam Lambda UV/Vis/NIR Spectrometer of Hitachi (U-3000). Reference beam was delivered through an optical cell filled with TDW. The spectra were recorded from 800 to 400 nm with a slit of 0.5 nm.

Conventional backscattering Raman spectra excited with the 441.6 nm line of an air-cooled HeCd laser (Kimmon Electric Co.), were collected by the UV-Vis Labram HR-800 spectrograph (J.Y).

SERS spectra were excited with a water-cooled Ar+ laser (Spectra physics model 2017, 5 W all lines) at 514.5 nm and with a He-Ne laser (Optronics Technologies S.A. model HLA-20P, 20 mW) operating at 632.8 nm. The specific laser line (632.8 nm) has been selected to generate an even larger to the expected surface enhancement Raman scattering due to molecular resonance Raman estimated from the analyte/MB UV-vis absorbance spectra. The power of the laser beam measured at the sample was 5 mW for the 632.8 nm excitation line. Raman spectra were collected using the T-64000 spectrometer of Jobin Yvon (ISA-Horiba group). The Raman system was used in the single spectrograph configuration for the collection, analysis and detection of the scattered light. The spectrometer was calibrated using the standard 992 cm\(^{-1}\) Raman band position of the ring breathing mode of benzene or/and the 801.3 cm\(^{-1}\) band of cyclohexane. Reproducible and improved Raman scattering collection measurements were allowed by the use of an “oscillating cell” in combination with the advantage of utilizing the right angle light scattering collection geometry. As aforementioned in the previous chapter, the advantage of this design, which permits the collection of the scattered Raman light at 90° of the excitation optics, is that during oscillation (“shaking”) the linear focusing field of the excitation line of the laser probes/scans a quite broad volume of the cell and the spectra obtained represent an overall volume as well as a large number of hot-spots of the sample even with a 1-s accumulation; moreover, due to the shaking, a continuous mixing of the solution also occurs.
8.2.3 Results and discussion

UV-Vis absorption study
Initially, absorption spectra of dye solutions, in the concentration range 7.863 µg/mL to 250 ng/mL were collected; the main absorption band maxima ($\lambda_{\text{max}}$) of methylene blue are located at 664 nm and at 615 nm shown in Figure 8.2.

![UV-Vis absorption spectra of aqueous solutions of MB at various concentrations. Inset: The calibration curve plot absorbance vs concentration extracted from the spectra.](image)

Figure 8.2 - UV-Vis absorption spectra of aqueous solutions of MB at various concentrations. Inset: The calibration curve plot absorbance vs concentration extracted from the spectra.

In the inset of Figure 8.2 the absorbance of the aqueous solutions of the dye at 664 nm is plotted versus concentration, constituting the UV-Vis absorption calibration curve ($R^2 = 99.93 \%$) that obeys a linear Beer's law behavior, with a limit of detection, LOD= 15 ng/mL and a limit of quantification, LOQ= 50 ng/mL.

The LOD value is given by the equation,

$$x_L = x_{bi} + ks_{bi}$$

Where $x_{bi}$ is the mean of the blank measures, $s_{bi}$ is the standard deviation of the blank measures, and $k$ is a numerical factor chosen accordingly to the confidence level desired (let $k = 3$). The conversion from measurement units, $x_L$, to concentration, $c_L$, is via the sensitivity,
\[ S = \frac{\Delta \text{concentration}}{\Delta \text{intensity}} \], the slope of the calibration curve. That is,

\[ c_L = c_{bi} + ks_{bi}S \]

But because the concentration of the blank is zero, this becomes

\[ c_L = 0 + ks_{bi}S, \text{ or } c_L = ks_{bi}S \]

Thus, quantitation is generally agreed to begin at a concentration equal to 10 standard deviations of the blank. This is called the limit of quantification (LOQ) or limit of determination. Therefore, \( \text{LOQ}=3.3\text{LOD} \).\(^{14}\)

**Resonance Effect**

Regarding the resonance effect study, in order SERRS to occur the analyte must contain a chromophore and the excitation frequency requires being close to or coincident with both an electronic transition of the chromophore and the plasmon absorption of the dye-dissolved silver nanocolloidal solution. To this end, absorption spectra of the silver colloid and the dye dissolved in silver colloid were recorded and are shown in **Figure 8.3**. Dye methylene blue (500μL) was added to colloid (1mL) aggregated with 1M NaCl (100μL). After 5 min, an aliquot (0.5 mL) was removed, placed into a 1 cm quartz cuvette and filled up with 2.5 mL TDW and the absorbance spectra were recorded.

**Figure 8.3** - Absorption spectra of silver colloid, of MB dissolved in silver colloid and of MB dissolved in silver colloid followed by 100 μL NaCl 1M.
Obviously, the addition of MB in the Ag nano-colloidal solution makes the absorption band to broaden to higher wavelengths, close to the excitation wavelengths of 514.5 and 632.8 nm turning that the resonant Raman effect will play an increasing role in the SERS signal.

SERS spectra were collected using both the excitation wavelengths at 514.5 and 632.8 nm as shown in Figure 8.4. One can see that the SERS signal for MB at 632.8 nm is 2 orders of magnitude higher compared to the one excited at 514.5 nm; despite the collection time is not the same, a clear indication of SERRS phenomenon is obvious.

![SERS spectrum of MB aqueous solution of concentration 37.2 μg/mL using excitation wavelength at 514.5 nm and SERRS spectrum of 0.52 μg/mL MB with excitation wavelength at 632.8 nm with much lower laser power and collecting time as indicated in the figure.](image)

**Figure 8.4** - a) SERS spectrum of MB aqueous solution of concentration 37.2 μg/mL using excitation wavelength at 514.5 nm and b) SERRS spectrum of 0.52 μg/mL MB with excitation wavelength at 632.8 nm with much lower laser power and collecting time as indicated in the figure.

Molecular resonance when using 632.8 nm excitation line enhanced ~2 orders of magnitude in sensitivity. Therefore, excitation with 632.8 nm wavelength was chosen to be as close as possible to the maximum absorbance of the dye and hence, to emphasize any contribution from molecular resonance enhancement.
**Figure 8.5** illustrates the normal Raman spectrum of MB aqueous solution at concentration 20.5 μg/mL collected with 441.6 nm excitation line and the SERRS spectrum of MB at concentration 486 pg/mL.

It is clear that the characteristic Raman bands of MB in the normal Raman spectra in aqueous solution are too weak to be observed because the concentration is too low. On the other hand, if the MB concentration in aqueous solution is increased, fluorescence covers the Raman spectra. Raman intensities are increased relatively to fluorescence by resonance Raman scattering. Strongly enhanced vibrational bands were observed at 454, 507, 778, 1185, 1400 and 1625 cm$^{-1}$ with the last-one to be the most intense; it can be assigned to the ring C-C stretching. Another mode at 454 cm$^{-1}$ arises from C-N-C skeletal bending.$^{13}$
**Effect of pH**

The effect of pH of MB solutions on SERRS measurements was studied and the intensity changes at different pH values of MB were observed. All conditions in this optimization were kept constant except the pH, which was adjusted adding sodium hydroxide and hydrochloric acid to lie between pH 0 and 12. The dye concentration under study was 34 ng/mL, MB dissolved in water (Milli-Q, Millipore 18 MΩcm) gives a solution at pH 5.5 (Fig. 8.6). Compared to normal Raman, only the molecules adsorbed on the metal surface are able to be monitored by SERS. From the molecular structure in scheme 1, methylene blue is a charged molecule and its ionization state depends on the pH of the surrounding medium.

![SERS spectra of MB aqueous solutions collected at different pH values for solution of concentration 34 ng/mL.](image)

**Figure 8.6** - SERS spectra of MB aqueous solutions collected at different pH values for solution of concentration 34 ng/mL.
The optimum conditions, with respect to pH, were determined at pH 5.5 where a strong increase of the peaks’ intensities was observed after 5 minutes of sample preparation—needed in order the aggregation processes to be completed—therefore, all spectra were collected 5 minutes post-aggregation. It is obvious that pH is one of the most important factors controlling the adsorption of a dye onto an adsorbent. Methylene blue is actually the salt of methylene blue chloride. When 5.4 < pH < 6.0 methylene blue is in the form MB+, for pH > 6 MB is a base and for pH < 5.4 is a binary acid (Fig. 8.7).\textsuperscript{15} Considering that own to the preparation method, citrate reduced silver colloid bears a negatively charged citrate layer ion that act as a surfactant stabilizer due to its negative charge, positively charged dye molecules will exhibit huge SERS signals under most experimental conditions due to binding of the analyte to the surface.\textsuperscript{16}

\textbf{Figure 8.7} - Structural formula of Methylene Blue as a function of pH.

\textbf{Quantification of MB}
The concentration dependence of the SERRS signal from MB was determined by plotting intensity (peak area) versus the MB concentration for 27 different concentrations ranging from 50.2 ng/mL to 16.8 pg/mL. Representatively, several spectra of different concentration are presented in Figure 8.8; a dependence of Raman peaks’ intensity with MB concentration is evident.
**Figure 8.8** - Dependence of the SERRS spectra on the concentration of MB. A few representative spectra are shown in the figure. The excitation wavelength was 632.8 nm and the laser power at the sample was 5 mW.

For the conventional quantitative analysis the area between 1570 and 1688 cm$^{-1}$ was used (**Fig. 8.9**).
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Figure 8.9 - Methylene blue in the concentration range from 16.8 pg/mL to 50.2 ng/mL. The area between 1570 and 1688 cm\(^{-1}\) was used for analysis. Four linear regions are observed. The excitation wavelength was 632.8 nm and the laser power at the sample was 5 mW.

The SERRS quantitative calibration curve is divided in four linear regions showing the progress of SERRS effect correlated with the concentration of the analyte. Thus, increasing the concentration of MB in the silver nano-colloidal solution results in a progressively slope decreasing, indicating the progressive saturation of “hot spots” in nano-colloidal solution by MB molecules, leading to saturated SERRS effect and finally, due to precipitation, probably to an inhibited SERRS phenomenon. The conditions the SERRS spectra were collected (e.g. concentration range, laser power) were selected in order to serve a sequent quantification of MB to the one constructed using the UV-Visible absorption method. In this way, there is a quantification sequence of MB using both methods comparing the sensitivity of each one and demonstrating the advantages of SER(R)S.

Parallel to the SERRS results, the OPUS/QUANT2 quantitative analysis software package was applied which uses partial least squares, PLS, to develop quantitative models. To obtain the optimized results of the PLS analysis, various mathematical pre-treatments were applied to the data to maximize the correlation coefficient R\(^2\) and minimize the root-mean square error of the cross-validation (RMS-
ECV). Four sample sets of SERRS spectra, corresponding to each linear region used for the conventional calibration curve of aqueous solutions of MB, were utilized for the PLS analysis over the wavenumber range 420-1800 cm\(^{-1}\), cross-validated internally by the leave-one-out method.\(^{17}\) No spectral pre-processing gave obviously better results. Five ranks can be extracted for each linear region, characteristically for the region corresponding to the lowest concentration range, the predicted versus known values of the concentration of the dye shown in Figure 8.10 allow for \(R^2 = 0.995\) and RMSE= 25 pg/mL.

![Graph showing correlation between predicted and known concentrations of methylene blue](image)

**Figure 8.10** - Correlation between predicted versus known concentration of methylene blue dissolved in Ag nano-colloid suspensions measured by SERRS spectra for a concentration range 50 pg/mL to 1.0 ng/mL, edited via PLS analysis.

### 8.2.4 Conclusions

Citrated reduced silver colloid was used for Surface Enhanced Resonance Raman scattering measurements. It is extremely unlike that there will be a single set of experimental conditions that are optimum for all type of analytes. The size of the colloidal particles, aggregation agent, pH, concentration of the analyte as well as the kind
of analyte, scattering collection geometry and also the excitation wavelength employed are factors affecting the SERS signal.

Surface Enhanced Resonance Raman scattering was performed for the quantification of the dye molecule methylene blue using silver colloid as SERRS substrate aggregated with NaCl. Linear correlation between band area and concentration of the analyte resulted at certain concentration regions. PLS analysis was applied to develop quantitative models. This study reveals the huge potential of SERS technique as a detection and quantification method being capable of detecting signals from very small analyte concentrations replacing other analytical methods like UV-Vis absorbance where detection limits are not that low.

**8.3 COMPARATIVE STUDY OF AGGREGATION AGENTS ON SERS MEASUREMENTS OF REMAZOL BRILLIANT BLUE R**

Positively charged dye molecules have been extensively studied with SERS under most experimental conditions. Instead, there are very few studies dealing with SERS of anionic analytes using simple citrate-reduced Ag colloids. Large, aromatic, positively charged molecules exhibit huge SERS signals. However, few studies have been fulfilled associated to anionic analytes using citrate-reduced Ag colloids. Anionic analytes exhibit week signal or no enhancement and this is probably due to the poor binding of the analyte to the Ag surface. It is in that sense that in spite of the high stability of the citrate-reduced Ag colloids, usually a partial aggregation is necessary to activate enhancement in the study of certain analytes. In several cases, self-aggregation is produced by the adsorption of the analyte under study, however, most of the time, the use of aggregation agents is required for SERS observation.\(^4,7,18\) Many studies have been reported indicating the importance of SERS enhancement of citrate-reduced silver colloids by the addition of salts like alkali halides contributing to the silver suspension activation-aggregation. Nevertheless, aggregation leads to less stable systems with limited or at best controlled use in time.

In the present subchapter, factors affecting the SERS signal are studied and described, like the excitation wavelength employed and also the use of aggregating agents in silver nano-colloidal
suspending, using as analyte the organic dye Remazol Brilliant Blue R (RBBR) (MW: 626.54 g/mol), an anionic molecule. SERS spectra of RBBR are presented and the effects of different aggregating agents on SERS measurements are investigated as well.

### 8.3.1 Preparation of silver nano-colloidal suspensions and analyte aqueous solutions

For the preparation of silver nano-colloidal suspensions, analytical grade silver nitrate (>99.99%) and sodium citrate tribasic dihydrate (99.0%) were purchased from Sigma-Aldrich; the same holds for sodium perchlorate (NaClO₄) (CAS 7601-89-0) and sodium chloride (NaCl) (EC No. 2315983) chosen as aggregating agents. Remazol Brilliant Blue R (R 8001) utilized as model analyte was also purchased from Sigma-Aldrich and its chemical structure is shown in Figure 8.11.

![Figure 8.11 - Chemical structure of Remazol Brilliant Blue R.](image)

The colloid utilized to collect the SERS spectra was prepared by the chemical reduction of silver nitrate with sodium citrate according to a modified Lee and Meisel procedure,¹² already described in a previous chapter. All glassware was purged with aqua regia solution followed by extensive rinsing with TDW prior to use. Triply distilled water (Milli-Q) was used for colloid and analyte solutions preparation.

### 8.3.2 Instrumentation

The UV-Vis absorption spectra were recorded by a double beam Lambda UV/Vis/NIR Spectrometer of Hitachi (U-3000). Reference
beam was delivered through an optical cell filled with TDW. The spectra were recorded from 800 to 190 nm with a slit of 0.5 nm.

The Raman spectra were excited either with a He-Ne laser (Optronics Technologies S.A. model HLA-20P, 20 mW) operating at 632.8 nm or a water-cooled Ar+ laser (Spectra physics model 2017, 5 W all lines) operating at 514.5 nm. An achromatic doublet (f: 145 mm; φ: 35 mm) was utilized to focus the laser beam into a Pyrex test tube filled with nano-colloidal silver suspensions and the power of the laser beam measured on sample was ~17 mW for both the 514.5 and the 632.8 nm excitation lines. Raman spectra were collected using the T-64000 spectrometer of Jobin Yvon (ISA-Horiba group). The Raman system was used in the single spectrograph configuration for the collection, analysis and detection of the scattered light.

All SERS spectra presented in this study were collected from solutions in test tubes containing 2 mL of Ag colloid, 100 μL aggregation agent (1M NaCl or 1M NaClO4) and 200 μL analyte under vortex agitation. Acquisition time for all spectra was 1s.

8.3.3 Results and discussion

Colloid characterization
The absorbance band of silver nano-colloidal suspension is appeared at approximately $\lambda_{\text{max}} = 407$ nm. A note is made of the fact that in order to obtain accurate UV-Vis absorption spectra, 0.5 mL of the corresponding nanocolloidal suspension has been diluted to 2 mL of TDW. UV-Vis absorbance spectra of the Ag colloid have been recorded just after preparation and after 1 month of storage, as shown in Figure 8.13. The stable position and shape of the absorbance peak at $\lambda_{\text{max}} = 407$ nm indicates Ag nanoparticles of approximately 5-10 nm in size being stable within this period of time. As it is shown in scheme 2, silver colloid particles possess a negative charge due to the adsorbed citrate ions with pendant negative groups, as a consequence of the colloid preparation process; due to this, a repulsive force works along particles preventing aggregation.
Figure 8.12 - A schematic model to illustrate the interaction of citrate ions (C6H5O7\(^{3-}\)) with Ag nanoparticles in the colloidal suspension.

Figure 8.13 illustrates UV-Vis absorption spectra of the citrate reduced silver colloid and the colloid activated with the aggregating agents NaCl and NaClO\(_4\). The violet-blue extinction band of silver colloid proves the existence of silver nanoparticles as well as the strong interaction of violet-blue light with surface plasmons localized in these nanoparticles. Preliminary measurements have shown that the analyte under study, RBBR/silver colloid do not generate any Raman signal in the absence of chloride and perchlorate ions. The aggregation of nanoparticles differentiates the conditions for the Raman signal enhancement. The absorbance peak changes shape when the aggregating agent is added to the silver colloid; after addition of the small amount of NaCl 1M (100 μL) in 2 mL of Ag nanocolloidal solution, the main absorption peak of silver colloid related to the dipole plasmon resonance is reduced and broadened to the green/red/NIR side. If further amount of anions is added, the stability of colloidal suspension is affected and after a few minutes gradual precipitation of colloid is observed. The enhancement of the absorption at ~700 nm indicates relevant formation of silver aggregates\(^{19}\).
Figure 8.13 - Absorbance spectra of citrate reduced silver colloid. Effect of addition of 100 μL of 1M NaCl (red line) and 1M NaClO₄ (green line). In addition, absorbance spectra of Ag colloid just after preparation (black line) and after 1 month of storage (grey line) indicating their stability in time.

**SERS study of RBBR**

Figure 8.14 presents the Raman spectra of citrate reduced Ag colloid using two different aggregation agents: sodium chloride, NaCl, and sodium perchlorate, NaClO₄. It is observed that the two aggregating agents display two different band patterns.
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SERS of organic dyes-pollutants

**Figure 8.14** - Raman spectra of citrated-reduced Ag colloid on addition of 100 μL NaCl or 100μL NaClO₄.

The addition of NaCl to the citrate reduced silver colloid displays basically the profile of water band. When NaClO₄ is added, bands corresponding to citrate appear with the principal band at ~1400 cm⁻¹ assigned to νₗ(COO).²⁰ A surface-enhanced Raman phenomenon is obviously occurring since the addition of just 100 μL of NaClO₄ to 2 mL Ag colloid produces much more intense bands than the spectra of simple aqueous citrate solution with the same concentration (not shown here).

Citrate is always present in citrate reduced silver colloids, although not always observed; so when recording relevant SERS spectra attention should be paid since the resulting SERS signal will depend on the species that occupy the surface sites. This can be explained in terms of free energy change associated with the replacement of one anion bound to the silver citrate colloid by a different anion. ClO₄⁻ ions are considered to be weakly or non-specifically absorbed at the Ag surface²¹; on the other hand, Cl⁻ ions are known to be specifically adsorbed to Ag (that is, to form chemical bonds with Ag). The fact that
the strongest citrate band at ~1400 cm\(^{-1}\) is not observed in untreated silver colloid is not surprising since many analytes give weak spectra with non-aggregated colloids. When adding NaCl as aggregating agent, the citrate on the surface is displaced by Cl\(^{-}\) which has high affinity to silver surface, so despite citrate is still present in the solution only a strong band at 235 cm\(^{-1}\) is detectable which is attributed to AgCl. The addition of ClO\(_4^-\) produces aggregation of the silver colloid without displacing the citrate and SERS from citrate is observed. The addition of Cl\(^{-}\) however causes aggregation of colloid and loss of citrate signal. Although the silver colloid itself may not show any/many bands, the addition of specific aggregating agent can generate “anomalous” bands which may obscure bands from the analyte under study.

Remazol Brilliant Blue R, RBBR, is an anthraquinone dye with a broad absorbance that extends from approximately \(\lambda = 590\) nm to \(\lambda = 680\) nm with maxima at 590 and 620 nm as shown in Figure 8.15.

![Remazol Brilliant Blue R](image)

**Figure 8.15** - UV-Vis absorption spectrum of Remazol Brilliant Blue R of concentration 50 ng/mL.

In an attempt to collect conventional Raman spectra of RBBR aqueous solutions fluorescence obscured the collected light using both the 514 and the 632 nm as excitation wavelengths (Fig. 8.16). The Raman scattering of RBBBR in solution containing non-aggregated silver
nanoparticles did not exhibit enhancement, so partial aggregation of colloid is necessary for practical SERS applications. Aliquots of 2 mL Ag colloid, 100 μL of aggregating agent NaClO₄ 1M and 200 μL of RBBR 1.6 mM where prepared in a test tube for SERS measurements with excitation lines at 514 and 632 nm. Since aggregation makes the colloid less stable, the addition of aggregation agent needs to be carefully controlled to obtain reproducible SERS spectra. If a large amount of aggregating agent is added, the colloid particles precipitate and no SERS is observed.

Figure 8.16 - Equal aliquots were examined with both excitation lines, 514 and 632 nm. (a) The conventional Raman spectra of a 1.0 mg/mL RBBR aqueous solution and (b) its SERS spectra using Ag colloid and NaClO₄ as aggregating agent.

The first conclusion coming up is that SERS measurements are very dependent on excitation wavelengths. This is due to the very broad absorption band of the RBBR analyte which is more close to 632 nm excitation wavelength. So, the difference in Raman intensity for the same concentration of analyte when exciting with 514 and 632 nm laser line is due to electronic resonance. When the analyte contains an absorption maximum of a chromophore approximately coincident with the excitation wavelength, leads to resonance enhancement, it is in that case that Surface Enhancement Resonance Raman Scattering (SERRS) occurs. Spectrum (b) of Figure 8.16, using excitation line
514.5 nm, shows that the citrate pattern is dominant, however a weak feature at ~1640 cm\(^{-1}\) is observed.

Since excitation line of 632.8 nm stimulates SERRS phenomenon, and spectra of higher intensity are collected, we proceeded to colloid aggregation-activation effect study making use of that laser line.

Aggregation of the silver nano-colloidal suspension by sodium chloride (NaCl) led to no SERRS enhancement; however Raman intensity of the analyte was increased relatively to fluorescence when sodium perchlorate (NaClO4) was added to the silver colloid as typically shown in Figure 8.17.

Although the citrate bands are intense when the Ag colloid is activated with sodium perchlorate (shown in Fig. 8.14), they are replaced by the RBBR analyte bands. Characteristic bands of anthraquinone dyes like the band at around 1640 cm\(^{-1}\) assigned to the C=O bonds\(^{22}\) of the ring and bands attributed to C-N stretching vibrations of aromatic amines at ~1330 cm\(^{-1}\)\(^{23}\) are present in the RBBR SERRS spectrum. Furthermore, bands at around 1270 cm\(^{-1}\) attributed to the C-O stretch\(^{24}\) are intensely present as shown in Figure 8.17.

![SER(R)S spectra of RBBR](image)

**Figure 8.17** - SERS from an aliquot containing: 2mL citrate-reduced Ag colloid, 100 μL NaCl or NaClO4 and 200 μL Remazol Brilliant Blue R aqueous solution 1.0 mg/mL.
The SERRS spectrum of Remazol Brilliant Blue R is reported here for the first time; neither conventional Raman spectra has been found in the literature and it is hard to collect a conventional Raman spectrum of RBBR. It should be emphasized that RBBR is an anionic dye, while citrated reduced silver colloids are widely exploited for SERS studies of cations since their metal surface sustain a negatively charged citrate layer. The immense majority of published studies are cases where the analyte is a cation, with the ability to displace the citrate that is present on the Ag surface and where aggregation of silver colloid enhances the spectra of low concentration of the analyte but does not noticeably increase the intensity of the citrate bands.

Chloride ions present large affinity to silver and adsorb directly on the surface, replacing citrate anions. When the incoming analyte is positively charged, it means that the Cl\(^-\) promotes chemisorptions of the analyte on silver together with aggregation as long as the concentration of chloride does not exceed a critical value which induces destabilization of the silver colloid and precipitation. The co-adsorption of the positively charged analyte with the chloride allows the molecules to directly interact with the silver surface and leads to additional SERS enhancement than in the absence of NaCl. When the analyte is not a cation the above explanation is not applicable, the chemisorption is not promoted. The success when trying to obtain SERS from anionic dyes using citrated reduced silver colloids is to find the appropriated “aggregating-activation” agent that will modify the metal surface and will made possible the SERS of the incoming analyte. Perchlorate can be used as aggregating agent; in this case, SERS from the citrate surface layer is observed. However its effectiveness is probed since even though the silver colloid is negatively charged due to the citrate surface layer, SERRS from the anionic analyte is observed. Munro et al. have studied and observed SERS spectra of low concentration citrate using nitric acid as aggregation agent\(^{25}\).

When the analyte under study is not absorbed to the Ag surface, only the effect of aggregation is observed; this is an explication why positively charged dye molecules show huge SERS signals under most experimental conditions.
8.3.4 Conclusions

In the present chapter SERS measurements of the anionic dye molecule Remazol Brilliant Blue R were studied and presented. It is concluded that cationic analytes can easily adsorb on the negatively charged silver surface of citrate reduced silver nano-colloids but in the case of neutral and anionic molecules further modification of the surface potentially is mandatory. Citrate-reduced silver colloids are not normally used to enhance the Raman spectra of anions but they can be used under appropriate conditions.

The characterization of the silver colloid prior to use is critical giving the opportunity to differentiate band patterns from the analyte and those originated to the colloid in the presence of an aggregating agent. Analytes adsorbed at the colloid surface may replace citrate and complex with silver, form bonds with the negatively charged citrate groups or physically adsorb at the citrate layer. The aggregation procedure requires further examination than that presented here in terms of salt concentrations. Addition of low concentration of aggregating agents may have no effect until the concentration is sufficiently high to aggregate the colloid but not high enough to produce precipitation of the colloid.

REFERENCES


20 Yaffe, N.R., Blanch, E.W., “Effects and anomalies that can occur in SERS spectra of biological molecules when using a wide range of aggregating agents for hydroxylamine-reduced and citrate-reduced silver colloids”, Vibrational spectroscopy, 2008, Vol.48, Pag.196-201
9

Synopsis, general conclusions and future areas for research

The present thesis was elaborated upon implementation of the projects BioNexGen and Synergasia-MEKKA and targeted at the study of the application of Carbon nanotubes in membrane science and technology. The general aim was to engineer membranes for separation processes based on Carbon Nanotubes for their potential application in Membrane Bioreactors as an alternative technology for the nano-filtration processes during industrial, municipal and agricultural wastewater treatment. The main focus of this work was the study of the parameters influencing the efficient incorporation of CNT into porous polymeric membranes, the fabrication of potently advanced composite membranes following different preparation approaches, as well as the use of advanced spectroscopic techniques as the Surface Enhanced Raman Scattering (SERS) in the efficiency control of the fabricated CNT membranes. The outcomes of these studies are outlined.

Three approaches concerning the fabrication of CNT-membranes were studied:

- Asymmetric PES membranes with CNTs infiltrated through their porosity (CNT-infiltrated-membranes), commercial and tailor-made PES membranes.
- Mixed matrix CNT-membranes (MM-CNT-membranes), where CNTs are mixed with the polymeric matrix into the polymeric solution and,
Membranes made by arrays of vertically aligned CNT (VA-CNT-membranes), where the VA-CNTs were incorporated into a PVDF matrix.

9.1 CNT-infiltrated commercial membranes

The experimental parameters influencing the efficient binding of CNTs in the thin selective layer of the ultra-filtration PES commercial membrane with pore diameters of ~40 nm in order to transform/render it to a nano-filtration one with pores to be defined exclusively by the hollow CNT-internal diameters were studied.

Only certain types of CNTs with respect to their diameters were appropriate for the rejection of small organic molecules of molecular weight ranging from ~200-1000 Da. The transformation of the UF membrane to a NF one preconditioned the decrease of the pores from ~40 nm to less than 2 nm.

The morphology and structure of the PES membrane was characterized in terms of SEM and Raman Spectroscopy. The gradient pore structure of the membrane seemed to facilitate the CNTs intrusion using filtration methods.

A variety of carbon nanotubes, SW-CNTs, DW-CNTs, Thin-MW-CNTs and MW-CNTs, with different features concerning the diameters, the length and the existence or/not of chemical functionalities, were utilized in the study aiming at the efficient binding of CNTs into the pores of the commercial PES membrane. Raman spectroscopy was utilized for the characterization of the CNTs.

Chemical modification, by the use of acids, and mechanical modification, by the use of tip-sonicator, were applied for the decrease of CNTs’ length and their uncapping (opening of the closed ends). SEM micrographs of the CNTs indicated that the chemical treatment process led to CNT-length ~320 nm near the values that mechanical treatment led to (average ~500 nm).

The membrane conformation in the filtration apparatus, the volume of the feed solution (i.e. the CNT-suspension) and the concentration of the CNT-suspensions to be infiltrated through the polymeric membrane, and the position of the tip-sonicator-probe were parameters studied since they appeared to affect the CNT-infiltration process through the membranes.
Further treatment of carboxyl-functionalized CNTs was proceeded to lead to deprotonation of the carboxylic groups in order to maintain good dispersion in aqueous media facilitating the CNT-infiltration. Two comparative studies between Thin MWCNTs and same CNTs functionalized with carboxyl groups, and between SWCNTs and carboxyl-functionalized CNTs, by the use or not of surfactant, were carried out. The CNTs, either Thin MWCNTs or SWCNTs bearing carboxylic anions showed much improved stability in water due to the chemical affinity between the polar modified groups and water and the electrostatic repulsion.

For the membranes infiltrated through the support side only few CNTs seem to protrude the surface area while the majority of the CNTs appeared to stack just before reaching the porous skin layer of the membrane. Therefore, the black imprint of CNTs on the surface of the membranes was attributed to their existence beneath the ~2 μm skin layer.

Laser Raman spectroscopy was implemented for the characterization of the CNT-membranes. The presence of D and G bands in the spectra of the CNT-infiltrated membranes is a clear evidence for their existence near or on the skin layer. A note is made of the fact that Raman penetration depth is of the order of 1-2 μm as much about the thickness of the selective layer of the commercial UF membranes.

The CNT-infiltrated membranes showed a tendency for enhanced flow rate, however, the results were not repeatable.

Adsorption effects contributed to the high retention of dye foulants.

The fabrication of CNT-membranes by the subsequent embedment of CNTs in the selective layer of specific commercial UF membranes by filtration turned partially inevitable. Taking into consideration the dense sponge-like structure of the skin layer containing the active membrane pores and its thickness of ~2 μm, the extrusion of CNTs proved challenging. However, through the experimental processes, many results for the understanding of the mechanism thrusting CNTs to embody in the selective layer of an asymmetric membrane were extracted. In addition, filtration and treatment protocols of CNTs were extracted and used for further studies.
9.2 CNT-infiltrated tailor-made membranes

- The immersion precipitation phase separation technique was studied aiming at the preparation of PES UF membranes similar to the commercial ones, however of tailored properties with respect to skin layer-thickness.
- Concerning the formation of the pores and the thickness of the selective layer, the polymer concentration in the casting solution was studied.
- Morphological characterization through SEM was carried out. The size of the pores ranged between 15-40 nm. Cross-sectional images indicate the asymmetric structure of the membranes by the formation of finger-type channels, potentially favoring the CNTs-infiltration. The thickness of the skin layer determined at 60-100 nm, fairly lower than that of the commercial membrane (~2 μm) and of similar order of magnitude to the length of CNTs.
- CNT-infiltrations to the prepared membranes showed that the higher the composition of polymer into the polymer solution for the preparation of membranes with the phase inversion technique, the more difficult CNTs to reach the selective layer.
- Decreasing the polymer amount into the polymer solution, the formation of the specific selective layer served/facilitated the infiltration of CNTs.
- The presence of D and G bands in the spectra of the CNT-infiltrated membranes is a clear evidence for their existence near or on the skin layer.
- The performance of the new PES membranes was evaluated by permeation experiments. tailor-made PES membranes bearing a thin selective layer of ~100 nm showed high fluxes. However, the embedment of SWCNT-COOH in the thin selective layer of the membranes contributed to the decrease of the flux, yet/although limited. The membranes remained functional and with high fluxes, even the dried ones.
- Additionally, the performance of the membranes was measured in terms of solute rejection. The CNT-infiltrated membranes exhibited a higher tendency to reject sizes of the higher molecular weight (200 kDa and 100 kDa), while a pure PES tailor-made membrane exhibited a similar rejection behavior to that of the commercial one. The presence of CNTs in the thin selective layer of the PES membranes increased the selectivity of the membrane, decreasing the MWCO from 150-200 kDa to ~40 kDa. However, taking into account the decreased pure water
flux the CNT-infiltrated tailor-made membranes exhibited, it was concluded that the presence of CNTs in the selective layer of the membranes did not contribute to the overall enhancement of the counterbalance between flux and selectivity.

An approach for the potential application of a polymeric coating aiming at the filling of empty pores and/or vacant spaces between CNTs and support pores walls and at the same time at the binding of nanotubes protruding the pores of the selective layer was studied. A polymeric coating of calcium alginate was synthesized by the addition of calcium chloride solution to the dilute solution of sodium alginate by gellification method and deposited over the surface area of the CNT-infiltrated membrane.

### 9.3 Mixed matrix CNT-membranes

- Nanocomposite membranes composed of PES and deprotonated carboxyl-functionalized Thin MWCNTs/SWCNTs were prepared. The functionalized CNTs were embedded in PES matrix during the immersion-induced phase separation method.
- The MM-CNT membranes exhibited most of the times increased fluxes compared to the pure PES membranes.
- The MM-Thin MW-COO− membranes exhibited an enhanced tendency of rejecting polymers of high molecular weight compared to the pure PES membrane.
- A comparative study of membranes loaded with different amounts of CNTs was carried out in order to investigate and elucidate the effect of CNTs’ presence in MMMs.
- The pure water flux measurements revealed that the order of increasing rate of water flow through the membranes according to the percentage of CNT loading is: 0.2%>0.4%>pure PES>0.6%>commercial PES>0.8%>1.0%.
- It is concluded that the pure water flux observed to increase for MM-CNT membranes loaded with small amount of CNTs (0.2, 0.4% w/w) is probably due to the increased hydrophilicity the Thin-MWCNT-COO− offered(provided) to the membranes. Higher amounts of CNTs, increase the viscosity of the selective layer of the PES membranes hindering the permeance of water molecules.
- The behavior of the membranes with respect to the permeability of the industrial wastewater was similar to that exhibited for water. The above results suggest that the pore size as well as
the pore density of a MM-membrane are determined largely by the CNT content.

- The membranes loaded with 0.2 and 0.4% w/w CNTs exhibited enhance permeation properties compared both to the pure PES membranes and the ones loaded with higher contents of CNTs.
- Rejection experiments using industrial wastewaters, revealed that the membranes loaded with higher percent of CNTs exhibited higher rejection capacity.
- The MM-CNT membranes with CNT-load 1.0% w/w exhibited enhanced water uptake properties while MM-CNT loaded with 0.2% w/w CNTs exhibited the lower percentage. These results provided an evidence that the increase in carboxylic group in the membrane component increases the hydrophilic nature of the membrane.
- Conclusively, the blending of hydrophilic CNTs into the polymeric matrix led to an increase in the hydrophilicity of the membranes, altering the porosity and increasing the pore density in certain cases that caused the migration of Thin-MWCNT-COO- to the surface of the membranes during their synthesis by the phase separation method. The permeation properties of the membranes-mixtures were found to be influenced and enhanced by adding a small amount of Thin-MWCNT-COO- in the polymer matrix with respect to the permeation rate of water and organic waste. More specifically, for the membranes with CNT-content 0.2% w/w, the water flow rate increased by 44% compared with the pure PES membranes and 220% compared with the corresponding commercial ones. Regarding the waste rejection from the membranes, it was observed that increasing the CNT-content the rejection capacity was increased with maximum rejection ~13% attributed to membranes containing Thin-MWCNT-COO- 1.0% w/w over commercial or pure PES membranes ranging between 5-6%.

### 9.4 Vertically aligned CNT-membranes

- Vertically aligned CNTs were incorporated into a PVDF casting solution. After evaporation of the DMF solvent, the specimen of VA-CNTs was enclosed into polymeric film containing.
- Plasma etching was carried out for the removal of the excess PVDF so as to obtain a membrane that the pores would be defined exclusively by the internal diameters of the CNTs.
9.5 SERS of pyridine-functionalized MWCNTs

A thorough study for the identification and quantification of small concentrations of multi-walled CNTs (MWCNTs) in water suspensions via SERS was performed. The functionalization of MWCNTs with pyridine groups seems to favor the surface enhancement of relevant Raman signal. This study constitutes the first step for the characterization of CNTs at quite low concentration range by SERS in any water suspension. The SERS study revealed that the identification of the pyridine moiety was proven to be directly related to the presence of the relevant functionalized carbon nanotubes. The initial intention of collecting SERS spectra of CNTs indirectly, having decorated them with a SERS active group like pyridine, led to a direct detection and also quantification of MWCNTs in aqueous suspensions even at low concentration, for instance at 1.0 μg/mL.

9.6 SERS of Methylene Blue

Citrated reduced silver colloid was used for Surface Enhanced Resonance Raman scattering measurements. It is extremely unlike that there will be a single set of experimental conditions that are optimum for all type of analytes. The size of the colloidal particles, aggregation agent, pH, concentration of the analyte as well as the kind of analyte, scattering collection geometry and also the excitation wavelength employed are factors affecting the SERS signal. Surface Enhanced Resonance Raman scattering was performed for the quantification of the dye molecule methylene blue using silver colloid as SERRS substrate aggregated with NaCl. Linear correlation between band area and concentration of the analyte resulted at certain concentration regions. PLS analysis was applied to develop quantitative models. This study reveals the huge potential of SERS technique as a detection and quantification method being capable of detecting signals from very small analyte concentrations replacing other analytical methods like UV-Vis absorbance where detection limits are not that low.


\section*{9.7 SERS of Remazol Brilliant Blue R}

SERS measurements of the anionic dye molecule Remazol Brilliant Blue R were studied. It is concluded that cationic analytes can easily adsorb on the negatively charged silver surface of citrate reduced silver nano-colloids but in the case of neutral and anionic molecules further modification of the surface potentially is mandatory.

The characterization of the silver colloid prior to use is critical giving the opportunity to differentiate band patterns from the analyte and those originated to the colloid in the presence of an aggregating agent.

The aggregation procedure requires further examination than that presented here in terms of salt concentrations.

Addition of low concentration of aggregating agents may have no effect until the concentration is sufficiently high to aggregate the colloid but not high enough to produce precipitation of the colloid.

\section*{9.8 Potent future areas for research}

In the context of studies on CNT-membranes, despite the fact that CNTs’ embedment into polymeric matrices generally did not exhibit the expected enhanced properties concerning the performance of the membranes, significant results were extracted, useful for further studies. Focusing on the optimization of the employed techniques, future studies may be based on the present thesis on the following topics:

Preparation of polymer asymmetric membranes with tailored morphological properties to serve as host for the encapsulation of carbon nanotubes. Study on the parameters contributing on the synthesis of the selective layer of controlled thickness would expect to be a step forward for the efficient fabrication of CNT-infiltrated membranes.

Extended study on the membrane properties using appropriate techniques for the characterization of the CNT-membranes, such as contact-angle measurements, porosimetry, AFM.

Study on appropriate coating application on CNT-membranes in order to fill-up the empty spaces between CNTs and those between CNTs and membrane walls.
Concerning membranes formed by vertically-aligned carbon nanotubes, plasma etching experiments would contribute to the optimization of the whole process in order to obtain functional membranes.
APPENDIX I

Dead-end filtration apparatus for large membranes

In the context of CNT-infiltration through PES membranes, due to the need of treating membranes of dimensions 6.5x12 cm (active surface) in order to match the cross-flow unit of BioNexGen partners that tested our membranes too, a home-made dead-end filtration cell was used. A rectangular-shaped dead-end filtration cell was built up in the framework of the present thesis by the workshop of the Technical Support Service Department at the Institute of Chemical Engineering Sciences, ICE/HT.

The home-made filtration cell, shown in Figure I.1, consists of a Plexiglas rectangular-shaped cell equipped with a metallic sieve operating as the basis of the membrane allowing the infiltration of membrane surface equal to 78 cm$^2$ using a volume of CNT-suspension to 1800 mL. It was designed to match the tip-sonicator device allowing the control of the distance between sonicator-probe and the membrane surface.
Figure I.1 – Images of the home-made filtration unit.

By the use of the home-made filtration cell, CNT-infiltrations through commercial and tailor-made PES membranes (Figure I.2) were carried out as well and the samples were sent to the laboratory of Jan Hoinkis at the Karlsruhe University of Applied Sciences and tested in terms of pure water flux and selectivity with respect to dye molecules.
Figure I.2 – (a) Commercial PES membrane infiltrated with CNT suspension from the substrate, the view is from the selective layer. (b) Commercial PES membrane infiltrated with CNT suspension towards the selective layer, the view is from the selective layer. (c) Comparison between the two different CNT-infiltration methods and (d) representative SEM micrographs corresponding to the CNT-infiltrate membranes.
**APPENDIX II**

**A. Scanning Electron Microscopy (SEM)**

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample’s surface topography, composition, and other properties such as electrical conductivity.

![Scanning Electron Microscope LEO SUPRA 35VP of Institute of Chemical Engineering Sciences (ICE/HT).](image)

**Figure II.1** Scanning Electron Microscope LEO SUPRA 35VP of Institute of Chemical Engineering Sciences (ICE/HT).

The types of signals produced by an SEM include secondary electrons, backscattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing
details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

**Scanning process and image formation**

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost.

The electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the interaction volume depends on the electron’s landing energy, the atomic number of the specimen and the specimen’s density. The energy exchange between the electron beam
and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronized with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor and saved to a computer's hard disk.

B. Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC), also called gel permeation chromatography in the case of lipophilic macromolecules or gel filtration chromatography in the case of hydrophilic macromolecules, is at present by far the most common method for separation and molecular characterization of synthetic polymers. As a technique, SEC was first developed in 1955 by Lathe and Ruthven.\(^{ii,iii}\) The term gel permeation chromatography can be traced back to J.C. Moore of the Dow Chemical Company who investigated the technique in 1964.\(^{iv}\) SEC is also widely used for separation of various natural polymers and for the purification of complex samples. The method is fast, simple, rather cheap, and well repeatable. Sample consumption for analytical purposes is small. SEC is a separation method for high polymers, similar to but advanced in practice over gel filtration as carried out by biochemists, that has become a prominent and widely used method for estimating molecular-weight distributions. The separation takes place in a chromatographic column filled with beads of a rigid porous “gel”; for polymer molecular-weight determinations, highly crosslinked porous polystyrene and porous glass are preferred column-packing materials. The pores in these gels are of the same size as the dimensions of polymer materials.\(^{v}\)

A sample of a dilute polymer solution is introduced into a solvent stream flowing through the column. As the dissolved polymer
molecules flow past the porous beads, the can diffuse into the internal pore structure of the gel to an extent depending on their size and the pore size distribution of the gel. Larger molecules can enter only a small fraction of the internal portion of the gel, or are completely excluded; smaller polymer molecules penetrate a larger fraction of the interior of the gel. The different molecular species are eluted from the column in order of their molecular size. Therefore, the larger molecules leave the column first, and the smaller molecules, latter.

A specific column or set of columns (with gels of different pore sizes) is calibrated empirically to give such a relationship, by means of which a plot of amount of solute versus retention volume, such as the ones obtained for this laboratory, can be converted into a molecular-size-distribution curve. For convenience, commercially available narrow-distribution polystyrenes are often used as standards.

The sample solution is then carried through the column(s) where the size separation process takes place. When the sample elutes from the column(s) it passes through a detector or series of detectors and the output is analyzed by a GPC/SEC software package on the computer.

**Figure II.2** - Size exclusion chromatography instrumentation.

The extent of the data analysis depends on the type and number of detectors used in the experiment. Depending on the choice of detectors, various types of calibrations and/or calculations are
employed to compute parameters like molecular weight (MW),
molecular weight distribution (MWD), intrinsic viscosity (IV) or
molecular density, hydrodynamic radius (Rh), and radius of gyration
(Rg). It is also possible to obtain additional information on
macromolecular structure, conformation, aggregation, branching and
copolymer/conjugate composition.

In order to obtain relevant information from the SEC chromatogram, it
is necessary to convert it into a Molar Mass Distribution Curve (MMD)
curve. Knowledge of the relationship between molar mass (M) and
elution volume (Ve) – volume of solvent required to elute a particular
polymer species from the point of injection to the detector – is needed
to do so. Such relationship comes from the expression for total elution
volume (Ve),

\[ Ve = V_0 + V_i e^{-\frac{A_s L}{2}} \]  

(1)

Where \( Ve \) = Total Elution Volume

\( V_0 \) = Void Volume (Volume in the system outside the porous
beads)

\( V_i \) = Internal Volume (Volume of solvent inside the beads)

\( A_s \) = Surface area per unit pore volume

\( L \) = Mean molecular projection of the molecule when free in
solution. Since \( L \) is proportional to the molar mass (M), this is the
elution volume to molar mass relationship needed.

This expression arises from the thermodynamics on which the Gel
Permeation Chromatography is based on. First, it is known that for
separations exclusively performed by size exclusion, the enthalpy
change should be zero. Recalling that \( \Delta G = \Delta H - T\Delta S \), if \( \Delta H=0 \), then \( \Delta G = - T\Delta S \). It is also known that the relationship between the Gibbs Free
Energy and the equilibrium constant is \( \Delta G = - RT \ln K \). Then if we
equate this two Gibbs Free Energy expressions we have \( -T\Delta S = - RT \ln K \). Solving for \( K \) we have the following expression for \( K \) as a function
of Entropy (\( \Delta S \)), \( K = \exp (\Delta S/R) \). But what is all this effort in
calculating \( K \)? The answer comes from the original expression for the
total elution volume, which is the sum of the void volume (volume in
the system outside the porous beads) and the internal volume (volume
of solvent inside the beads). However, the term for internal volume is
dependent of how deep the molecule penetrates inside the pores in the
bed. Thus, the term \( K \) represents the fraction of internal pore volume
which has been occupied by the molecule, but it is also viewed as an
equilibrium constant. Then \( V_e = V_0 + V_i \times K \). If the expression for \( K \) in terms of entropy is substituted in this equation, we have

\[
V_e = V_0 + V_i e^{(dS/R)}
\]  

(2)

Methods of statistical thermodynamics based on models of coils entering pores of different shapes are used to obtain an alternative expression for \( \Delta S \). The result has the general form \( \Delta S = -R \Delta s_{i} \times L/2 \), which is inserted in equation (2) to give equation (1) described above.

Now, SEC is not a primary method as usually practiced. As it is mentioned above, it requires calibration in order to convert raw experimental data into molecular weight distribution. The raw data in gel permeation chromatography consist of a trace of detector response (e.g. differential refractometer, continuous viscometer, etc) – which is proportional to the amount of polymer in solution – and the corresponding elution volumes.

A series of commercially available anionically polymerized polystyrenes is particularly well suited to be used as standard for calibration, since anionic-polymerized polystyrene can be produced as closely monodisperse polymers and for a wide range of molecular weights. When such sample is injected into the SEC column set, the resulting chromatogram is narrower than that of a whole polymer, but is not a simple spike because of band broadening effects and dispersion along the columns, and because the polymer standard is itself not exactly monodisperse. Since the distribution is very narrow, no serious error is committed by assigning the elution volume corresponding to the peak of the chromatogram to the molecular weight of the particular polystyrene. The peaks appear in decreasing order of molecular weight, being the larger molecules the first to be eluted. A “cocktail” of several polystyrenes covering different molecular weights is usually used and result in a peak of each one of them.

Once every molecular weight is assigned to its elution volume, a plot of \( \log(M) \) versus elution volume can be constructed. A straight line should result and this is known as the calibration curve.

After having the calibration curve ready, an analysis of the unknown polymer can be performed. Again a plot of the reading signal at the end of the set of columns versus the elution time is the result of the run. Elution time can be converted into elution volume if the pump flow is known. Note that the calibration curve to be used must cover
the same range of elution volume as the known sample. It is also important to consider a baseline to which the detector response will be referred; this will be considered the origin (y=0) and the deviation will be proportional to the concentration of polymer. These recorder divisions are in fact the product NiMi, the product of the number of molecules of “i” molecular weight times “i” molecular weight. If the unknown sample and the standard are compared at the same elution volume, it is possible to obtain Mi for such volume, applying the linear fitting expression for log(M) as a function of Ve. Once all Mi’s are determined, two columns – Ni and NiMi² - can be obtained for each molecular weight. Therefore,

\[ Mn = \frac{\sum_i (NiMi)}{\sum_i (Ni)} \]  \hspace{1cm} (3)
\[ Mw = \frac{\sum_i (NiMi^2)}{\sum_i (Ni)} \]  \hspace{1cm} (4)

and

\[ PDI = \frac{Mw}{Mn} \]  \hspace{1cm} (5)

Where \( Mn \) stands for Number Average Molecular Weight, \( Mw \) for Weight Average Molecular Weight and \( PDI \) is the Polydispersity Index.

The most common RI detector in use today is based on the deflection of a beam of light as it passes through a dual compartment flow cell as shown in Figure II.3. One side of the compartment contains the reference solvent of refractive index \( n_0 \), which is static during the measurement process. The other side contains the sample solution, i.e., the column eluent, having refractive index \( n \).

The beam is refracted at the liquid-glass interfaces separating the two compartments and also at the liquid-glass interface on the exit wall, and again at the glass-air interface on the exit wall. A rigorous analysis must take each of the refractions into account. Fortunately, a simplified analysis that ignores the glass interfaces as shown in Figure II.3(b) yields substantially the same result as the rigorous analysis, so that derivation will be reviewed instead.
Snells law of refraction is applied to the hypothetical liquid-liquid interface shown in Figure II.3(b).

\[ n_0 \cdot \sin(45) = n \cdot \sin\theta = n \cdot \sin(45 - \theta) \]  \hspace{1cm} (6)

For the very small angles of deflection encountered here we may approximate with no loss of accuracy as follows.

\[ \sin(45 - \theta) = \sin(45) - \tan\theta = \sin(45) - \frac{x}{L} \] \hspace{1cm} (7)

Combining equations 6 and 7 shows that the incremental refractive index is proportional to the deflection x.

\[ \frac{n-n_0}{n} = \frac{x}{L \cdot \sin(45)} \] \hspace{1cm} (8)

The differential signal will likewise be proportional to x because the beam, which actually has a finite width, will deliver more light to one photo-detector and less to the other as the beam is moved across the beam splitter due to refraction. So we can combine instrument
constants into one detector calibration factor. And we can replace \( n \) by \( n_0 \) because they are very nearly the same value at low concentrations.

\[
RL_{signal} = RL_{Cal} \cdot \frac{n-n_0}{n_0} \tag{9}
\]

C. Basic principles of Closed Reflux, Colorimetric method for the determination of COD

Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate (\(K_2Cr_2O_7\)). After digestion, the remaining unreduced \(K_2Cr_2O_7\) is titrated with ferrous ammonium sulfate to determine the amount of \(K_2Cr_2O_7\) consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent.

Colorimetric reaction vessels are sealed glass ampoules or capped culture tubes. Oxygen consumed is measured against standards at 600 nm with a spectrophotometer.

Reagents

(a) Digestion solution: 10.216 g \(K_2Cr_2O_7\), primary standard grade, dried at 103 °C for 2 h, 167 mL conc. \(H_2SO_4\), and 33.3 g \(HgSO_4\), are dissolved in 500 mL distilled water. The solution is cooled at room temperature and diluted to 1000 mL.
(b) Sulfuric acid reagent: \(Ag_2SO_4\) reagent are added to conc. \(H_2SO_4\) at the rate of 5.5 g \(Ag_2SO_4\)/kg \(H_2SO_4\) and left stand for 1-2 days to dissolve \(Ag_2SO_4\).
(c) Potassium hydrogen phthalate (KHP) standard: Potassium hydrogen phthalate is lightly crushed and dried to constant weight at 120 °C. 425 mg are dissolved in distilled water and diluted to 1000 mL. KHP has a theoretical COD of 500 \(\mu g\) \(O_2\)/mL. This solution is stable when refrigerated for up to 3 months in the absence of visible biological growth.

COD calculation

The COD is calculated as:

\[
mg \frac{O_2}{L} = \frac{mg \ 0_2 \ in \ final \ volume \times 1000}{ml \ sample}
\]

C. Plasma etching

Plasma is the forth state of matter. Heating a gas may ionize its molecules or atoms thus turning it into a plasma, which contains charged particles: positive ions and negative electrons. (99.9% of matters in the space).

Atmospheric plasma technology finds application in many scientific fields in recent decades. The Atmospheric Pressure Plasma Jets (APPJ) particularly, have aroused interest due to their ability in the processing of metallic and polymeric surfaces with plasma atmospheric pressure and under low temperature. They have found application in areas such as dry cleaning surfaces, improving sorption of protective coatings on vulnerable surfaces, improving quality printing and dyeing of hydrophobic surfaces, but even at the
enhancement of biocompatibility of materials intended as biomaterials, and also at direct treatment of human tissues.

**Argon-Oxygen discharges**

The chemical species appear during discharge reactions of Argon-Oxygen are:
\[ e, Ar, Ar^+, Ar^+, O_2, O_2^+, O^+, O^-, O^+ \]

**Table II.1 – Volume reactions Argon-Oxygen.**

<table>
<thead>
<tr>
<th>Volume reaction</th>
<th>Rate Coefficient k (m³s⁻¹)</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ( e + Ar \rightarrow Ar + e )</td>
<td>Cross Section</td>
<td>Momentum Transfer</td>
</tr>
<tr>
<td>2 ( e + O_2 \rightarrow O_2 + e )</td>
<td>Cross Section</td>
<td>Momentum Transfer</td>
</tr>
<tr>
<td>3 ( e + Ar \rightarrow Ar^+ + 2e )</td>
<td>Cross Section</td>
<td>Ionization</td>
</tr>
<tr>
<td>4 ( e + Ar^+ \rightarrow Ar^+ + 2e )</td>
<td>( 1.725 \times 10^{-14} )</td>
<td>Ionization</td>
</tr>
<tr>
<td>5 ( e + Ar^+ \rightarrow Ar + e )</td>
<td>( 2 \times 10^{-13} )</td>
<td>Electronic Deexcitation</td>
</tr>
<tr>
<td>6 ( 2Ar^+ \rightarrow Ar^+ + Ar + e )</td>
<td>( 5 \times 10^{-16} )</td>
<td>Ionization (Met.Pooling)</td>
</tr>
<tr>
<td>7 ( e + O_2 \rightarrow O^- + O )</td>
<td>( 0.98 \times 10^{-17} )</td>
<td>Dissociative Attachment</td>
</tr>
<tr>
<td>8 ( e + O_2 \rightarrow 2O + e )</td>
<td>( 0.26 \times 10^{-15} )</td>
<td>Dissociation</td>
</tr>
<tr>
<td>9 ( e + O_2 \rightarrow O^- + O + e )</td>
<td>( 0.34 \times 10^{-15} )</td>
<td>Dissociative Excitation</td>
</tr>
<tr>
<td>10 ( e + O_2 \rightarrow O_2^- + 2e )</td>
<td>Cross Section</td>
<td>Ionization</td>
</tr>
<tr>
<td>11 ( e + O_2 \rightarrow O + O^+ + 2e )</td>
<td>( 4.49 \times 10^{-20} )</td>
<td>Dissociative Ionization</td>
</tr>
<tr>
<td>12 ( e + O_2^- \rightarrow 2O )</td>
<td>( 2.6 \times 10^{-15} )</td>
<td>Dissociative Recombination</td>
</tr>
<tr>
<td>13 ( e + O^- \rightarrow O + 2e )</td>
<td>( 0.13 \times 10^{-13} )</td>
<td>Neutralization</td>
</tr>
<tr>
<td>14 ( e + O \rightarrow O^- + e )</td>
<td>( 1.42 \times 10^{-15} )</td>
<td>Electronic Excitation</td>
</tr>
<tr>
<td>15 ( e + O \rightarrow O^+ + 2e )</td>
<td>( 0.16 \times 10^{-16} )</td>
<td>Ionization</td>
</tr>
<tr>
<td>16 ( e + O^+ \rightarrow O^+ + 2e )</td>
<td>( 0.44 \times 10^{-16} )</td>
<td>Ionization</td>
</tr>
<tr>
<td>No.</td>
<td>Reaction</td>
<td>Rate Constant</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>----------------</td>
</tr>
<tr>
<td>17</td>
<td>$O^+ + O_2^* \rightarrow O + O_2$</td>
<td>$2 \times 10^{-13}$</td>
</tr>
<tr>
<td>18</td>
<td>$O^- + O_2^* \rightarrow 3O$</td>
<td>$2.01 \times 10^{-13}$</td>
</tr>
<tr>
<td>19</td>
<td>$O^- + O^+ \rightarrow 2O$</td>
<td>$2.7 \times 10^{-13}$</td>
</tr>
<tr>
<td>20</td>
<td>$O^+ + O \rightarrow 2O$</td>
<td>$8 \times 10^{-18}$</td>
</tr>
<tr>
<td>21</td>
<td>$O^+ + O_2 \rightarrow O + O_2$</td>
<td>$4.8 \times 10^{-18}$</td>
</tr>
<tr>
<td>22</td>
<td>$O^+ + O_2 \rightarrow O + O_2^+$</td>
<td>$2 \times 10^{-17}$</td>
</tr>
<tr>
<td>23</td>
<td>$e + Ar \rightarrow Ar^* + e$</td>
<td>$1.99 \times 10^{-17}$</td>
</tr>
<tr>
<td>24</td>
<td>$e + O_2 \rightarrow O_2^* + e$</td>
<td>$0.36 \times 10^{-15}$</td>
</tr>
<tr>
<td>25</td>
<td>$e + O_2^* \rightarrow O_2^* + 2e$</td>
<td>$0.11 \times 10^{-16}$</td>
</tr>
<tr>
<td>26</td>
<td>$O_2^* + O_2 \rightarrow 2O_2$</td>
<td>$3 \times 10^{-24}$</td>
</tr>
<tr>
<td>27</td>
<td>$Ar^* + O_2 \rightarrow Ar + O_2^*$</td>
<td>$5.1 \times 10^{-17}$</td>
</tr>
<tr>
<td>28</td>
<td>$Ar^* + O \rightarrow Ar + O^*$</td>
<td>$6.4 \times 10^{-18}$</td>
</tr>
<tr>
<td>29</td>
<td>$Ar^* + O^+ \rightarrow O^+ + Ar$</td>
<td>$6.4 \times 10^{-18}$</td>
</tr>
<tr>
<td>30</td>
<td>$Ar^* + O_2 \rightarrow Ar + O^+ + O$</td>
<td>$2.1 \times 10^{-16}$</td>
</tr>
<tr>
<td>31</td>
<td>$Ar^* + O \rightarrow Ar + O^*$</td>
<td>$4.1 \times 10^{-17}$</td>
</tr>
<tr>
<td>32</td>
<td>$O^- + Ar^* \rightarrow O + Ar$</td>
<td>$3 \times 10^{-13}$</td>
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<tr>
<td>33</td>
<td>$O_2 + Ar^* \rightarrow Ar + O_2$</td>
<td>$1.12 \times 10^{-15}$</td>
</tr>
<tr>
<td>34</td>
<td>$O + Ar^* \rightarrow Ar + O$</td>
<td>$8.1 \times 10^{-18}$</td>
</tr>
<tr>
<td>35</td>
<td>$O_2 + Ar^* \rightarrow Ar + 2O$</td>
<td>$5.8 \times 10^{-17}$</td>
</tr>
</tbody>
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Table II.1 – Surface reactions Argon-Oxygen.

<table>
<thead>
<tr>
<th>Surface reaction</th>
<th>Sticking Coefficient</th>
<th>Reaction Type</th>
</tr>
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<tr>
<td>$1\quad Ar^+ \rightarrow Ar$</td>
<td>1</td>
<td>Deexcitation</td>
</tr>
<tr>
<td>$2\quad Ar^+ \rightarrow Ar$</td>
<td>1</td>
<td>Neutralization</td>
</tr>
<tr>
<td>$3\quad O_2^+ \rightarrow O_2$</td>
<td>1</td>
<td>Deexcitation</td>
</tr>
<tr>
<td>$4\quad O^- \rightarrow O$</td>
<td>1</td>
<td>Deexcitation</td>
</tr>
<tr>
<td>$5\quad O_2^+ \rightarrow O_2^+$</td>
<td>1</td>
<td>Neutralization</td>
</tr>
<tr>
<td>$6\quad O^+ \rightarrow O$</td>
<td>1</td>
<td>Neutralization</td>
</tr>
<tr>
<td>$7\quad O^- \rightarrow O$</td>
<td>1</td>
<td>Neutralization</td>
</tr>
</tbody>
</table>

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APPENDIX III

Supporting Information of Chapter 7
DLS Measurements

In DLS, intensity time autocorrelation functions

\[ g^{(2)}(q,t) = \frac{\langle I(q,t) I(q,0) \rangle}{\langle I(q,0) \rangle^2} \]

of the four dispersions in water at 25 °C were measured (n ≥ 3) over a broad time scale (10^{-7} s – 10^4 s) using a full multiple tau digital correlator with 280 channels spaced quasi-logarithmically (ALV-5000/FAST) and the 671 nm line of a diode pumped solid state laser, operated at low power, <1 mW. The scattered light was collected by a single-mode optical fiber, transferred to an avalanche photodetector and then to the digital correlator for analysis. In dilute suspensions the normalized electric field time autocorrelation function

\[ g^{(1)}(q,t) = \frac{\langle E(q,t) E^*(q,0) \rangle}{\langle E(q,0) \rangle^2} \]

is related to the experimentally recorded \(g^{(2)}(q,t)^2\) through the Siegert relation\(^\dagger\)

\[ g^{(2)}(q,t) = B \left[ 1 + f^* \left| g^{(1)}(q,t) \right|^2 \right] \]

where \(B\) describes the long delay time behavior of \(g^{(2)}(q,t)\) and \(f^*\) is an instrumental factor (in our system \(f^* \sim 0.95\)). Hence, \(g^{(1)}(q,t)\) (for simplicity we drop the \(q\)-dependence) was analyzed as a weighted sum of independent exponential contributions

\[ g^{(1)}(q,t) = \int L(t) \exp(-t/\tau) d\tau = \int L(\ln \tau) \exp(-t/\tau) d\ln \tau \]

The distribution of relaxation times \(L(\ln \tau) = \tau L(t)\) was obtained by inverse Laplace transformation of \(g^{(1)}(q,t)\) using the CONTIN algorithm.\(^\ddagger\) The apparent hydrodynamic radii of the suspended particles were determined using the Stokes-Einstein relation \(R_h = k_B T / 6 \pi \eta D\), where \(k_B\) is the Boltzmann constant, \(\eta\) is the viscosity of
the solvent, and $D$ is the diffusion coefficient of the particle which is equal to $D = 1/\tau q^2$, where $\tau$ is the relaxation time of $g^{(1)}(q,t)$.

Representative normalized intensity autocorrelation functions for the various dispersions investigated are shown in Fig. 3. The decay time of each curve is characteristic of the particle size; the faster the decay, the smaller the probed particle.

**Figure III.1** - Normalized Intensity autocorrelation functions of the four following dispersions. AgNPs: 120 μL of Ag colloid in 1mL TDW; AgNPs/NaCl: 120 μL of NaCl activated Ag colloid (from 1 mL Ag colloid + 40 μL NaCl 1M) in 1 mL of TDW; MWCNT-pyr: 120 μL from a 100 μg/mL pyridine functionalized MWCNTs aqueous suspension in 1 mL of TDW; AgNPs/NaCl/MWCNT-pyr: 120 μL of a dispersion containing 1 mL Ag colloid + 40 μL NaCl 1M + 0.5 mL of 100 μg/mL pyridine functionalized MWCNTs aqueous suspension in 1 mL TDW.

The data reveal that the dispersion of Ag NPs in the absence of the salt is the smallest one. Addition of NaCl has a strong effect on the agglomeration of Ag NPs. In analogy, the interaction of NaCl activated Ag NPs with pyridine functionalized MWCNTs results in “particles” which are larger than the pure MWCNT-pyr particles.
To provide a more quantitative picture of these results, the experimental data are analyzed by the inverse Laplace transformation, which provides the distributions of particle sizes in each case. In all cases, we observe a bimodal particle size distribution. It is obvious that the addition of NaCl into the dispersion which contains Ag NPs, Fig. 4 (a) and (b) alter drastically the particle size distributions. Agglomeration of individual Ag NPs takes place towards larger particle clusters. In the case of neat MWCNT-pyr dispersion, we observe a bimodal size distribution; the two peaks are centered at ~65 and 232 nm.

**Figure III.2** - Intensity autocorrelation function of (a) AgNPs, (b) NaCl activated Ag NPs, (c) pyridine functionalized MWCNTs, and (d) AgNPs/NaCl/MWCNT-pyr dispersions and the corresponding particle size distributions $L(\ln t)$. The solid lines through the experimental data points stands for the best fit curves using the ILT technique. The mean (most probable) particle sizes for each distribution are shown in the labels.

The presence of NaCl activated Ag NPs into the MWCNT-pyr dispersion creates larger particles owing to their mutual interactions, as is evident from the intensity increase of the larger population and its
broadening in comparison to the corresponding peak of the neat MWCNT-pyr dispersions.

**XPS**

In XPS, the surface analysis studies were performed in a UHV chamber (P<10⁻⁹ mbar) equipped with a SPECS LHS-10 hemispherical electron analyzer. The XPS measurements were carried out at room temperature using unmonochromatized MgKα radiation under conditions optimized for maximum signal (constant ΔE mode with pass energy of 36 eV giving a full width at half maximum (FWHM) of 1.1 eV for the Cu2p₃/₂ peak). The analyzed area was an ellipsoid with dimensions 2.5 x 4.5 mm². The XPS core level spectra were analyzed using a fitting routine, which allows the decomposition of each spectrum into individual mixed Gaussian-Lorentzian components after a Shirley background subtraction. The samples were drop casted in a silicon substrate with dimensions 1x1cm² and were dried at 70°C.

In order to investigate eventual interaction between Ag nanoclusters and pyridine functionalized MWCNTs, XPS measurements have been carried out mainly on two samples, the NaCl activated Ag-nanocolloid (AgCol/NaCl: 1 mL Ag colloid + 40 μL NaCl 1M) and the pyridine functionalized MWCNTs in NaCl activated Ag-nanocolloid (AgCol/NaCl/MWCNT-pyr: 1 mL Ag colloid + 40 μL NaCl 1M + 0.5 mL of 100 μg/mL pyridine functionalized MWCNTs aqueous suspension). For comparison, Ag-nanocolloid (AgCol: 120 μL of Ag colloid) and pyridine functionalized MWCNTs (MWCNT-pyr: 120 μL from a 100 μg/mL pyridine functionalized MWCNTs) were also investigated. The C1s, N1s, Ag3d and Ag MVV signals have been acquired. Figure 5 shows the N1s peak of the two samples. N1s peak of MWCNT-pyr consists of one component centred at 399.3eV assigned to N in pyridine.iii The N1s of AgCol/NaCl/MWCNT-pyr sample again has one main peak at the same binding energy and the same FWHM with the MWCNT-pyr sample indicating that there is no strong chemical interaction between the Ag nanoparticles and pyridine N. It has to be mentioned that the literature E_B values for the N1s originating from N atoms in the Ag-N bonds is 396.8eV.iv
Moreover, Figure 6 shows the XP spectra of the Ag3d doublet from the AgCol/NaCl and the AgCol/NaCl/MWCNT-pyr samples. The binding energy of both Ag3d_{5/2} peaks is at 368.2eV. The kinetic energy of the AgM_{4VV} peak (not shown) is at 357.8eV. From the sum of 3d_{5/2} binding energy and M_{4VV} kinetic energies the modified Auger parameter can be calculated which is found to be 726.1±0.1eV, assigned to Ag^0. The only difference between AgCol/NaCl and AgCol/NaCl/MWCNT-pyr Ag3d peaks is that the width of the peak from AgCol/NaCl/MWCNT-pyr sample (FWHM=1.35eV) is greater than that from the pure AgCol/NaCl suspension (FWHM=1.15eV).
Appendix III

![Figure III.4](image)

**Figure III.4** - XP spectrum of Ag3d photoelectron peak for (a) AgCol/NaCl and (b) AgCol/NaCl/MWCNT-pyr.

Although the conventional standard deviation/error in XPS is of 0.05 eV and the difference in FWHM here is of 0.2 eV, it is not possible with the XPS results to claim conclusively that there is chemical interaction of Ag with pyridinic nitrogen.

**REFERENCES**


Curriculum Vitae

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Academic Background

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<td>Department of Chemical Engineering, University of Patras &amp; Institute of Chemical Engineering Sciences (ICE-HT), Greece. 2011-now</td>
<td>Thesis Title: Development of carbon nanotube membranes for wastewater treatment and surface enhanced Raman scattering study of the membrane efficiency and eventual contamination caused. Supervisor: Dr. G. Voyiatzis</td>
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<tr>
<td><strong>MSc</strong></td>
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<td>Thesis Title: Use of SERS to the controlled release studies of low molecular weight substances from polymer matrices. Supervisor: Dr. G. Voyiatzis</td>
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<td><strong>BSc Degree</strong></td>
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Participation in Research & Development projects

1. Development of the next generation membrane bioreactor system (BioNexGen) (September 1, 2010 – February 28, 2014) Funded by CEU, FP7-NMP-2009-2.6-1 Novel membranes for water technologies (SICA)
2. Implantation of CNTs in Permeable Polymer Matrices (MEKKA) (May 3, 2011 – May/November 2, 2014) Funded by GSRT, SYNERGASIA program, Nanotechnology applications to the environment

Awards

- 1st Prize for outstanding poster presentation, 29th EMS Summer School, Membranes for liquid separations, Essen, Germany (2013)
- Young Researcher Award for the best Poster Presentation, 11th Int. Conf. on Nanosciences & Nanotechnologies (NN14), Thessaloniki, Greece (2014)

Didactic Experience

Participation in the organization and co-teaching of the following courses at the Department of Chemical Engineering, University of Patras:
- Instrumental Chemical Analysis, Co-teaching of Organic Chemistry, University of Patras (2014, 1 semester)
- Analytical Chemistry, Laboratory of Analytical Chemistry, University of Patras (2012-2013, 2 semesters)

Participation in the organization and co-teaching of the following laboratory courses at the Department of Materials Science, University of Patras:
- Chemistry II, Laboratory of Organic Chemistry, University of Patras (2011, 1 semester)
- Materials Science IV, Laboratory of Materials Science, University of Patras (2010-2011, 2 semesters)
- CV _ Anastasopoulos Ioannis -

Participation in the organization and co-teaching of the following laboratory courses at the Department of Chemistry, University of Patras:

- Analytical Chemistry, Laboratory of Analytical Chemistry, University of Patras (2009, 1 semester)

### Employment History

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<tr>
<td></td>
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### Publications


### Conferences


Where my name is underlined I was the speaker (oral or poster presentation).

Language Proficiency

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