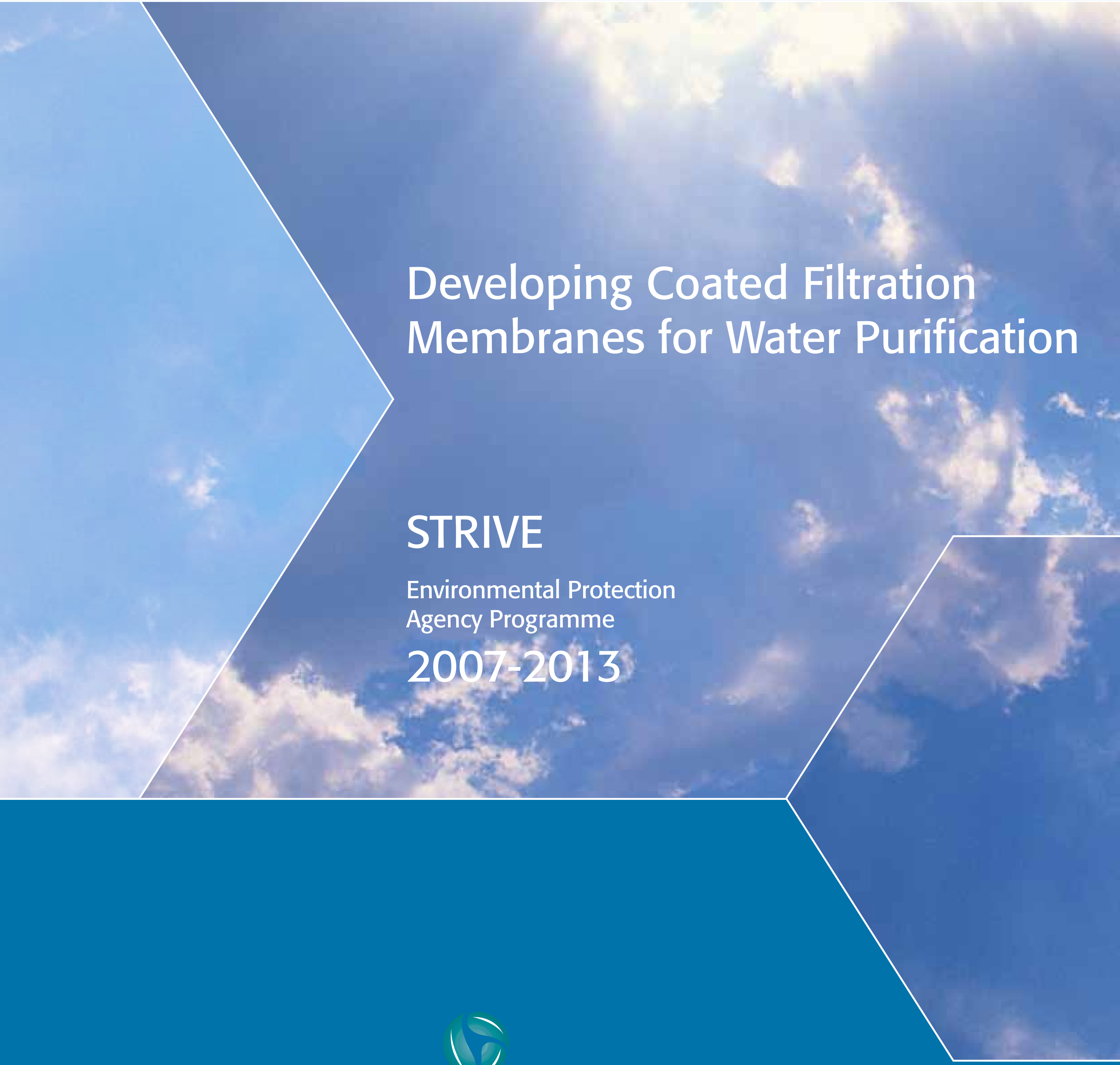
Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

STRIVE
Report Series No.116



Developing Coated Filtration Membranes for Water Purification

STRIVE

Environmental Protection
Agency Programme

2007-2013

SSTI
Strategy for Science, Technology and Innovation

Comhshaol, Pobal agus Rialtas Áitiúil
Environment, Community and Local Government

Environmental Protection Agency

The Environmental Protection Agency (EPA) is a statutory body responsible for protecting the environment in Ireland. We regulate and police activities that might otherwise cause pollution. We ensure there is solid information on environmental trends so that necessary actions are taken. Our priorities are protecting the Irish environment and ensuring that development is sustainable.

The EPA is an independent public body established in July 1993 under the Environmental Protection Agency Act, 1992. Its sponsor in Government is the Department of the Environment, Community and Local Government.

OUR RESPONSIBILITIES

LICENSING

We license the following to ensure that their emissions do not endanger human health or harm the environment:

- waste facilities (e.g., landfills, incinerators, waste transfer stations);
- large scale industrial activities (e.g., pharmaceutical manufacturing, cement manufacturing, power plants);
- intensive agriculture;
- the contained use and controlled release of Genetically Modified Organisms (GMOs);
- large petrol storage facilities;
- waste water discharges;
- dumping at sea.

NATIONAL ENVIRONMENTAL ENFORCEMENT

- Conducting over 1200 audits and inspections of EPA licensed facilities every year.
- Overseeing local authorities' environmental protection responsibilities in the areas of - air, noise, waste, waste-water and water quality.
- Working with local authorities and the Gardaí to stamp out illegal waste activity by co-ordinating a national enforcement network, targeting offenders, conducting investigations and overseeing remediation.
- Prosecuting those who flout environmental law and damage the environment as a result of their actions.

MONITORING, ANALYSING AND REPORTING ON THE ENVIRONMENT

- Monitoring air quality and the quality of rivers, lakes, tidal waters and ground waters; measuring water levels and river flows.
- Independent reporting to inform decision making by national and local government.

REGULATING IRELAND'S GREENHOUSE GAS EMISSIONS

- Quantifying Ireland's emissions of greenhouse gases in the context of our Kyoto commitments
- Implementing the Emissions Trading Directive, involving over 100 companies who are major generators of carbon dioxide in Ireland.

ENVIRONMENTAL RESEARCH AND DEVELOPMENT

- Co-ordinating research on environmental issues (including air and water quality, climate change, biodiversity, environmental technologies).

STRATEGIC ENVIRONMENTAL ASSESSMENT

- Assessing the impact of plans and programmes on the Irish environment (such as waste management and development plans).

ENVIRONMENTAL PLANNING, EDUCATION AND GUIDANCE

- Providing guidance to the public and to industry on various environmental topics (including licence applications, waste prevention and environmental regulations).
- Generating greater environmental awareness (through environmental television programmes and primary and secondary schools' resource packs).

PROACTIVE WASTE MANAGEMENT

- Promoting waste prevention and minimisation projects through the co-ordination of the National Waste Prevention Programme, including input into the implementation of Producer Responsibility Initiatives.
- Enforcing Regulations such as Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS) and substances that deplete the ozone layer.
- Developing a National Hazardous Waste Management Plan to prevent and manage hazardous waste.

MANAGEMENT AND STRUCTURE OF THE EPA

The organisation is managed by a full time Board, consisting of a Director General and four Directors.

The work of the EPA is carried out across four offices:

- Office of Climate, Licensing and Resource Use
- Office of Environmental Enforcement
- Office of Environmental Assessment
- Office of Communications and Corporate Services

The EPA is assisted by an Advisory Committee of twelve members who meet several times a year to discuss issues of concern and offer advice to the Board.

EPA STRIVE Programme 2007-2013

Developing Coated Filtration Membranes for Water Purification

(2009-ET-MS-8-S2)

STRIVE Report

Prepared for the Environmental Protection Agency

by

National University of Ireland Maynooth

Authors:

Denise Rooney, Orla Power, Catherine Fox, Carmel Breslin,

Bernadette Alcock-Earley

ENVIRONMENTAL PROTECTION AGENCY

An Ghníomhaireacht um Chaomhnú Comhshaoil
PO Box 3000, Johnstown Castle, Co.Wexford, Ireland

Telephone: +353 53 916 0600 Fax: +353 53 916 0699
Email: info@epa.ie Website: www.epa.ie

ACKNOWLEDGEMENTS

This report is published as part of the Science, Technology, Research and Innovation for the Environment (STRIVE) Programme 2007–2013. The programme is financed by the Irish Government under the National Development Plan 2007–2013. It is administered on behalf of the Department of the Environment, Community and Local Government (DECLG) by the Environmental Protection Agency (EPA) which has the statutory function of co-ordinating and promoting environmental research. We would like to gratefully acknowledge the steering committee, Prof. John Cassidy, Dublin Institute of Technology (DIT), Darragh Page, EPA, Darren Byrne, DECLG and Lisa Sheils (EPA), for their advice and direction which have overall added value to the project as a whole. We are also grateful to Raymond Murphy from Emerald Environmental Services for providing us with river water samples and to Dr Richard Doyle for his scientific input. We would like to thank Dr. Patrick Carolan for recording electron micrographs as part of the SFI National Access Programme to the Tyndall Institute.

DISCLAIMER

Although every effort has been made to ensure the accuracy of the material contained in this publication, complete accuracy cannot be guaranteed. Neither the Environmental Protection Agency nor the author(s) accept any responsibility whatsoever for loss or damage occasioned or claimed to have been occasioned, in part or in full, as a consequence of any person acting, or refraining from acting, as a result of a matter contained in this publication. All or part of this publication may be reproduced without further permission, provided the source is acknowledged. The EPA STRIVE Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

EPA STRIVE PROGRAMME 2007–2013

Published by the Environmental Protection Agency, Ireland

ISBN: 978-1-84095-516-3

Price: Free **Online version**

Details of Project Partners

Denise Rooney
Department of Chemistry
National University of Ireland Maynooth
Tel.: +353 1 7083 616
Email: Denise.Rooney@nuim.ie

Carmel Breslin
Department of Chemistry
National University of Ireland Maynooth
Tel.: +353 1 7083 677
Email: Carmel.Breslin@nuim.ie

Bernadette Alcock-Earley
Department of Chemistry
National University of Ireland Maynooth
Tel.: +353 1 7086 850
Email: Bernadette.Alcock@nuim.ie

Catherine Fox
Department of Chemistry
National University of Ireland Maynooth
Email: Catherine.Fox@nuim.ie

Orla Power
Department of Chemistry
National University of Ireland Maynooth
Email: Orla.Power@nuim.ie

Table of Contents

Acknowledgements ii

Disclaimer ii

Details of Project Partners iii

Executive Summary vii

1 Introduction 1

2 Results and Discussion 2

- 2.1 Modification of Membranes using Polypyrrole Nanofibers 2
- 2.2 Investigation on the Ion-exchange Properties of *p*-Sulfonatocalix[4]-arene-Polypyrrole using Electrochemical Quartz Crystal Microbalance 7
- 2.3 Investigating Copper Ion Removal from Solution using *p*-Sulfonatocalix[4]arene-Polypyrrole-coated Nanofibers on a Membrane 13
- 2.4 Development of a Smart Membrane for Anion Transport using Polypyrrole Nanofiber-coated Membranes 14
- 2.5 Removal of Cr(VI) from Water using Polypyrrole Nanofiber-coated Membranes 15
- 2.6 Development of Anti-fouling Coatings for Water-filtration Membranes 20

3 Conclusions and Recommendations 30

References 31

Acronyms and Annotations 34

Appendix: Conference Presentations and Publications 35

Executive Summary

A significant challenge of the twenty-first century is to supply water of sufficient quality for drinking, for other requirements such as agriculture, energy and industry, and to sustain healthy aquatic ecosystems. Water security is a key issue for modern Ireland to ensure the health of its citizens and ecosystems and to aid economic growth. Protecting the quality of water resources and the sustainable use of resources, including water, are key environmental goals in the Environmental Protection Agency (EPA, 2007) 2020 *Vision* strategy document, and are also in line with the Flagship initiative of the Europe Union (European Commission, 2011) strategy for a resource-efficient Europe. The fifth 'State of Environment' EPA report (O'Lehane and O'Leary, 2012) Ireland's *Environment 2012 – An Assessment*, reports that Ireland has better than average water quality in comparison to other EU member states, and there is evidence of overall improvement in water quality. However, Ireland faces major challenges in meeting targets set for 2015, 2021 and 2027 as required by the Water Framework Directive. A strategic priority of the EPA (2013) *Strategic Plan 2013–2015* is to maintain a vibrant and relevant environmental research programme to influence policy, identify pressures and develop solutions to key environmental challenges, such as water quality and a sustainable environment. The EU Joint Programming Initiative 'Water Challenges for a Changing World' is a strategic initiative to pool national research resources of member states in this important area. In addition, the support of research into nanotechnologies will enable Ireland to benefit from the growth forecasted for the economic impact of these technologies, as highlighted by the Forfás 2010 report, *Ireland's Nanotechnology Commercialisation Framework 2010–2014*.

Membrane technologies are an established means for producing potable water from surface water, groundwater and industrial wastewaters. The research described herein set out to develop polymer-coated membrane-based technologies that could be used to remove the heavy metals chromium and copper from aqueous systems. The membranes were modified to investigate their potential for the selective transport of nitrate ions across the membrane, and studies were carried out to investigate if the polymer coating had the ability to exchange nitrate ions. There is considerable concern about the level of nitrate in water, and this is underlined by the Nitrates Directive (1991/676/EEC), the National Nitrates Action Programme, the ongoing public consultation on Ireland's Nitrate Plan, and the EU Water Framework Directive (2000/60/EC). The mandatory safe level of nitrate in drinking water is set at 50 mg L^{-1}.

The Water Framework Directive outlined clearly a requirement that the levels of Cr(VI) and Cu(II) be monitored in Irish water. Chromium commonly exists in either its hexavalent or trivalent forms. Chromium (VI) is a highly toxic metal ion that is well known for its contribution to a variety of health problems such as cancers, mucosal ulcerations and chronic dermatitis. It is a dangerous pollutant, which can be leached into groundwater from industries such as tanning, stainless steel production and metal finishing. Chromium can be readily transported in soil, and leached into water bodies far from the original sites of contamination, so its removal from industrial waste to within the regulatory limits is vital. Copper is generally found in the environment in its divalent or monovalent forms. Ingested in relatively high concentrations, it can induce symptoms of severe food poisoning: long-term exposure can result in damage to the liver and kidneys and is linked to cognitive impairment and Alzheimer's disease. Copper is toxic to fish and aquatic life with high levels of bioaccumulation. Often used in electrical and plumbing systems, it is known to corrode under certain circumstances, resulting in leaching into soils and water sources. In addition, copper is a waste product of a number of industries such as pig farming and electroplating. The European Communities (Drinking Water) (No. 2) Regulations 2007 set out a mandatory limit of 50 µg L^{-1} chromium and 2 mg L^{-1} copper in drinking water. The studies reported here showed that the polypyrrole nanofiber-coated membranes could be used to convert Cr(VI) to Cr(III) (7.6 mg L^{-1}) in acidified solution and to deposit copper (240 mg/g) from water.

A disadvantage of membrane technologies is that they can suffer from fouling due to dissolved organic matter, such as proteins and humic acid, in the water. These adhere to the membrane surface, blocking the pores and reducing the membrane's performance. The current research set out to develop methodologies to form polymer coatings on polyamide membranes to reduce this fouling. The study showed membranes containing chemically attached poly(poly(ethylene glycol) methacrylate) and those coated using the bio-inspired polydopamine-based films successfully reduced the extent of protein fouling using the model protein, bovine serum albumin.

1 Introduction

Separation technology is a very important and well-established industry, and membrane-based separations have a number of attractive features over other technologies, such as chromatography or distillation, in terms of energy requirement, ease of scale-up and the ability to operate a continuous flow system. Modern membrane polymeric materials are becoming increasingly sophisticated, and the development of membranes based on electronically conducting polymers has been an area of significant research interest for a number of years (Akieh, et al., 2010) (Jeon, et al., 2011) (Reece, et al., 2005) (Ariza & Otero, 2007). The desirable features of conducting polymers (such as polypyrrole and polyaniline) that make them desirable as membrane materials are properties such as conductivity, ion exchange, stored charge and volume, which can be altered using electrochemical control. Therefore, these membranes have the potential to alter their properties as a function of changes in their environment or because of an external stimulus. Research has been carried out on both free-standing and composite polypyrrole membranes as switchable ion-exchange membranes. This project grew conducting polypyrrole nanofibers on polyamide water-filtration membranes in order to make the membrane electroactive, and studied the electrochemically induced ion-exchange properties of the conducting polymer coating. There is current research interest in employing conducting polymers, particularly in the nanoparticle or nanofiber morphology, as a means of removing hexavalent chromium from solution. For example, iron (III) oxide polypyrrole nanocomposite and polypyrrole nanotubes have been used as adsorbents for Cr(VI) (Bhaumik, et al., 2011) (Li, et al., 2012). Polyaniline nanofiber/tubes have been shown to be effective at reducing Cr(VI) to Cr(III) (Guo, et al., 2011). As part of the present research the polypyrrole nanofiber-polyamide composite membrane was investigated as a material for both the chemical or electrochemical reduction of Cr(VI) from aqueous solution. In addition, as some transition metal cations will undergo electrochemical reduction within the potential window of polypyrrole reduction, a number of studies have investigated the potential of using polypyrrole as a means of extracting toxic or precious metals from water (Shamaeli & Alizadeh, 2012) (Antilen et al., 2012) (Ding et al., 2003). Therefore, as part of the current research, investigations were carried out using polypyrrole nanofiber-coated membranes to remove Cu(II) ions from aqueous solution.

In the second part of the project polymers were attached onto the polyamide water-filtration membranes in order to increase the hydrophilicity of the membrane so as to improve their protein anti-fouling properties. Studies have shown that polymer materials that show protein anti-fouling properties generally exhibit some of the following properties: they are hydrophilic and are uncharged or contain both negative and positive charges, or contain H-bond acceptors (Ostuni, et al., 2001). Many materials have been considered for their anti-fouling properties (Yu, et al., 2011). In the present study an investigation was carried out on the anti-fouling properties of the polyelectrolyte polystyrene sulfonate (PSS), and the hydrophilic polymer poly(poly(ethylene glycol) methacrylate), which were grown using atom-transfer polymerisation from the activated membrane surface. In addition, a study was carried out on polydopamine-based polymers which were grown in solution and then deposited on the membrane surface.

2 Results and Discussion

2.1 Modification of Membranes using Polypyrrole Nanofibers

2.1.1 Introduction

Polypyrrole belongs to a class of polymers known as ‘conducting polymers’. These materials have the intrinsic ability to conduct electric current and feature a wide variety of structures and properties. Polyacetylene was the first example of a conducting polymer to be fully characterised (MacDiarmid, 2001): however, since then polymers containing heteroatoms such as polyaniline, polypyrrole, polythiophene and their derivatives have become more important (Reynolds, 2007). Of these, polypyrrole is one of the conducting polymers that has been most extensively studied and applied. The ease of preparation, high conductivity and relative stability of polypyrrole has led to its use in a diverse range of applications such as chemical sensors (Wei, et al., 2012) (Pirsa & Alizadeh, 2011), batteries (Wang, et al., 2005) (Liu, et al., 2013), supercapacitors (Mao, et al., 2012) (Li, et al., 2012), smart membranes (Jeon, et al., 2011) (Akieh, et al., 2010) and heavy metal remediation (Tian, et al., 2010) (Tian, et al., 2012). The important role that conducting polymers such as polypyrrole have come to play in modern chemistry is shown by the 2000 Nobel Prize in Chemistry awarded to Heeger, MacDiarmid and Shirakawa for their initial work on polyacetylene.

Polypyrrole is a black insoluble material consisting of a chain of repeating pyrrole monomer rings connected by carbon-carbon σ bonds. It is readily oxidised, resulting in the formation of polarons (semi-oxidised form) and bipolarons (fully oxidised form) (Fig. 2.1). A polaron is a radical cation formed by the loss of a single electron from the polymer and a bipolaron is the result of the loss of a further electron to form a dication (Bredas, et al., 1984) (Bredas & Street, 1985).

Oxidised polypyrrole is said to be doped by anions taken into the bulk polymer in order to preserve its charge neutrality. This process is reversible for small mobile anions such as chloride. The oxidation of polypyrrole is accompanied by an influx of anions which are then expelled from the polymer when it is reduced back to a neutral state. This ability to be either doped or undoped depending on the oxidation level is unique to conducting polymers (MacDiarmid, 2001). When oxidised polypyrrole is doped with larger anions such as dodecylbenzene sulfonate and poly(styrene sulfonate) the anions become anchored permanently in the polymer matrix. In this situation the electroneutrality of the polymer on reduction is maintained by the incorporation of mobile cations from the electrolyte solution. Thus, polypyrrole can act as an anion or cation exchange polymer depending on the size of the dopant (Weidlich, et al., 2005) (Syritski, et al., 2003) (Skaarup, et al., 2003).

Polypyrrole can be synthesised using either chemical or electrochemical methods (Feast, et al., 1996) (Toshima & Hara, 1995) (Scheme 2.1). One of the easiest and most common ways of synthesising polypyrrole chemically is by adding an oxidising agent such as $FeCl_3$ or a Cu^{2+} salt to pyrrole in solution, resulting in the precipitation of polypyrrole (Toshima & Hara, 1995). The anion of the salt is incorporated into the polymer to balance the positive charge carried by the polymer during the polymerisation: in this way, it is relatively simple to dope the polymer with different anions. Electrochemical polymerisation of pyrrole is achieved when an anodic potential is applied to a conducting substrate that has been immersed in a solution containing the pyrrole monomer and a suitable electrolyte. The polymer is formed in the positively charged oxidised state with the charge counterbalanced by dopant anions inside the bulk polymer.

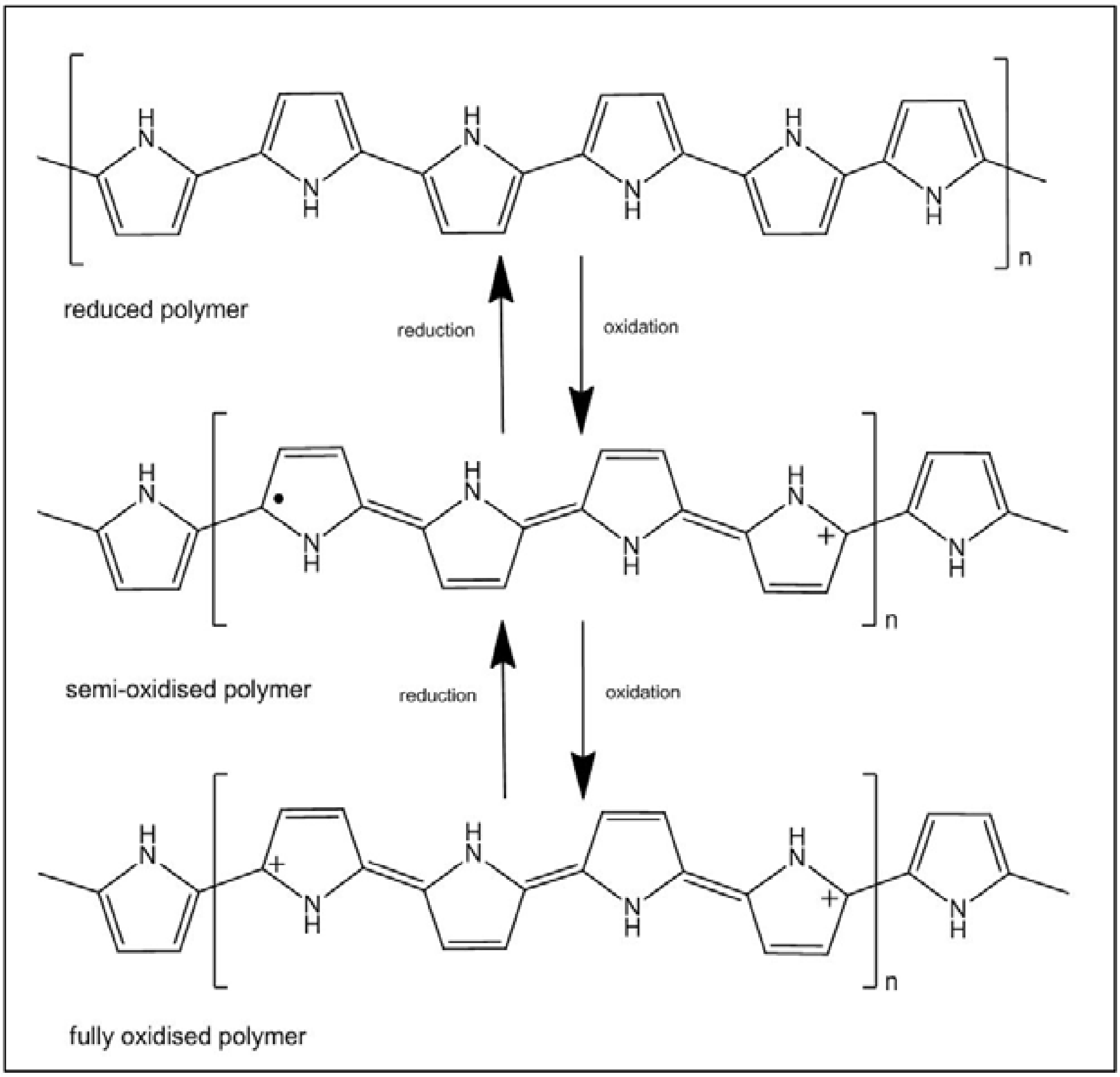
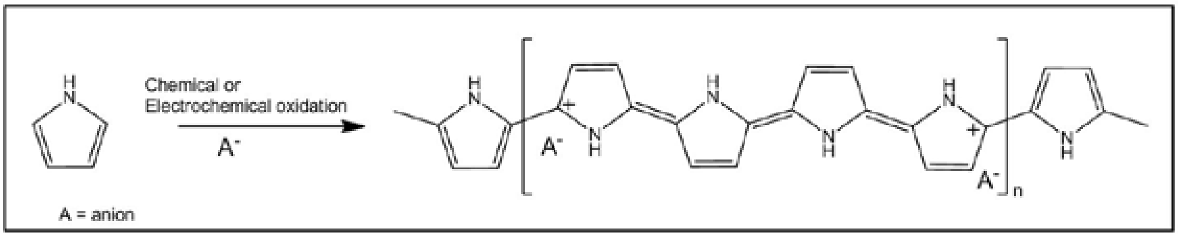


Figure 2.1. Different oxidation states of polypyrrole.



Scheme 2.1. Formation of polypyrrole by oxidative polymerisation.

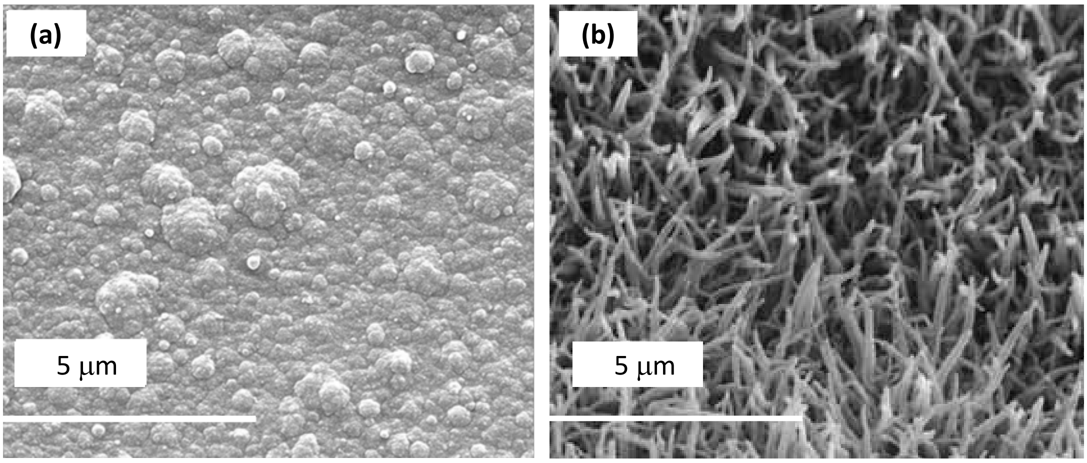


Figure 2.2. Scanning electron microscopy (SEM) micrographs showing polypyrrole in (a) bulk and (b) nanofiber morphology.

Extensive research has been carried out to find methods for controlling the growth of conducting polymers, as many studies have illustrated that their physical properties are a consequence of their morphology (MacDiarmid, 2001) (Reynolds, 2007). Polypyrrole nanofibers can be grown by a number of template methods, but in recent years a number of authors have reported template-free electrochemical methods for the formation of polypyrrole nanofibers. Template-free deposition methods have certain advantages as the formation of the nanofibers is fast and no additional steps are required to remove the hard template. Nanofibers have a higher surface area and shorter diffusion lengths than the analogous bulk materials, providing the fibres with more attractive properties (Bredas, et al., 1984). Figure 2.2 (a) and (b) depicts scanning electron microscopy (SEM) micrographs showing the difference in the morphology of typical bulk and nanofiber polypyrrole films.

2.1.2 *Chemical Oxidation*

Using an adaptation of the method outlined by Lin et al. (2005), a polyamide microfiltration membrane was stirred in an aqueous solution of pyrrole, anthraquinone-2-sulfonic acid sodium salt at 0°C for 30 mins. The iron-oxidising agent was then added to the reaction mixture with vigorous swirling. This was allowed to react for 2 hours (0–4°C), resulting in a fully coated membrane. This allowed a thin layer of bulk polymer to grow across the membrane surface to which the nanofibers could become attached. The membranes were then removed from the solution and placed in a new aqueous solution containing a mixture of methyl orange and pyrrole which was then cooled to 0°C with stirring for 30 mins. A pre-cooled solution of the iron-oxidising agent was added drop-wise with stirring and the solution again allowed to polymerise for 2 hours (0–4°C) (Yang & Li, 2010). The membranes were then removed from the reaction mixture and washed extensively with deionised water. The polymer formation on the membrane surface was indicated by the formation of a thin black polymer layer on the membrane (Fig. 2.3). Confirmation that the polymer was in the nanofiber morphology was obtained using SEM (Fig. 2.4). The average nanofiber diameter was approximately 180 nm, with a range of diameters of 100–400 nm. As can be seen from the SEM micrographs in Fig. 2.4, nanofiber lengths can only be estimated as being about 5 μm, as they form a mesh at the membrane surface. The flow rate measured, under gravity, of deionised water through the modified membranes decreased by 20% compared to their unmodified counterparts. However, it was observed that the methyl orange template was leached from the nanofibers, indicating that it was not completely immobilised within the polymer matrix.

Figure 2.3. Photograph of a polyamide membrane coated in polypyrrole.

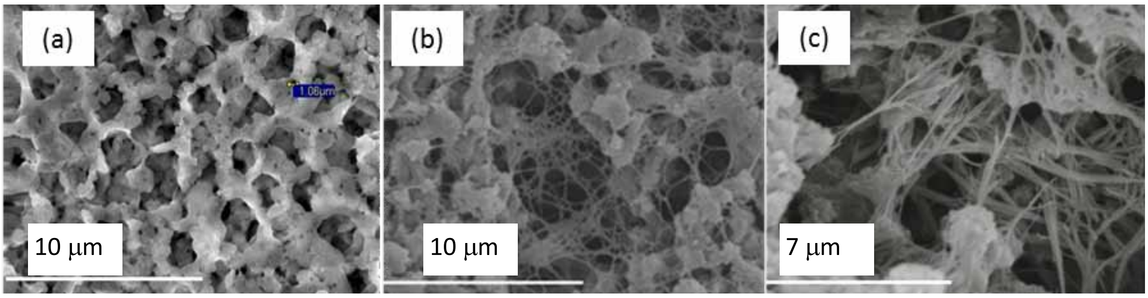


Figure 2.4. Scanning electron microscopy (SEM) micrographs of (a) unmodified polyamide filtration membrane (b) and (c) polyamide filtration membrane coated with polypyrrole nanofibers at low and high magnification.

2.1.3 Electrochemical Oxidation

2.1.3.1 Nanofiber Growth on Conventional Electrodes

A number of studies have shown that polypyrrole nanofibers can be grown directly on a surface using an electrochemical template-free approach (Debiemme-Chouvy, 2009) (Wang, et al., 2006). Preliminary experiments were carried out to investigate the optimum conditions of growth of polypyrrole nanofibers on an electrode. Two different electrolyte mixtures were employed: (i) pyrrole, Na_2HPO_4 and $LiClO_4$ and (ii) pyrrole, Na_2CO_3, $NaHCO_3$ and $LiClO_4$. Studies showed that the applied potential was critical in the successful formation of the nanofibers. Figure 2.5 shows SEM micrographs recorded for a typical set of experiments in which the applied potential was changed from 0.70 to 0.80 V vs saturated calomel electrode (SCE). At the lower applied potential the polypyrrole grows in a shark-tooth morphology, changing to a fibrillar morphology at an applied potential of 0.75 V vs SCE and finally forming the nanofiber morphology at 0.80 V. The nanofibers could be formed on a range of electrode surfaces, including gold, platinum, glassy carbon and indium tin oxide (ITO). The optimum potential for the formation of nanofibers from both electrolyte mixtures was 0.80 V vs SCE. Using Electrolyte Mixture 1 polypyrrole nanofibers were formed with lengths of between 0.6 and 1.5 µm and diameters of between 110 and 380 nm, whereas using Mixture 2 the lengths were between 1.0 and 1.5 µm and diameters were between 150 and 400 nm. In both cases SEM micrographs recorded of the cross sections of the polymer film showed that they formed from a thin base layer of bulk polymer (Fig. 2.6), which enables them to adhere well to the substrate. The nanofibers were conditioned to remove mobile phosphate by electrochemically cycling the modified electrode in NaCl. Alternatively, the carbonate containing nanofibers were soaked in a solution of sulfuric acid for 24 hours to remove the excess carbonate.

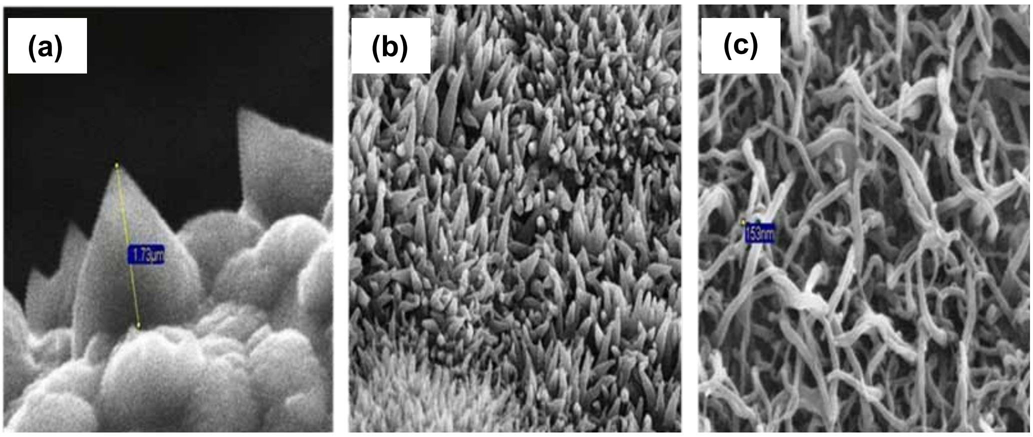


Figure 2.5. Scanning electron microscopy (SEM) micrographs showing the (a) shark-tooth, (b) fibrillar and (c) nanofiber morphologies.

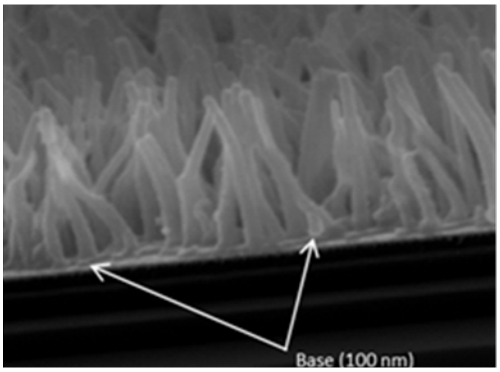


Figure 2.6. Scanning electron microscopy (SEM) micrograph showing the nanofibers growing from a base layer.

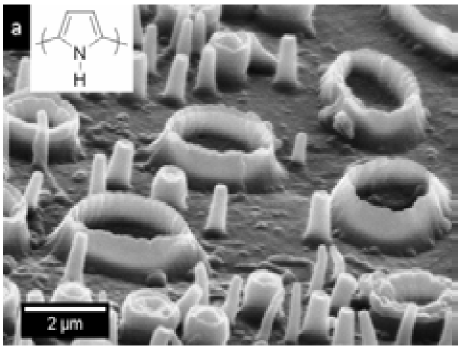


Figure 2.7. Scanning electron microscopy (SEM) micrographs showing a polypyrrole film grown in a microtubule morphology.

Interestingly, in some cases microtubular structures were formed on the electrode surface (Fig. 2.7) as for the nanofiber films, this morphology should have advantages compared to the bulk morphology with respect to an increased surface area. Further studies showed that it is possible to form this morphology reproducibly on the electrode surface using electrodeposition from an acoustically formed emulsion of the polymerisation mixture which contained a small quantity of a nonpolar solvent. These studies are the first observation of a facile means of depositing hollow polypyrrole microtubes directly onto an electrode. Moreover, the methodology could be applied to a number of conducting polymers.

It is not possible to directly add large immobile anions to form the nanofibers using a template-free electrochemical approach. Therefore, in order to form nanofibers containing these dopants, the nanofibers were first grown using Electrolyte Mixture 1. They were then removed from this solution, washed and immersed in a new polymerisation mixture containing an aqueous solution of pyrrole, *p*-sulfonatocalix[4]arene sodium salt (a large immobile anion); a layer of this polymer was then grown on the existing nanofibers. The surface of the nanofibers was characterised using energy dispersive X-ray (EDX) analysis, which was shown to contain sulfur atoms confirming the incorporation of the calixarene into the polymer. SEM micrographs

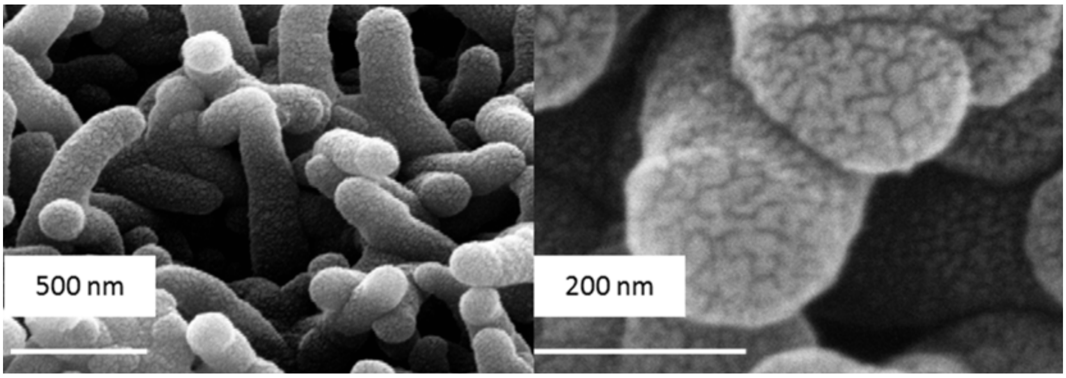


Figure 2.8. Scanning electron microscopy (SEM) micrographs showing polypyrrole nanofibers coated in a layer of *p*-sulfonatocalix[4]arene-polypyrrole at two magnifications.

were then recorded of the nanofibers before and after the additional coating, and showed that the nanofibers had increased in thickness by approximately 50 nm (Fig.2.8).

2.1.3.2 Nanofiber Growth on Polyamide Membranes

In order to make the membranes conductive they were first sputter-coated with a thin layer of gold. However, the studies on the conventional electrodes had indicated that tuning the conditions (including the concentration of the monomer, the electrolyte concentration, adding a small amount of co-solvent and the applied potential) allowed the nanofibers to grow on a range of substrates, so cheaper conducting materials such as graphite could be employed. Studies on the resistivity on the membranes coated with different thicknesses of gold indicated that a 70 nm coating was sufficient to lower the resistance across the membranes to approximately 200 ohms and to allow polypyrrole to be electrochemically deposited on the membrane surface. Using similar conditions to those outlined in Section 2.1.3.1, nanofiber formation was successfully achieved from Electrolyte Mixture 1 at an applied potential of 0.80 V vs SCE. A SEM micrograph of a typical membrane after electrochemical deposition of polypyrrole nanofibers is given in Fig. 2.9. In a final step the membranes were conditioned to exchange any mobile anions for chloride. Polypyrrole nanofiber-coated membranes could also be coated in an additional layer of *p*-sulfonatocalix[4]arene-polypyrrole in order to form nanofibers that contained an immobile dopant. The electroactivity of the membranes was determined using cyclic voltammetry which showed that the membrane could conduct electricity.

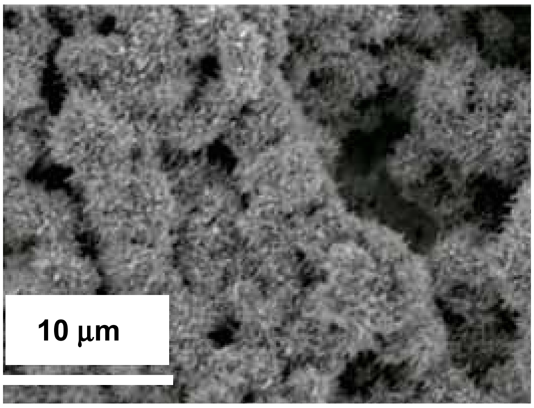


Figure 2.9. Polypyrrole nanofibers grown on a polyamide membrane using electrochemical deposition.

2.2 Investigation on the Ion-exchange Properties of *p*-Sulfonatocalix[4]-arene-Polypyrrole using Electrochemical Quartz Crystal Microbalance

2.2.1 Introduction

Sulfonated calixarenes (Fig. 2.10) are a versatile class of water-soluble supramolecules with the ability to bind with a wide range of metal cations, organic ammonium cations and neutral organic molecules (Guo, et al., 2008). Studies have shown that *p*-sulfonatocalix[4]-arene has high binding constants for divalent and trivalent metal cations (Guo, et al., 2008). As they are

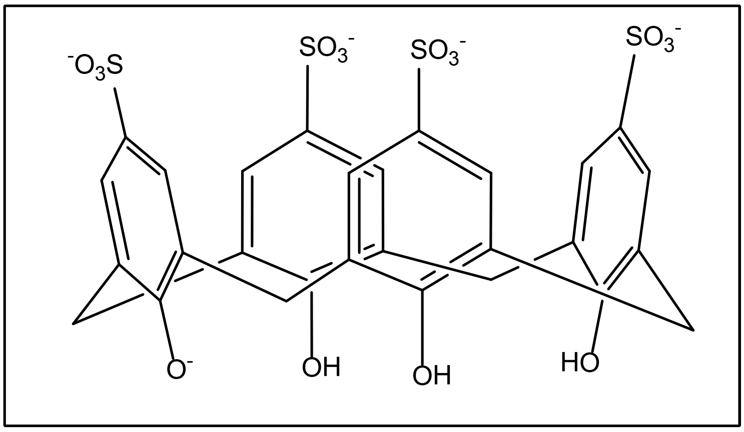


Figure 2.10. Structure of *p*-sulfonatocalix[4]arene.

anionic *p*-sulfonated calixarenes can be doped into polypyrrole as it forms and electrochemical impedance studies (EIS) studies carried out by our group have shown that *p*-sulfonatocalix[4]arene acts as an immobile dopant within the polypyrrole matrix (Doyle, et al., 2012). Moreover, Bidan and Niel (1997) showed that the *p*-sulfonatocalix[6]arene retained its inclusion properties when it was immobilised in the polymer film. *p*-Sulfonatocalix[4]arene-polypyrrole was chosen as a coating for the nanofibers formed in the present research as previous studies have shown that the formation of a membrane from polypyrrole containing a chelating ligand, such as a calixarene or a cyclodextrin, can alter the cation-transport properties across the membrane and can enhance selective permeability to a number of transition metal cations (Akieh, et al., 2010) (Reece, et al., 2005).

Polypyrrole's ability to behave as an electrochemically controllable ion-exchange material has enabled it to be used in a range of applications such as membrane separation, the recovery of toxic or precious metals from solution, or in analytical applications. Therefore, it is important to understand the processes which occur upon oxidation or reduction of the polymer. An investigation of the ion-exchange properties of the *p*-sulfonatocalix[4]arene-polypyrrole coating was carried out using an electrochemical quartz crystal microbalance (EQCM). In order to apply this technique to the *p*-sulfonatocalix[4]arene-polypyrrole coating, it is necessary to ensure that the coating is uniform, rigid and thin. A linear relationship was observed between the change in mass of the coating with charge consumed as the polymer was formed, indicating that the film was uniform, rigid and thin.

2.2.2 *Cyclic Voltammograms of* p-*Sulfonatocalix[4]-arene-Polypyrrole*

In the first instance, the cyclic voltammogram of the *p*-sulfanotocalix[4]arene-polypyrrole film grown to different charges was recorded in order to determine the film's oxidation and reduction potentials. The polymer was grown from a solution of *p*-sulfonatocalix[4]arene sodium salt and pyrrole. The films were then cycled in sodium sulfate and the reduction peak (-0.40 to -0.65 V) shifts to lower potentials with thicker films. The oxidation peak occurs between -0.40 and -0.20 V and shifts to higher potentials with thicker films. This behaviour is indicative of a cation-exchange polymer. The reduction peak is distinctly sharper than that observed for the oxidation peak and this has been attributed to the high mobility of the cations and to the ionic concentration gradient between the bulk electrolyte and the film (Baker, et al., 1991). Therefore, the reduction of the *p*-sulfonatocalix[4]arene-polypyrrole film, which involves the incorporation of Na^+ ions from the solution phase into the film, is a relatively fast and efficient process, whereas oxidation of the polymer is slower due to the slow release of Na^+ ions.

2.2.3 *Effect of Scan Rate on the Massograms of* p-*Sulfonatocalix[4]arene-Polypyrrole*

In order to investigate if *p*-sulfonatocalix[4]arene-polypyrrole films did exhibit metal cation-exchange properties, studies were carried out using Na^+ as a test ion. Three separate *p*-sulfonatocalix[4]arene-polypyrrole films were grown on a gold electrode using pyrrole and *p*-sulfonatocalix[4]arene sodium salt. The three films were cycled in a NaCl solution at scan rates of 10, 50 or 100 mV s^{-1} respectively, and the mass change and current response were recorded as a function of potential. The size of the anodic and cathodic peak currents for the *p*-sulfonatocalix[4]arene-polypyrrole film decreased as a function of scan rate which is a generally observed phenomenon in cyclic voltammetry. The shape of the massograms for the three scan rates are quite similar and are typical for polypyrrole doped with an immobile anion (Akieh, et al., 2009). Initially, upon reducing the potential from 0.10 V to approx. -0.40 V vs. Ag/AgCl, the mass of the film decreased steadily. This is consistent with the expulsion of mobile Cl^- ions and associated water which had been absorbed into the polymer from the electrolyte solution. However, when the potential reached a value of approximately -0.40 to -0.50 V vs. Ag/AgCl, at which point the polypyrrole backbone was significantly reduced, the mass of the polymers started to increase and continued to increase as the polymers were further reduced to -0.85 V vs. Ag/AgCl. Over this potential window, Na^+ ions and associated water molecules from the electrolyte solution influx into the polymers to balance the charge on the immobile anionic calixarene dopants. The opposite processes (i.e. loss of Na^+ and influx of Cl^-) occur as the polymer was cycled back in the anodic direction.

A quantitative analysis of the data acquired from the EQCM experiments was then carried out by relating the change in mass of the polymer to the total amount of charge passed in order to identify the molar mass of the ion being incorporated or egressing from the polymer. Data were obtained from the linear regions of the massograms and the mass change was then plotted as a function of charge. The apparent molar mass of the species moving into or out of the polymer was determined from the gradient of the line. Upon carrying out this analysis, differences in the behaviour of the polymers as a function of the potential scan rate became apparent. The apparent molar mass of the species moving into each of the three polymers was determined as 39.39, 21.97 and 12.95 g mol^{-1}. If the only process occurring at this stage of the redox cycle was the movement of Na^+ ions, the molar mass would be 22.99 g mol^{-1}. While the apparent molar mass calculated at 100 mV s^{-1} was greater than the theoretical value, it is believed that this is because the Na^+ ions will be solvated. It is well established that the influx of cations into a polymer is accompanied by solvent uptake. Indeed, Akieh et al. (2009) have also observed mass changes greater than the theoretical values for a polystyrene sulfonate-polypyrrole film. They too attributed these elevated values to the influx of solvent molecules. Interestingly, at the slowest scan rate the apparent molar mass is lower than the molar mass of Na^+. The most likely explanation for this observation was that, at this scan rate, in addition to the movement of Na^+ ions into the polymer, there was also the movement of neutral species (salt or water) out of the polymer. This is again consistent with observations by Akieh et al. (2009) for polypyrrole doped with the immobile polystyrene sulfonate anion. In that work, it was proposed that the decrease in the apparent molar mass of the influxing species upon reduction of the potential scan rate arises due to increased movement of neutral species. It would appear that a similar effect was occurring for the *p*-sulfonatocalix[4]arene-polypyrrole system studied here. The massogram recorded at 100 mV s^{-1} in NaCl was the most similar in appearance to that of an ideal cation exchange polymer. In summary, it would appear that the ion-exchange behaviour of the *p*-sulfonatocalix[4]arene-polypyrrole is scan-rate dependent, with cation exchange becoming the dominant process at the higher scan rates. This indicates that it may be possible to control the ion-exchange properties of the membranes by choice of potential scan rate and so favour the removal of certain ions from water.

2.2.4 *Effect of Dopant Concentration on the Massograms of* p-*Sulfonatocalix[4]arene-Polypyrrole*

Polymers were grown from two solutions containing pyrrole and two different concentrations of *p*-sulfonatocalix[4]arene. The general features of the massograms were similar for both polymers for each scan rate studied. Both films showed a similar loss of mass between 0.10 and -0.40 V vs Ag/AgCl on the forward scan, and an increase in mass between -0.40 and -0.80 V vs Ag/AgCl. However, the mass increase is greater for the polymer containing the higher amount of calixarene dopant, indicating that an increase of dopant concentration does enable a greater number of cations to enter the polymer.

2.2.5 Metal Cation-exchange Properties of p*-Sulfonatocalix[4]arene-Polypyrrole*

In order to investigate the metal ion-exchange properties of the films against a range of metal ion, they were cycled in aqueous solutions containing CsCl, NaCl, $CaCl_2$, $NiCl_2$, $CuCl_2$ or $CrCl_3$. The experiments were carried out at scan rates of both 10 and 100 mV s^{-1} between a potential of -0.80 and 0.10 V vs Ag/AgCl. Table 2.1 gives a summary of the peak potentials for the redox couple of the polymer in the different solutions.

Table 2.1. Peak potentials for the *p*-sulfonatocalix[4]-arene-polypyrrole coating recorded in metal chloride solution.

Compound	E_p^A/ V vs. Ag/AgCl	E_p^C / V vs Ag/AgCl
NaCl	-0.28	-0.46
CsCl	-0.28	-0.41
$CaCl_2$	-0.29	-0.40
$NiCl_2$	~	-0.64
$CrCl_3$	-0.01	~

The actual mass differences were recorded in the massograms at reduction potentials in both forward and reverse scan. The mass increase in the forward scan occurs because as the polypyrrole backbone is reduced the cations must ingress into the polymer to balance the negative charges on the calixarene. The mass loss in the reverse scan occurs because as the polypyrrole backbone is oxidised the cations egress from the polymer as they are no longer required to achieve charge neutrality. In general, the shapes of the cyclic voltammograms and massograms show similar features, although the loss in mass observed in the region 0.10 to -0.40 V in the forward and reverse scan of the polymer cycled in NaCl and $CaCl_2$ was not evident when the experiment was repeated in CsCl. This may reflect the higher mobility of the Cs^+ ion compared to Na^+ or Ca^{2+}, both of which will have a higher number of hydration shells, enabling a great number of Cs^+ ions to move into the polymer. This causes the mass change in the polymer in the region of -0.4 to -0.8 V vs Ag/AgCl to be substantially higher for CsCl than for NaCl or $CaCl_2$ so that the small change in mass in the region of 0.1 to 0.4 V may not be noticeable.

The data were analysed in order to investigate if the mass increase or loss corresponded to the known molar mass for that cation. Table 2.2 summarises the results obtained from this study. For the s-Block metal salts CsCl, $CaCl_2$ and NaCl it was observed that the actual mass change of the polymer was greater at the

Table 2.2. Data obtained from changes in mass recorded on the 5th cycle for *p*-sulfonatocalix[4]-arene-polypyrrole cycled at reduction potential in a range of salt solutions.

Compound	Scan rate (mV s^{-1})	Cation ingress (forward scan, polypyrrole reduced)			Cation egress (reverse scan, polypyrrole oxidised)		
		Actual Δmass (μg cm^{-2})	Apparent molar mass (g mol^{-1})	Expected molar mass (g mol^{-1})	Actual Δmass (μg cm^{-2})	Apparent molar mass (g mol^{-1})	Expected molar mass (g mol^{-1})
CsCl							
	10	1.19	69.07	Cs: 132.91	1.15	78.03	Cs: 132.91
	100	1.26	91.52	Cs: 132.91	1.22	88.04	Cs: 132.91
$CaCl_2$							
	10	0.04	17.62	Ca: 40.08	0.03	-	Ca: 40.08
	100	0.37	89.61	Ca: 40.08	0.23	42.40	Ca: 40.08
$NiCl_2$							
	10	0.44	86.65	Ni: 58.69	0.06	32.85	Ni : 58.69
$CrCl_3$							
	10	0.05	1.95	Cr: 52.00	0.02	0.55	Cr: 52.00
NaCl							
	10	0.07	12.95	Na: 22.99	0.07	4.43	Na: 22.99
	100	0.18	39.39	Na: 22.99	0.15	31.30	Na: 22.99
$CuCl_2$							
	10	0.61	95.44	Cu: 63.55	0.08	51.23	Cu: 63.55

100 mV s^{-1} scan rate than at the 10 mV s^{-1} scan rate. This indicates that at the slower scan rates, as the cations ingress or egress from the polymer, other species – such as water molecules or salts – move in the opposite direction. The molar mass determined for the three cations is higher at the higher scan rate, indicating that the competing processes compete less favourably at this scan rate. However, in all cases it is likely that this movement of neutral species is still occurring and that even at the high scan rate the molar mass determined for the cesium ion is lower than the known mass – showing that the movement of the species in the opposite direction is still occurring. This molar mass determined for the calcium and sodium ions at 100 mV s^{-1} is higher than the known molar mass of these ions and this is accounted for by the presence of solvent shells around the ions. Interestingly, for the transition metal salts $CuCl_2$, $NiCl_2$ and $CrCl_3$, it was observed that the mass of the polymer increased with each cycle, indicating that the metal was being trapped within the polymer. Moreover, the mass increase for the nickel and copper in the forward scan was significantly higher than that recorded in the calcium chloride solution. It was determined that the nickel and copper cations were undergoing reduction at the polymer surface at the reduction potential, and although some were then reoxidised and egressed from the polymer a component remained in the polymer matrix as metal(0) particles.

2.2.6 *Anion-exchange Properties of* p-*Sulfonatocalix[4]arene-Polypyrrole*

From the EQCM studies carried out in the previous sections it was clear that the *p*-sulfonatocalix[4]arene-polypyrrole film was not permselective, that is, it did not act exclusively as a cation-exchange polymer and the massograms did not exactly match the 'ideal' behaviour of a cation-exchange polymer. Moreover, this deviation from being a selective cation-exchange polymer deviated to a greater extent at lower scan rates. As a result, a study to investigate the anion exchange behaviour of the film was conducted. Three anions were used for this study: (i) nitrate, (ii) perchlorate and (iii) chloride. Table 2.3 gives the peak potentials for the redox processes of polymer recorded in solution of each of these ions.

Table 2.3. Peak potentials for the *p*-sulfonatocalix[4]-arene-polypyrrole coating recorded in sodium salt solutions.

Compound	Ep^A/ V vs. Ag/AgCl	E_p^C / V vs. Ag/AgCl
NaCl	-0.28	-0.46
$NaNO_3$	-0.26	-0.40
$NaClO_4$	-0.20	-0.41

Table 2.4 summarises the results of the EQCM study. For each anion studied it can be observed that the mass loss (egress of anions) of the polymer is higher than the mass gain (ingress of anions) of the polymer at the two scan rates studied. This indicates clearly that other exchange process – such as the movement of solvent

Table 2.4. Data obtained from changes in mass recorded on the 5th cycle for *p*-sulfonatocalix[4]-arene-polypyrrole cycled at oxidation potential in a range of salt solutions.

Compound	Scan Rate (mV s^{-1})	Anion ingress (reverse scan polypyrrole oxidised)			Anion egress (forward scan polypyrrole reduced)		
		Actual Δmass (μg cm^{-2})	Apparent molar mass (g mol^{-1})	Expected molar mass (g mol^{-1})	Actual Δmass (μg cm^{-2})	Apparent molar mass (g mol^{-1})	Expected molar mass (g mol^{-1})
NaCl							
	10	0.08	12.57	Cl: 35.45	0.14	15.49	Cl : 35.45
	100	0.03	9.68	Cl: 35.45	0.10	22.52	Cl : 35.45
$NaNO_3$							
	10	0.16	26.15	NO_3 : 62.01	0.23	29.23	NO_3: 62.01
	100	0.10	23.14	NO_3: 62.01	0.17	27.90	NO_3: 62.01
$NaClO_4$							
	10	0.34	42.43	ClO_4 : 99.45	0.39	52.77	ClO_4 : 99.45
	100	0.34	46.31	ClO_4 : 99.45	0.39	52.50	ClO_4 : 99.45

– must be taking place at the polymer interface and that the mass change does not simply reflect the movement of anions. This deduction is confirmed by analysis of the data which shows that the apparent molar masses are less than the known molar masses for the anions. This indicates that neutral species are being transported in the opposite direction to the anions. Interestingly, the mass changes observed for the anions (in particular the perchlorate ion) did not show a significant dependence on the scan rate.

In summary, it would appear that *p*-sulfonatocalix[4]-arene-polypyrrole acts as a mixed cation–anion exchange material at slow potential scan rates and as predominantly a cation-exchange polymer at high potential scan rates. For the two concentrations of *p*-sulfonatocalix[4]arene used to grow the polymer, it would appear that the cation-exchange properties are slightly favoured when using a higher concentration of dopant. However, the exchange behaviour for both anions and cations is complicated by the movement of other species (solvent or neutral salts) in the opposite direction. The movement of these other species would appear to be more significant at slow potential scan rates as indicated by the smaller apparent molar masses determined for Na^+, Cs^+ and Ca^{2+} at the scan rate of 10 mV s^{-1} compared to the values determined when the experiment was repeated at 100 mV s^{-1}. The electrochemistry of Cu^{2+}, Ni^{2+} and Cr^{3+} overlapped with that of the polymer and there was evidence that two of these metals were deposited on the coating in the zero oxidation state. This observation is consistent with the known standard reduction potentials for these ions (which are given in Table 2.5) and the three metals would be expected to be deposited on the polymer when it is cycled down to -1.0 V vs Ag/AgCl. As a result, the nanofiber-coated membranes coupled with electrochemical reduction could be used as a means of removing these ions from water.

2.2.7 *Investigations of Cation Exchange in Real-water Samples*

The electrochemical activity of the *p*-sulfonatocalix[4]-arene-polypyrrole coating was studied using cyclic voltammetry in a sample of river water spiked with NaCl or $CaCl_2$. The known contents of the water sample are given in Table 2.6.

Fresh polymer coatings were grown for each experiment and the resulting polymer was then cycled in a spiked real water sample. The redox activity with its associated ion-exchange properties of the polymer was still present in the real water samples. The shape of the cyclic voltammograms indicate that the polymer still acts predominantly as a cation-exchange material. This is because at the high scan rates the cyclic voltammograms of the polymer show a more defined peak for the reduction process than the oxidation processes. This indicates that *p*-sulfonatocalix[4]arene-polypyrrole system will act as an electrochemically induced ion-exchange polymer in real water samples, if the conductivity of the solution is sufficient to enable them to do so.

Table 2.5. Standard reduction potentials for a number of transition metal ions.

Reduction reaction at 25°C in water	E° (V)
$Cu^{2+} + 2e \rightarrow Cu$	+0.34
$Ni^{2+} + 2e \rightarrow Ni$	-0.25
$Cr^{3+} + 3e \rightarrow Cr$	-0.74

Table 2.6. Data on the properties and content of the river water sample.

Sample	Solid (mg L^{-1})	pH	Total Phosphorus (mg L^{-1})	Ammonia (mg L^{-1})	Nitrate (mg L^{-1})	Nitrite (mg L^{-1})	Orthophosphate (mg L^{-1})	Chloride (mg L^{-1})	Potassium (mg L^{-1})	Sodium (mg L^{-1})
River water	< 1	6.6	0.05	<0.02	<0.3	<0.002	0.04	8.7	n/a	n/a

2.3 Investigating Copper Ion Removal from Solution using *p*-Sulfonatocalix[4]arene-Polypyrrole-coated Nanofibers on a Membrane

2.3.1 Introduction

As some transition metal cations will undergo electrochemical reduction within the potential window of polypyrrole reduction, a number of studies have investigated the potential of using polypyrrole as a means of extracting toxic or precious metals from water. For example, polypyrrole was used as an electrochemical system for the microextraction of Ni^{2+} from wastewater (Shamaeli & Alizadeh, 2012), while Antilen et al. (2012) showed that a polypyrrole-humic acid composite could be used for the extraction of Cu^{2+} from drinking water and Ding et al. (2003) showed that polypyrrole-coated fabrics could be used as an efficient means to extract gold from aqueous solution.

2.3.2 Copper Ion Extraction from Aqueous Solution

As outlined in Section 2.1.3.2, polypyrrole nanofibers were grown on the membrane. They were then conditioned to remove mobile phosphate ions and coated with a layer of *p*-sulfonatocalix[4]arene-polypyrrole. This was done to form a film that will favour the influx of metal cations. The membrane was washed extensively and placed between two compartments of a teflon cell (see Fig. 2.11). An aqueous solution of $Cu(NO_3)_2$ was placed in both compartments. The membrane was pulsed between the potentials of -0.80 V vs. SCE for 50 s, then 0.50 V vs. SCE for 50 s for a fixed period of time (25, 50, 75 and 100 min). The pulsed potential methodology was carried out in order to regenerate the polypyrrole material, although some of the copper would be expected to be oxidised during the positive potential pulses. The experiment was then stopped and the solutions in both the source and receiving cell were mixed together and the amount of copper which had been removed from the solution was then measured (Fig. 2.12). That the copper was deposited on the membrane was confirmed by carrying out an EDX analysis of the membrane at the end of each experiment. Over the time period of the experiment (100 min), 12.5% of the Cu(II) ions were removed from the solution. This efficiency of removal is lower than previous values for related systems reported in the literature (Piatnicki, et al., 2002) (Ying, et al., 2007). However, these literature studies involved much lower concentrations of Cu^{2+} ion and were carried out under acid conditions. An improved efficiency of Cu^{2+} ion removal would be expected for the membranes studied in the present research if the initial concentration of Cu^{2+} was reduced and the solution was acidified.

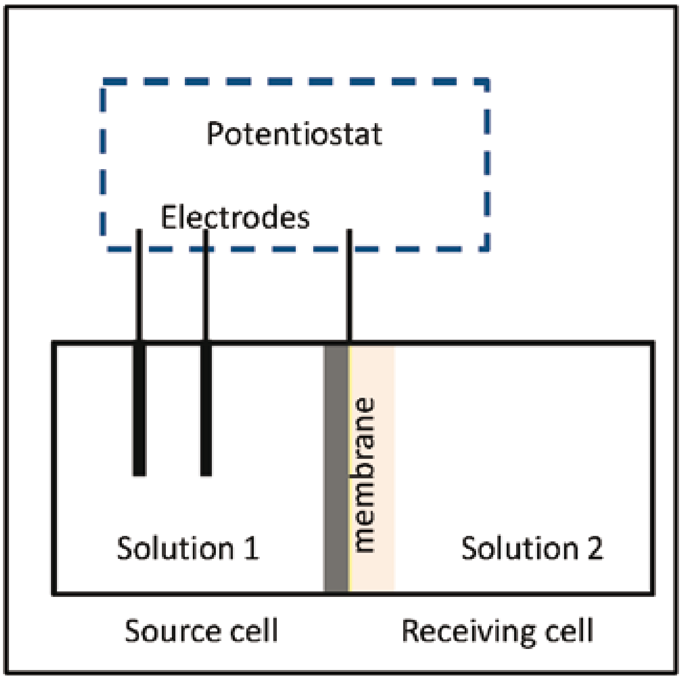


Figure 2.11. Schematic diagram of the cell used to test if the polypyrrole nanofiber-modified membrane removes copper Ions from solution.

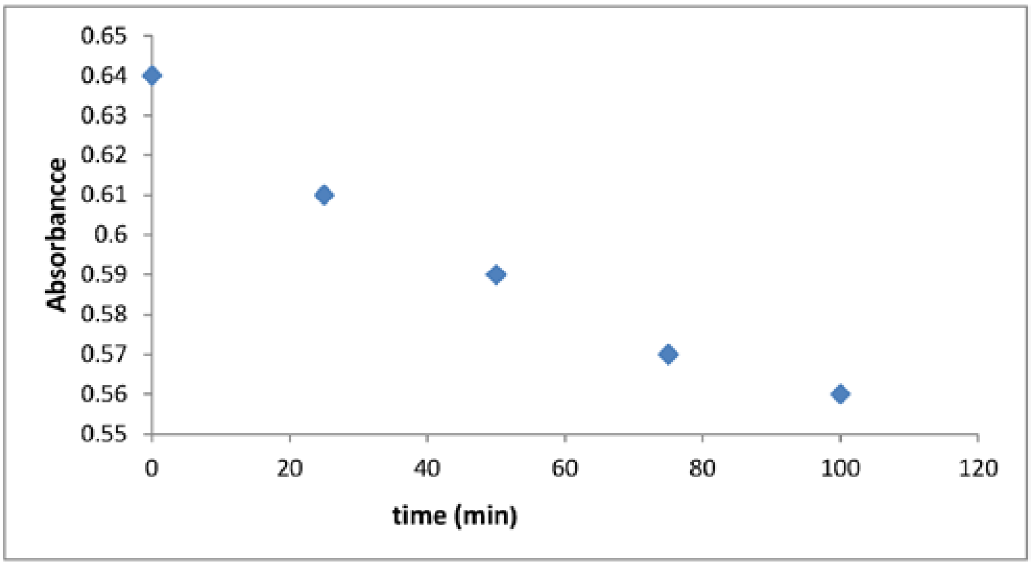


Figure 2.12. Decrease in the absorbance band for the Cu(II) ions monitored as a function of time for the electrochemical removal of Cu(II) ions from solution using a polypyrrole nanofiber-coated membrane.

2.4 Development of a Smart Membrane for Anion Transport using Polypyrrole Nanofiber-coated Membranes

2.4.1 Introduction

As the physical properties of polypyrrole – such as its charge, the nature of it doping ions, its porosity and water content – are known to change with applied potential, there has been significant interest in developing this polymer as a ‘smart’ material, the properties of which can be altered by the application of an external stimulus. One such application is to employ polypyrrole-based membranes as electrically switchable ion-exchange membranes. The use of polypyrrole as a switchable membrane occurs because, as discussed in Section 2.1.1, as polypyrrole is reduced in order for the polymer to retain its charge neutrality, either the anion that was incorporated during electrochemical synthesis must be expelled or, if the anion is immobile, cations from the surrounding solution must be incorporated into the polymer. When the polymer is reoxidised the opposite movement of the ions occurs. As a result, it is possible to switch the ion gate membrane from ‘off’ by reducing – and to ‘on’ by oxidizing – the polymer, so that the membrane becomes permeable to different ions during the ‘on’ period.

A significant number of researchers have investigated both free-standing and composite polypyrrole membranes as switchable ion-exchange membranes. The drawback to the free-standing membranes is that they have limited strength and porosity. Therefore, a number of researchers have developed composite membranes based on microfiltration membrane supports, such as the modified membranes developed in the current project. Interestingly, studies have shown that the selectivity of ion transport across the polypyrrole membrane can be enhanced by the choice of the dopant anion (Reece, et al., 2005). Less attention has been paid in the literature to the selective transport of anions across polypyrrole membranes, or to how the process is altered if the polypyrrole is in the nanofiber morphology. One study showed that free-standing oxidised polypyrrole films were highly permeable to nitrate ions, while the rejection of these ions was very high when the film was reduced (Ariza & Otero, 2007). The present study set out to investigate if polypyrrole nanofiber–polyamide composite membranes could be developed as a gated membrane for nitrate ions.

2.4.2 Anion Movement through Polypyrrole Nanofiber-Polyamide Composite Membranes

Polypyrrole nanofibers were grown on the membrane, as outlined in Section 2.1.3.2 without the calixarene over-layer. The membranes were conditioned by cycling in NaCl solution to exchange mobile phosphate ions and then extensively washed and placed in the transport cell (described previously in Section 2.3.2). Initial experiments were carried out using the same pulsed potential technique as described in Section 2.3.2

using an aqueous solution of $CaCl_2$ as the electrolyte. The membrane was allowed to equilibrate for 60 min and then pulsed between the potentials of -0.80 V vs SCE for 50 s, then 0.50 V vs SCE for 50 s for a fixed period of time (25, 50, 75 and 100 min). Tests were carried out to determine if the selected ion was present in the receiving cell. Depending on whether or not the potential was applied, it was found that the membrane would selectively allow transport of Cl^- over Ca^{2+}.

Having confirmed that anion transport through the membrane was possible, studies were carried out to determine the selectivity of the membrane when exposed to a mix of anions. Polypyrrole nanofibers were grown on the membrane and placed in a mixed solution of KNO_3 and KCl. It was found that while both Cl^- and NO_3^- permeate the membrane at negative applied potentials, NO_3^- permeation is slower than Cl^- permeation. It is anticipated an increased difference in the permeation rate of the Cl^- and NO_3^- anion will be achieved upon increasing the thickness of the polypyrrole nanofiber membrane, but no selective transport of the nitrate ion was achieved for the membranes as tested here.

2.5 Removal of Cr(VI) from Water using Polypyrrole Nanofiber-coated Membranes

2.5.1 Introduction

There is substantial current interest in investigating conducting polymer-based materials as a means of removing Cr(VI) from solution, and a variety of different approaches have been employed. For example, a number of researchers have used polypyrrole particles and micro- and nanocomposites of polypyrrole and iron oxides as adsorbents for Cr(VI) (Roy, et al., 2012) (Gao, et al., 2012) (Bhaumik, et al., 2011). Lei et al. (2012) have employed polypyrrole/cellulose fibres for the chemical reduction of Cr(VI) to the less toxic Cr(III) and a number of studies have been carried out on the electrochemical reduction of Cr(VI) to Cr(III) by polypyrrole coated on a variety of electrode substrates (Tian, et al., 2012) (Earley, et al., 2009). As polypyrrole nanofibers can have advantages over bulk polypyrrole with respect to the surface area of the polymer, a study was carried out to employ the polypyrrole-nanofiber-coated membranes as a porous electrode for the electrochemical reduction of Cr(VI), with the overall goal of removing Cr(VI) from water

2.5.2 UV/vis Spectroscopic Study on the Removal of Cr(VI) from Water

Polypyrrole nanofibers were grown on a membrane, as outlined in Section 2.1.3.2, without the calixarene overlayer. The membrane was then held in KCl and reduced at -0.80 V vs SCE for 30 mins. The membrane was then transferred to 10 mL of H_2SO_4 and $Na_2Cr_2O_7$ and the UV/vis spectra of the solution were recorded over 24 hours to monitor the loss of Cr(VI) from the solution. A typical series of UV/vis spectra is given in Fig. 2.13(a), which shows that no band associated with the Cr(VI) compound remained in solution after 24 hours of contact. Figure 2.13(b) shows a 50% loss of Cr(VI) from solution after approximately 8 hours of contact. The experiment was repeated three times and it can be observed in Figure 2.13(b) that there was good reproducibility in the amount of Cr(VI) that was removed from the solution at a given time.

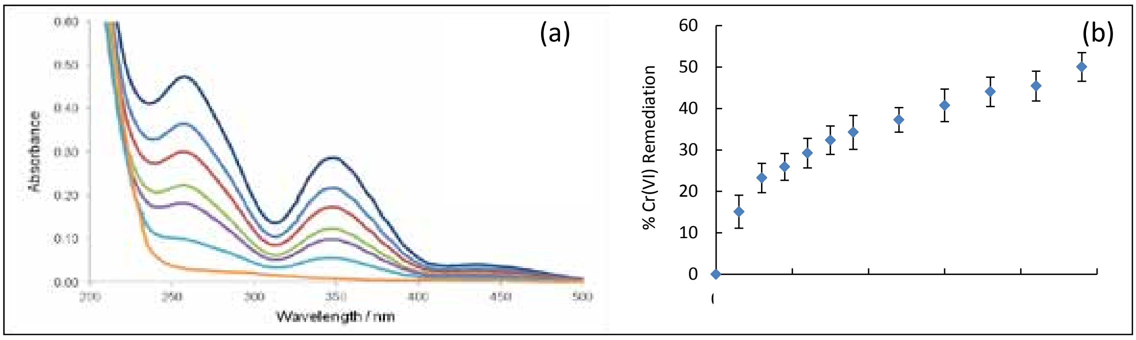


Figure 2.13. (a) UV/vis spectra showing decrease in the absorbance bands associated with Cr(VI) as function of time, (b) % loss of Cr(VI) from solution as function of time for solution of $Na_2Cr_2O_7$ in contact with polypyrrole-nanofiber-coated membrane, measured over 8-hour time period.

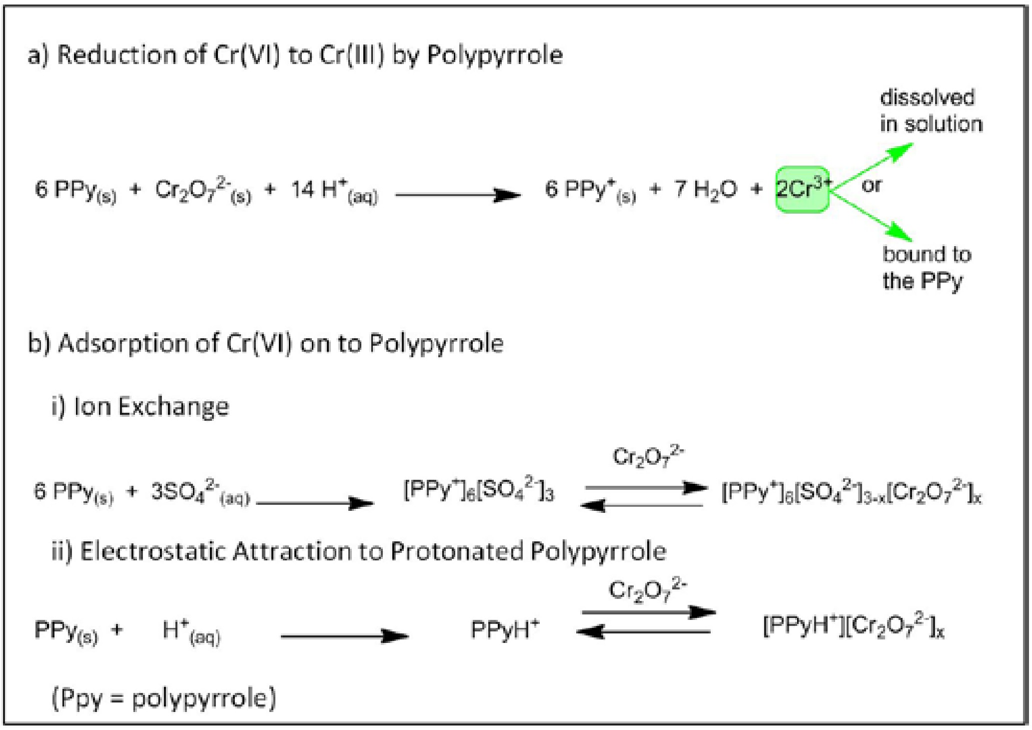


Figure 2.14. Possible processes that could occur between Cr(VI) and the polypyrrole nanofibers.

The membranes could be recycled by re-immersing them in KCl or H_2SO_4 and reducing them at -0.80 V vs SCE for 30 mins. There was a substantial loss of activity after the first immersion but thereafter the loss of activity levelled out. Significantly, a similar pattern of loss of activity was observed for the membranes that were not pre-reduced. However, the rate of loss of Cr(VI) at the early times of immersion was greater for the membranes that included the pre-reduction step. These findings suggest that prolonged exposure to the Cr(VI) solution was over-oxidising the polypyrrole coating, which causes a loss in its conductivity and reduces its ability to reform the neutral form. Therefore, it is likely when using polypyrrole for the electrochemical remediation of Cr(VI) that a potential pulsing methodology (as used in Section 2.3.2) – in which the membrane is pulsed with negative potentials – should increase the recyclability of the system.

2.5.3 Mechanism of Cr(VI) Removal from Solution by Polypyrrole Nanofibers

The studies carried out in Section 2.5.2 have shown that the reduction step altered the properties of the modified membrane, but that the polymer which was not pre-reduced could also remove Cr(VI) from solution. In addition, other processes such as ion exchange could be important in the polymer's activity and there was no information on the final fate of the chromium, that is whether it was adsorbed on the polymer in the +6 or +3 oxidation state or whether it was released in to solution in the +3 oxidation state. Therefore, studies were carried out to understand the processes by which the Cr(VI) is removed by the polypyrrole nanofibers. The possible processes by which the Cr(VI) can be removed from solution are summarised in Fig. 2.14.

2.5.3.1 Ion Exchange

If an ion-exchange step is important in the removal of the Cr(VI) from solution, then replacing the small mobile dopant with a large immobile dopant should stop the process. The dopant chosen for this study was sodium dodecyl sulfate (SDS) which, as is clear from Fig. 2.15, is a very large, and therefore immobile, anion.

Polypyrrole nanofibers (which contain a mixture of small mobile dopants) and bulk polypyrrole containing either the SDS dopant or a mobile Cl^- dopant were all grown on gold electrodes. The polypyrrole films were reduced and were then each placed in a solution containing $Na_2Cr_2O_7$ in H_2SO_4. Figure 2.16 gives the results for Cr(VI) removal, and shows that there is no significant

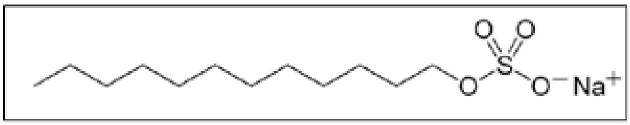


Figure 2.15. Structure of dodecyl sulfate sodium salt.

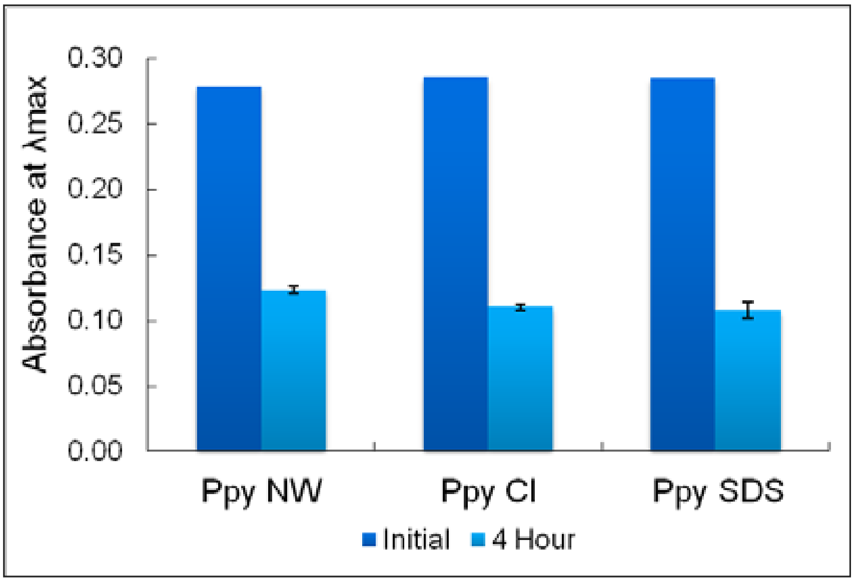


Figure 2.16. Absorbance of $Na_2Cr_2O_7$ in H_2SO_4 in contact with polypyrrole nanofibers (Ppy NW), polypyrrole doped with chloride ions (Ppy Cl) and polypyrrole doped with dodecyl sulfate ions (Ppy SDS).

difference between the amount of Cr(VI) removed from the solution in each case. This indicates that the nature of the dopant – whether mobile or immobile – does not have an important role to play in removing Cr(VI) from the solution. Therefore, this would not be an important consideration when developing such systems for removing Cr(VI) from water.

2.5.3.2 *Effect of pH*

As can be observed from Fig. 2.14, a low pH of the solution could promote Cr(VI) removal in two ways. First, acid is required for the reduction of Cr(VI) to Cr(III) and second at pH values below 3 the pyrrole nitrogen becomes protonated (Zhang, et al., 2006) so that the polypyrrole will carry a positive charge even when the polymer backbone is reduced. This will allow anions in the solution to be adsorbed onto the polymer surface by electrostatic attraction. The current study investigated the efficiency of the polypyrrole-nanofiber-coated membranes for removing Cr(VI) as a function of pH. The polypyrrole-nanofiber-coated membranes were first reduced and then each membrane was immersed in a solution of $Na_2Cr_2O_7$ held at pH 1.0, pH 3.5 and pH 6.0, respectively. The initial absorbance spectrum of the solution at pH 6.0 was different from that held at pH 1.0 and 3.5 as at this pH chromium is predominately in the CrO_4^{2-} form. The chemistry of chromium is very pH dependent and the $Cr_2O_7^{2-}$ and CrO_4^{2-} ions are in a pH dependent equilibrium as shown in Eq. 2.1, while at pH 1.0 the chromium exists as either the $Cr_2O_7^{2-}$ or $HCrO_4^-$.

$$Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons 2CrO_4^{2-}{}_{(aq)} + 2H^+{}_{(a)} \qquad \text{(eq 1)}$$

Equation 2.1

The absorbance spectrum of each of the Cr(VI) solutions was recorded after 1 and 8 hours in contact with the polypyrrole-nanofiber-coated membranes. There was only a drop in the amount of Cr(VI) for the solution, which was held at pH 1.0. Thus, the removal of Cr(VI) only occurs effectively at a pH value at which the electrochemically reduced polypyrrole nanofibers carry a positive charge through protonation. This indicates that electrostatic attraction between the chromate anion and the polymer coating is a step in the removal of Cr(VI) from solution. This finding is in contrast to that of other researchers who have observed that polypyrrole will remove Cr(VI) from solution at values of about pH 3.5 (Ansari & Fahim, 2007). However, the behaviour of the polymer is dependent on its morphology and the substrate on which it is grown. Significantly, our finding is consistent with the oxidative power of Cr(VI), which increases as the pH is lowered, and suggests that for the nanofibers a further step for the loss of Cr(VI) from solution is its reduction to Cr(III).

2.5.3.3 *Evidence of Oxidation of the Polypyrrole and Polypyrrole Nanofibers by Measuring their Open Circuit Potential*

An investigation was carried out in order to test if a chemical reaction was taking place between the polymer film and the chromate and whether the Cr(VI) was being reduced to the less toxic Cr(III). The polypyrrole nanofibers were grown on a gold electrode and their open circuit potential (OCP) was measured under a number of conditions. An increase in the OCP of the film is an indicator that the polymer is being oxidised. Initially, a control experiment was carried out to investigate what occurred at the gold substrate when it was immersed in the sulfuric acid solution and the sulfuric acid solution containing Cr(VI). There was no reaction between the gold and the H_2SO_4 and the OCP remains constant over the 1800 s of the experiment, whereas a small increase in the OCP (0.08 V vs SCE) was recorded when the same experiment was repeated in a solution containing Cr(VI). This indicates that Cr(VI) does have some ability to oxidise the gold surface.

Open circuit potential experiments were first carried out on bulk polypyrrole films with chloride dopant which were grown on the electrodes from solutions of pyrrole. The polymer film was either immersed in H_2SO_4 and reduced for 30 mins at -0.80 V vs SCE, or was simply immersed in deionised water with no applied potential for the same period of time. After this time the two polymers were transferred to a new solution of H_2SO_4 and the OCP of each polymer was measured. The resulting OCP traces showed that the pre-reduced polymer undergoes oxidation in the H_2SO_4 solution, whereas the non-reduced polymer film underwent a slight reduction. When the experiment was repeated – except that the second solution now contained the $Na_2Cr_2O_7$ – both polymers showed an increase in their OCP values. This indicates clearly that both polymers undergo oxidation in the Cr(VI) solution. A further experiment was carried out to investigate the role of oxygen dissolved in the solution as an oxidising agent. Two polypyrrole-chloride films were grown on gold electrodes, the polymers were both reduced at -0.8 V vs SCE for 30 mins in H_2SO_4 and one was then placed in a solution of H_2SO_4 which had been purged with nitrogen gas and one in an identical solution which had not been purged. The OCP results showed that oxygen dissolved in the acid did oxidise the polymer but not to the same extent as the Cr(VI).

Polypyrrole nanofibers were reduced in H_2SO_4 solution for 30 mins. The nanofibers were then immersed in a fresh solution of H_2SO_4 containing $Na_2Cr_2O_7$ and the OCP was recorded and is shown in Fig. 2.17(a). Similar behaviour was observed compared to the bulk polymer in that the OCP of the nanofibers increased rapidly over the first 30 mins and then reached a 'plateau' value. The amount of Cr(VI) removed from the same solution was also monitored (Fig. 2.17(a)). As can be observed from the figure the decrease in the amount of Cr(VI) occurred quite rapidly at the early stages of immersion – there was a 45% loss in $Na_2Cr_2O_7$ after 125 minutes of immersion. However, after this time the amount of $Na_2Cr_2O_7$ continued to be removed from the solution at a slower rate, even though the OCP of the nanofibers appeared to have reached a 'plateau' value. Therefore, the 'plateau' region of the OCP of the nanofibers was expanded using a small scale and a plot of OCP against time for this region is given in Fig. 2.17(b). It can be observed that there was actually a gradual increase in the OCP for the nanofibers over this region. This indicates that the polymer was slowly being oxidised by the solution over this time period, and it is likely that this reaction is occurring between the polymer and the remaining $Na_2Cr_2O_7$.

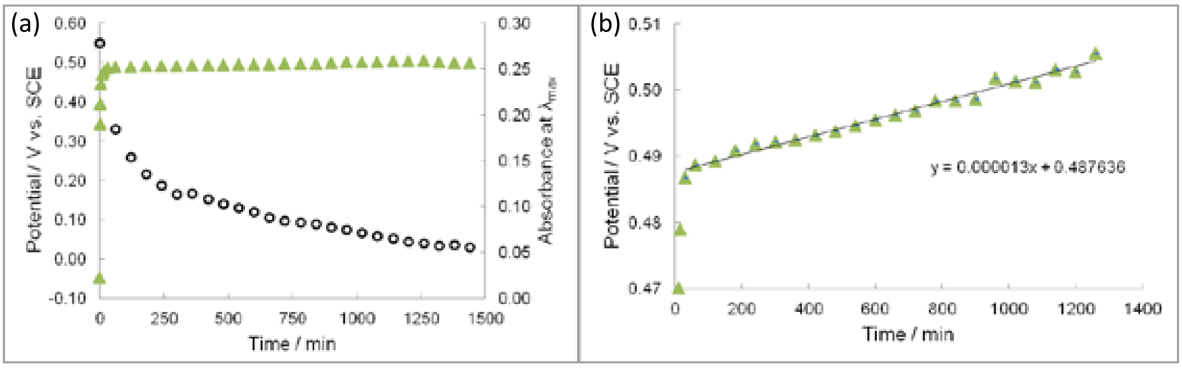


Figure 2.17. (a) Open circuit potential (OCP) (▲) of polypyrrole nanofiber and associated drop in absorbance band of $Na_2Cr_2O_7$ (o) for polypyrrole nanofibers immersed in solution of H_2SO_4 and $Na_2Cr_2O_7$. (—) nanofibers were reduced at -0.80 V vs SCE for 30 mins in H_2SO_4 before immersion. (b) Expansion of OCP.

The data obtained from the OCP studies suggests that both the bulk polypyrrole-chloride and the polypyrrole nanofibers were being oxidised in the solution containing $Na_2Cr_2O_7$. The rate of oxidation in the initial stages of the reaction was enhanced if the polymer was reduced before immersion. However, after a certain time period (approximately 30-mins immersion) all the polymers underwent a slow oxidation in the solution and, as highlighted for the nanofibers (Fig. 2.17), this corresponded to a slow decrease in the amount of $Na_2Cr_2O_7$ present in the solution. As the polymers were being continually oxidised over the course of the experiment, this would indicate that the Cr(VI) was being reduced to Cr(III). Therefore, at the pH at which the experiment was carried out the polypyrrole nanofibers were not simply acting as an adsorbent for Cr(VI) as has been proposed for related polypyrrole polymers.

2.5.3.4 The Location of the Cr(III)

The data obtained from the OCP studies carried out in Section 2.5.3.3 would indicate that the polypyrrole nanofibers were being oxidised over the 24 hours of the experiment and conversely the Cr(VI) must have been reduced to Cr(III). As depicted in Fig. 2.14 the Cr(III) could remain adsorbed on the nanofiber film or could be expelled back into solution. An EDX spectrum was recorded on the polypyrrole nanofiber-coated membrane after 24 hours of immersion in the acidified Cr(VI) solution and it was observed that a small peak for Cr was visible on the membrane. However, EDX is not a quantitative technique, so no information could be obtained on the amount of chromium adsorbed or the nature of its oxidation state.

If the Cr(VI) was reduced to Cr(III) this species could be present in solution as $Cr_2(SO_4)_3$. $Cr_2(SO_4)_3$ is a very pale colour and at the concentrations used would not have been detected using UV/vis spectroscopy. Therefore, a colorimetric test was developed from known procedures to investigate if the Cr(III) was present in the solution after the Cr(VI) solution had been in contact with the polypyrrole nanofibers for 24 hours. When the test was carried out on the solution that remained after the polypyrrole nanofibers had been immersed in an original solution containing H_2SO_4 and $Na_2Cr_2O_7$, it was determined that 85% of the chromium remained in the solution. This is in contrast to other studies, which have shown that the chromium is adsorbed onto the polymer. However, generally these studies have been carried out at a higher pH than the value of 1.0 used here (Ansari and Fahim, 2007). The findings described here are consistent with the findings of Guo et al. (2011) on polyaniline nanofibers, which showed that below a pH value of 2 polyaniline does not adsorb the chromium and it is expelled back into solution. We would propose that, as it is known that below a pH value of 3 polypyrrole is protonated, that for the polypyrrole nanofibers the positively charged Cr(III) ion once formed is repelled from the nanofiber surface. Therefore, while the polymer does remediate Cr(VI) from acidified water, ideally the chromium should remain adsorbed on the polymer so that both Cr(VI) and Cr(III) are removed from the water.

Table 2.7. Data on the properties and content of the bottled water sample.

Sample	pH	Bicarbonate (mg L^{-1})	Sulfate (mg L^{-1})	Nitrate (mg L^{-1})	Calcium (mg L^{-1})	Chloride (mg L^{-1})	Potassium (mg L^{-1})	Sodium (mg L^{-1})
Bottled water	7.3	400	15	9	114	28	3	15

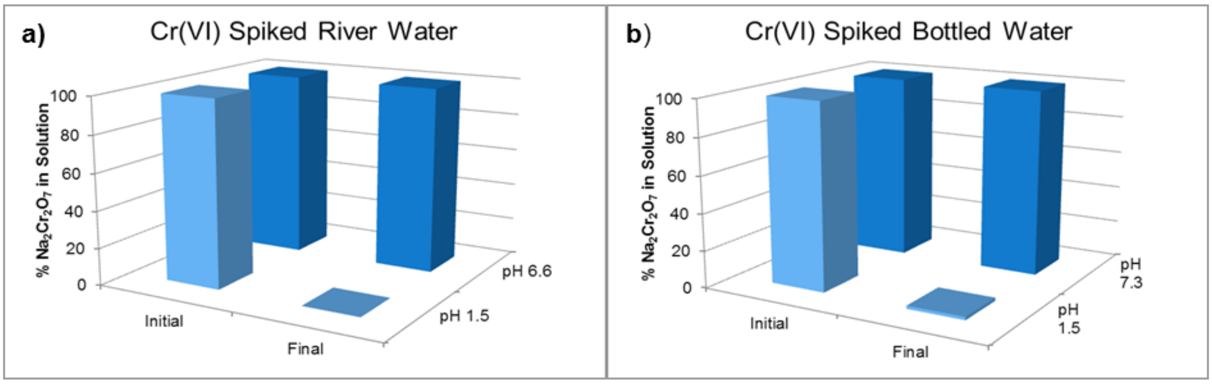


Figure 2.18. % $Na_2Cr_2O_7$ remaining in solution after 24 hours in contact with polypyrrole nanofiber-coated membranes at ambient pH and at pH 1.5 (a) river water, (b) bottled water.

2.5.4 Studies on Real Water Samples

A study was carried out to investigate if the Cr(VI) could be removed from real water samples spiked with $Na_2Cr_2O_7$. The water samples chosen were river water (properties given in Table 2.6 above) and bottled water (properties given in Table 2.7). The polypyrrole-nanofiber-coated membranes were immersed in Cr(VI) spiked samples held at their ambient pH or acidified with sufficient amounts of H_2SO_4 so that the solutions had a pH value of 1.5. The UV/vis spectrum of the solution was recorded at the start of the experiment and after the membranes had been immersed in the solutions for 24 hours. The results of the study are given in Fig. 2.18 and it can be seen that, as had occurred in the experiments carried out using deionised water, efficient removal of the Cr(VI) from the solution only occurred when the solution was at the lower pH value.

A study was carried out to investigate the effect the initial concentration of Cr(VI) had on the ability of the polypyrrole-coated nanofiber membranes to remove the Cr(VI) from acidified river water. The nanofiber-coated membranes were formed as outlined in Section 2.1.3.2. Samples of river water (10 mL) (properties given in Table 2.6) were acidified using H_2SO_4 and each sample contained a different concentration of $Na_2Cr_2O_7$. The membranes were each reduced for 30 mins at -0.80 V vs SCE in KCl and then placed in the prepared river water sample. The UV/vis spectrum of each solution was recorded after 24 hours of immersion and in each case there was no band observed to indicate the presence of Cr(VI) remaining in solution.

Clearly, the membranes are effective for removing Cr(VI) from real-water samples that contain added acid. Further studies would be required to enable the removal of Cr(VI) from real water samples without the need for the added acid.

2.6 Development of Anti-fouling Coatings for Water-filtration Membranes

2.6.1 Introduction

Most of the materials used in water-filtration membranes including polyamides (e.g. nylon), poly(sulfone), and poly(ethylene), will exhibit protein adsorption (Sarry & Sucker, 1993), (Beeskow, et al., 1997), (Briefs & Kula, 1992). The fouling of the membrane upon filtration of solutions containing proteins and other organic molecules negatively affects the performance of the membrane. One effective way to counteract this problem is to coat the membrane with an anti-fouling

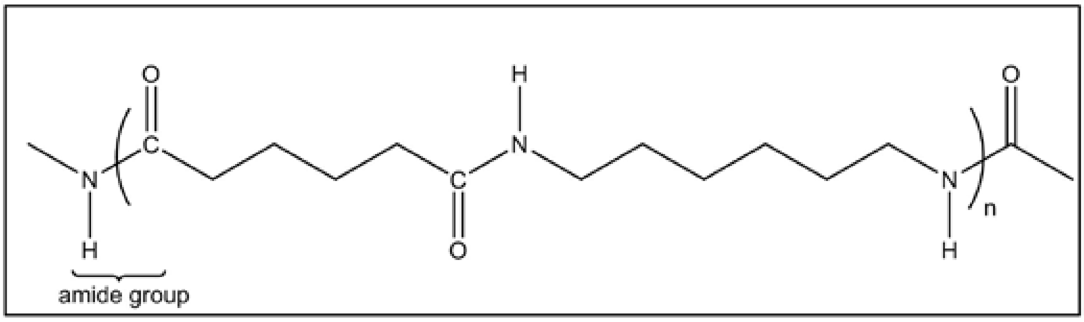


Figure 2.19. Polyamide structure, nylon 66.

coating. Many anti-fouling coatings are hydrophilic and are uncharged or contain both negative and positive charges, and contain H-bond acceptors (Ostuni, et al., 2001). A wide range of polymer materials have been considered for these coatings, including oligosaccharides (Ruegsegger & Marchant, 2001), polyacrylates (Tanaka, et al., 2002), poly(ethylene glycol) (Zhang, et al., 2001), polymer analogues of phospholipids (Lewis, et al., 2002), and mixed layers of polyelectrolytes (Wong, et al., 2012).

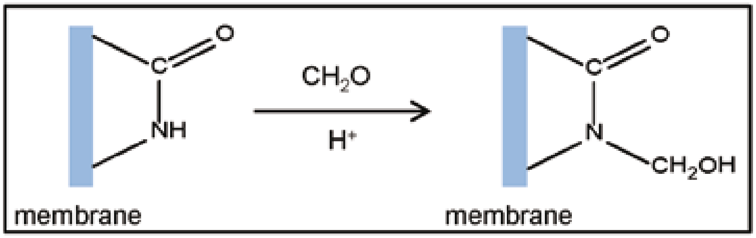
Membrane surfaces have been modified with anti-fouling coatings using two basic strategies. The first is a 'graft-to' approach in which a polymer is formed in solution and is then attached to the membrane surface. The second is a 'graft-from' approach in which the polymer is grown directly from the membrane surface. An essential requirement of both approaches is that the coating is strongly adherent to the membrane surface. The two main methods of anchoring the polymer coatings to the membranes are termed 'chemisorption' (attachment via a covalent bond) or 'physisorption' (non-covalent forces of attraction). Both approaches were applied in the current research. The coatings were first tested on polyamide microfiltration membranes and the most promising materials were then tested on nanofiltration membranes. 'Nylon' refers to a general class of polymeric polyamide materials made up of repeating units separated by amide groups. The structure of a common nylon (nylon 66) highlighting the amide functional groups is shown in Fig. 2.19.

2.6.2 Chemical Activation of Polyamides

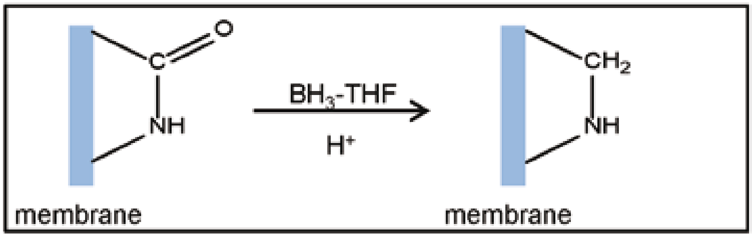
In order to chemisorb a polymer to a membrane surface, there must be a functional group present on the surface to which a covalent bond can be formed. In order to achieve this, the amide group (N-H functionality in Fig. 2.19) on the polyamide membranes was first activated using two approaches (described in Sections 2.6.2.1 and 2.6.2.2 below). Alternatively, the membrane was coated with a layer of a more reactive polymer polydopamine. The polyamide membranes were either soaked in acetone for 12 hours, or washed in alcohol before use to remove any surface coating, and then dried under atmospheric conditions until they achieved a constant weight.

2.6.2.1 Activation of Polyamide Membranes using Formaldehyde

Polyamide membranes were activated by formaldehyde (CH_2O) using an adaptation of a procedure described by Xu et al. (2007). The reaction to add reactive N-methylol groups to the membrane is given in Scheme 2.2. The membranes were extensively washed with water and used immediately or stored under nitrogen until used.



Scheme 2.2. Activation of the polyamide membrane using formaldehyde



Scheme 2.3. Activation of the polyamide membrane using borane-THF.

2.6.2.2 Activation of the Amide Group using Borane-THF

The membranes were activated using a solution of borane-THF (BH_3-THF) held at 0°C during the addition (Jia, et al., 2006) (Scheme 2.3). They were washed extensively with methanol and then water and dried under vacuum for 24 hours. This reaction converts the amide groups on the membrane surface to more reactive amine groups. The membranes were stored under nitrogen until used.

2.6.2.3 Coating the Membrane with Polydopamine

Polydopamine (two postulated structures are given in Fig. 2.20) has been shown to have excellent adhesion properties to a wide range of surfaces. Moreover, a number of the hydroxyl groups have been shown to be available for the covalent functionalisation of the polymer. Polyamide membranes were coated using a solution of dopamine in Tris-HCl buffer under atmospheric conditions at room temperature for 2 hours (Fig. 2.20) (Jiang, et al., 2011). The membranes were washed extensively with water and dried under vacuum. The membranes were stored under nitrogen in the dark until used, to ensure no further reaction of the dopamine.

2.6.3 Coating the Membranes using an Atom Transfer Radical Polymerisation 'Grafting-From' Approach

Atom transfer radical polymerisation (ATRP) generally requires a chemical mixture containing an initiator, a metal catalyst (a copper catalyst was employed in the current research) and ligand, which stabilises the metal catalyst and the monomer which is often a styrene or an acrylate. The polymerisation reaction is carried out by highly reactive radical species, and the source of the radicals is the initiator, which generally contains a bromine atom. In order to control the reaction so that the radicals only react with the monomer at the defined position to form straight chains of polymer, the catalytic mixture is set up so that only a small concentration of radicals are present in solution at any given time. The general mechanism of surface-initiated ATRP is given in Fig. 2.21. As Fig. 2.21 shows, in the reaction the copper is shuttled between Cu(I) which is the active catalyst and Cu(II) which is inactive. In the current research an adaptation of ATRP – Activators ReGenerated by Electron Transfer (ARGET)-ATRP – was used. This involves adding a reducing agent (usually ascorbic

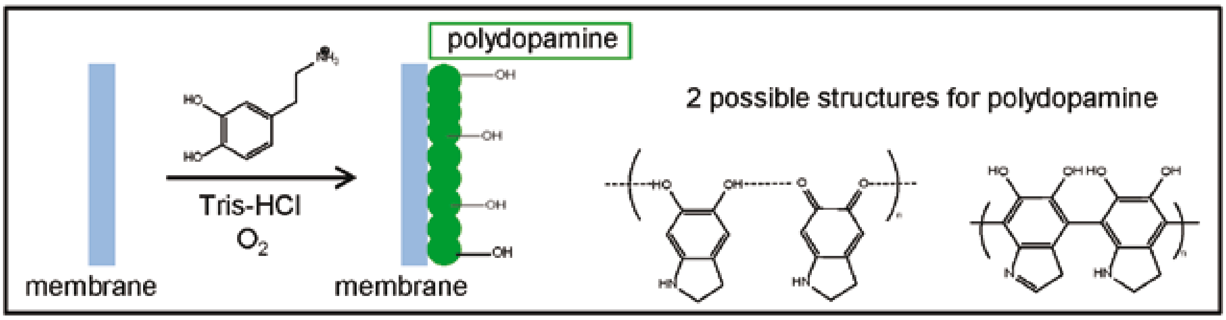


Figure 2.20. Schematic of reaction to coat polyamide membrane with polydopamine.

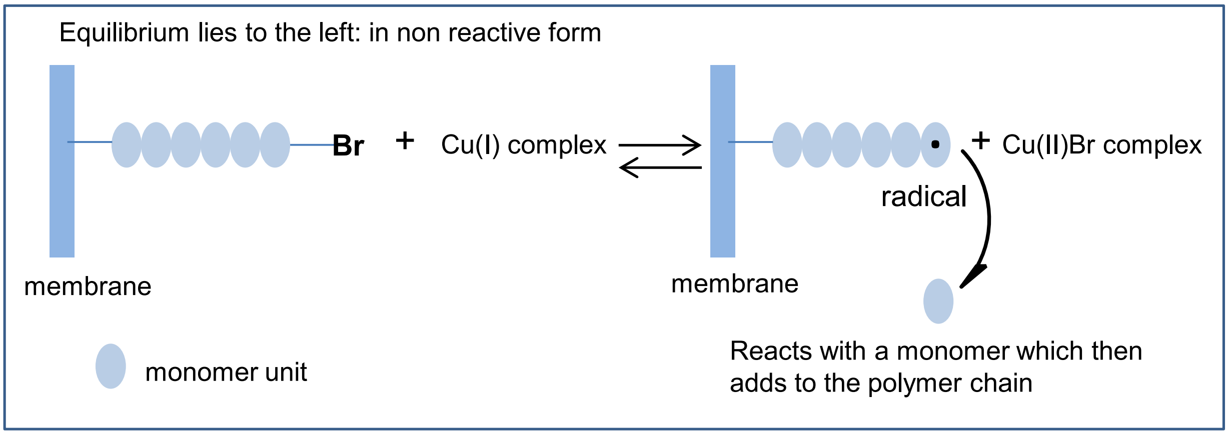


Figure 2.21. Mechanism of surface-initiated atom transfer radical polymerisation (ATRP).

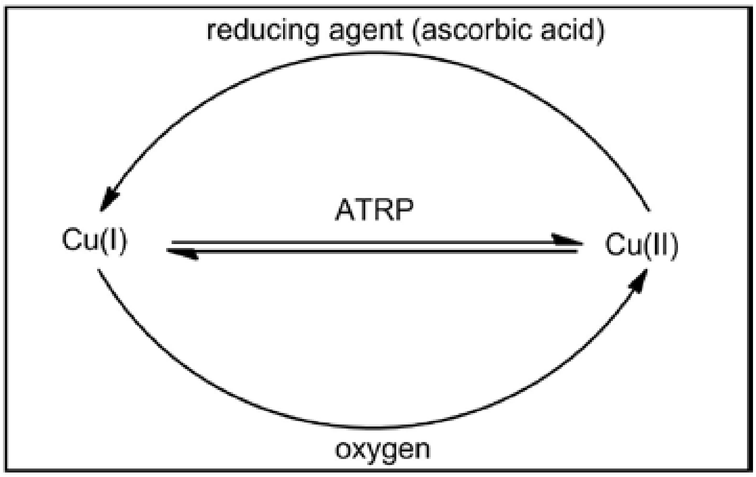


Figure 2.22. Schematic diagram showing the role of the reducing agent in ARGET-ATRP.

acid) to the polymerisation mixture (Bai, et al., 2012). The reducing agent's role is to reduce the Cu(II) back to the active Cu(I) form; using this methodology means that less rigorous air-free conditions and less copper catalysts are required for the polymerisation. Figure 2.22 gives a schematic showing the mechanism of ARGET-ATRP.

2.6.3.1 Attachment of the Initiator

The initiator used in the present study was 2-bromoisobutyryl bromide (BIBB) (Fig. 2.23). The reaction between the activated membranes and the BIBB takes place at the functionality highlighted in green in the chemical structure in Fig. 2.23 with the subsequent loss of HBr. The BIBB was attached to the membrane surfaces, which were activated by each of the methodologies outlined in Section 2.6.2. Using air-free conditions the membranes were reacted with a solution of BIBB with added base at 0°C. The mixture was stirred for 5 mins at 0°C and then, depending on the experiment, for time periods of 15 mins to 2 hours at room temperature. The membranes were washed extensively using acetone and then a 1:1 water:methanol mixture and dried under vacuum. Figure 2.24 shows a representation of the structure of the BIBB functionalised membranes. In addition, a variation of the above conditions was used to functionalise the nanofiltration membranes. These membranes were then washed using acetonitrile, followed by methanol and then extensively washed with deionised water and then dried. The attachment of the BIBB group to the membrane surface was monitored using EDX analyses. Figure 2.23 shows typical EDX

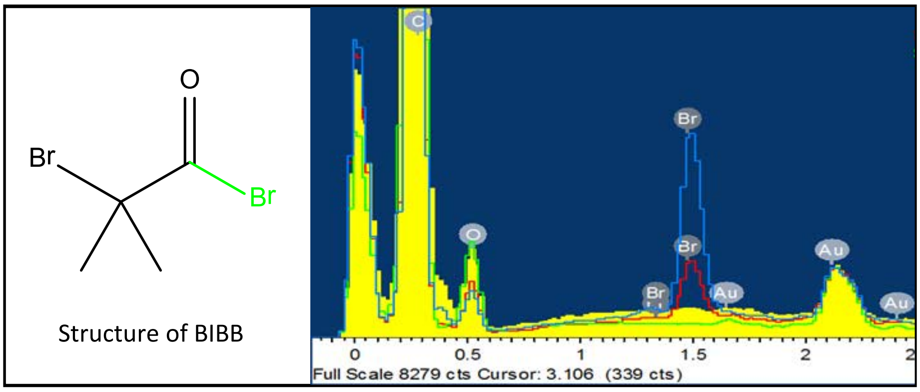


Figure 2.23. Energy dispersive X-ray (EDX) spectra of functionalised polyamide membranes (—) pristine membrane, (—) membrane reacted with 36.5% formaldehyde and then BIBB, (—) membrane reacted with 60% formaldehyde and then BIBB.

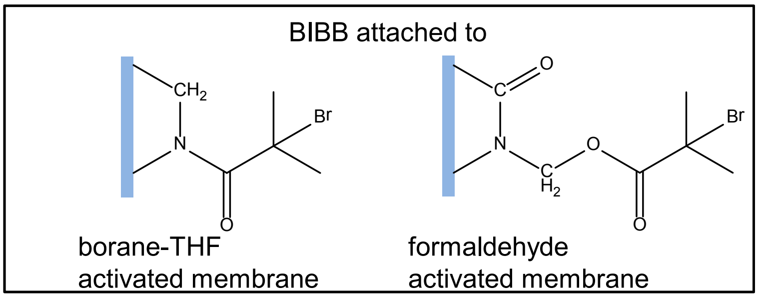


Figure 2.24. Representation of the BIBB initiator attached to the activated membranes.

spectra for the membrane before and after the reaction has taken place. By analysing the membranes using EDX at different stages of the washing procedure it was possible to ascertain that a significant proportion of the BIBB was simply physisorbed onto the membrane surface and not attached to the membrane through a chemical bond. This became apparent as the signal for Br was shown to decrease in intensity as a function of the extent of washing.

2.6.3.2 Polymerisation at the BIBB Functionalised Membranes

Monomers that were employed for the ATRP reaction were sodium styrene sulfonate, 2-hydroxyethyl methacrylate (HEMA), and poly(ethylene glycol) methacrylate (PEGMA). Figure 2.25 gives the chemical structure of these monomers and their respective polymers.

In order to control the rate of the polymerisation reaction for each monomer the reaction conditions were optimised. These studies involved altering the temperature of the reaction, the amount of monomer, copper catalyst, stabilising ligand, reducing agent and the solvent used. Using the optimised conditions the reaction was allowed to proceed for time periods of 15 mins to 2 hours. Experiments were also carried out to make co-polymers of PSS and P(HEMA) on the membrane surface. This was done by first carrying out the polymerisation on the BIBB-functionalised membrane using the polymerisation mixture for PSS and then removing the membrane from that solution, extensively washing it, and placing it in a solution containing the reaction mixture for P(HEMA). To ensure a more even coverage of the polymer over the membrane surfaces later experiments carried out the reaction on one membrane which was suspended in a gently stirred reaction mixture.

As would be expected from their known chemical reactivity the acrylate monomers were more reactive than the styrene monomer and it was found that the

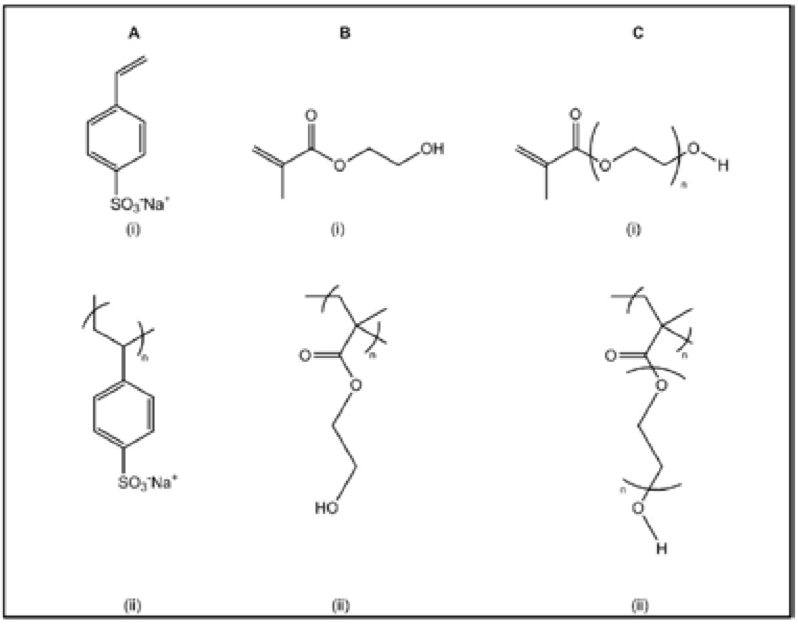


Figure 2.25. Chemical structure of (A) (i) sodium styrene sulfonate and (ii) polystyrene sulfonate (PSS), (B) (i) 2-hydroxyethyl methacrylate (HEMA) and (ii) P(HEMA) and (C) (i) poly(ethylene glycol) methacrylate (PEGMA) and (ii) P(PEGMA).

reaction proceeded more rapidly in the polar (methanol : water) solvent. For all cases, but especially for P(PEGMA), there were problems with macroscopic gelation at the surface of the membrane. This indicates that uncontrolled polymerisation is taking place. The P(PEGMA) was grown on both the micro and the nanofiltration membranes, but there were significant problems with getting the polymer to grow reproducibly. Studies have shown that the addition of a 'sacrificial' initiator (i.e. BIBB simply added to the polymerisation solvent) can lower the amount of macroscopic gelation (Hansson, et al., 2009). A study was carried out using the sodium styrene sulfonate. The reaction conditions were similar to those outlined above and the reaction was allowed to proceed for 80 mins. Different amounts of BIBB in mL were added to the 20 mL of reaction mixture. The 10 membranes in each reaction flask were extensively washed and dried to constant weight. The average mass of each sample of 10 membranes was then determined and plotted against the amount of BIBB which was added to the mixture. The addition of a 'sacrificial' initiator did slow down the rate of polymerisation at the membrane surface and this methodology could be applied to enable the growth of P(PEGMA) layers at the membrane surface in a more reproducible manner.

2.6.3.3 Characterisation of the Polymer Functionalised Membranes

That polymerisation of the three monomers had succeeded at the membrane surface was determined using Fourier transformation infra-red spectroscopy (FTIR), EDX and SEM. The most prominent bands in the pristine membranes appear at 1634 and 1538 cm^{-1} which are assigned as the amide(I) and amide(II) bands. Bands are observed at 1180 and 1038 cm^{-1} upon the growth of PSS on the membrane; these are assigned to the asymmetric and symmetric bands of the SO_3^- group. When P(PEGMA) is grown on the membrane surface, characteristic bands are observed at 1720 and 1113 cm^{-1}. These bands are assigned as arising from the C=O stretch of the ester groups and the C-O stretch of the large number of ether groups on the poly(ethylene glycol) chains respectively. The spectrum recorded on the membrane after it is functionalised with P(HEMA) also shows the band at 1720 cm^{-1}, indicating the attachment of the ester functional group to the membrane. PSS is the only one of the polymers studied that contained different elements from those of the base membrane. Therefore, EDX analysis was only carried out on the membranes functionalised with PSS. It was clear that the functionalised membrane contains both sulfur and sodium atoms, which identify the grafting of PSS to the membrane.

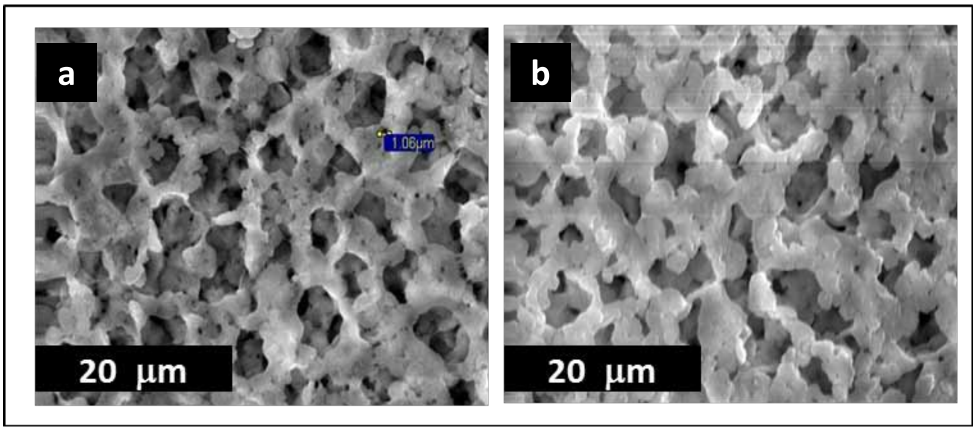


Figure 2.26. Scanning electron microscopy (SEM) micrograph of (a) pristine polyamide membrane and (b) membrane functionalised with polystyrene sulfonate (PSS).

The change in the surface morphology of the membranes was determined using SEM microscopy. In general, the SEM micrographs made clear that a layer of polymer was formed across the membrane surface. Figure 2.26 gives a SEM micrograph of a pristine membrane and one coated with a layer of PSS.

2.6.4 Anti-fouling Properties of the Membranes Coated with Polymers formed using ATRP

The fouling properties of the membranes were tested using a dead-end stirred Millipore-stirred ultra-filtration cell. The rate of flow of water was measured by determining the mass of deionised water/solution to pass through the membrane as a function of time. The anti-fouling properties of the membrane were studied using the model protein bovine serum albumin (BSA) in PBS buffer held at a pH value of 7.4; both types of membrane were significantly fouled by the model protein. This indicates that the PSS coating was not providing any added protection against protein fouling. However, it was shown that the coating did repel anionic dye compounds. When a fixed mass of a solution containing methyl orange was passed through the pristine or PSS-coated membranes it was visually apparent that the methyl orange did not adhere to the functionalised membrane as shown in the photograph recorded of the membranes after the experiment was carried out (Fig. 2.27). This indicates that the coating may have promise for protection against fouling by negatively charged organic matter, such as humic acid. In addition, it was shown that the sodium ions in the membrane could be exchanged for silver ions (as shown using EDX analysis), thereby giving the possibility of producing a membrane with anti-microbial properties.

Figure 2.27. Photograph of membranes after solution containing methyl orange has passed through them. Membrane on right is unmodified polyamide; left membrane is coated with PSS.

As shown in the results of the study using the model protein BSA, the P(PEGMA)-coated membrane showed good protein anti-fouling properties compared to the unfunctionalised polyamide membrane. However, there were significant difficulties in forming the P(PEGMA) coating reproducibly on the membranes, and it was observed that a random amount of polymer could be washed from the coating. This indicates that as well as the covalently attached polymer a certain amount of the polymer was simply physisorbed on the membrane and this amount varied from batch to batch. This lack of reproducibility would be a challenge in any future development of these membranes for real applications.

2.6.5 Coating the Membranes using Dopamine-based Compounds

During the course of the research project a number of bio-inspired coatings were tested for their protein anti-fouling properties: these included the naturally occurring carbohydrate polymer chitosan, functionalising the membranes with phosphorylcholine zwitterionic groups, and polydopamines. Preliminary studies showed that the most successful coatings were found to be based on polydopamine so the current research concentrated on these materials. As noted in Section 2.6.2.3, polydopamine was used as a means of activating the polyamide membrane for attachment of the BIBB initiator, due to its ease of formation and its good adhesion properties (Yang & Zhao, 2011). However, polydopamine has also shown promise as an anti-fouling coating (McCloskey, et al., 2012). A study was therefore carried out to investigate if coatings of polydopamine and a number of its derivatives could improve the anti-fouling properties of the membranes.

2.6.5.1 Synthesis of Functionalised Dopamines

Derivatives of dopamine were synthesised according to literature procedures in order to attach polar groups (succinyl dopamine) (Bonina, et al., 2003) or zwitterion species (zwitterionic dopamine sulfonate) (Wei, et al., 2012) to the amine group or the dopamine. Figure 2.28 gives the structures of the two compounds. At each step of the reaction the products were identified using nuclear magnetic resonance (NMR) spectroscopy and FTIR where appropriate.

1 Succinyl dopamine

In order to ensure that the functional group was added only at the amine group a series of protection steps were first carried out on the dopamine (Xu, et al., 2004) to form 2-(3,4-bis-Benzyloxy-phenyl)-ethylamine, in 80% yield. 2-(3,4-bis-Benzyloxy-phenyl)-ethylamine was reacted with succinic anhydride to form succinyl dopamine. Pure succinyl dopamine was obtained in 82% yield.

2 Zwitterionic dopamine sulfonate

Zwitterionic dopamine sulfonate was formed in a multi-step synthesis. The reaction is selective for the amine group so no protection of the hydroxyls is required. After extensive purification the product was formed as a white solid (50% yield).

2.6.5.2 Coating of the Membranes using the Dopamines

In each case the dopamine or functionalised dopamine was dissolved in a solution of Tris-HCl buffer and stirred with 10 membranes under atmospheric conditions for different periods of time. That a reaction was taking place was indicated by the change in the colour of the solution from clear to yellow to dark brown. When the membranes were removed from the solution they were clearly covered in a coating as indicated by their change in colour. Figure 2.29 is a photograph of a set of membranes that have been in contact with the dopamine-containing solutions. Simple visual inspection makes clear that the polydopamine formed a coating more rapidly than its functionalised analogues. A dark

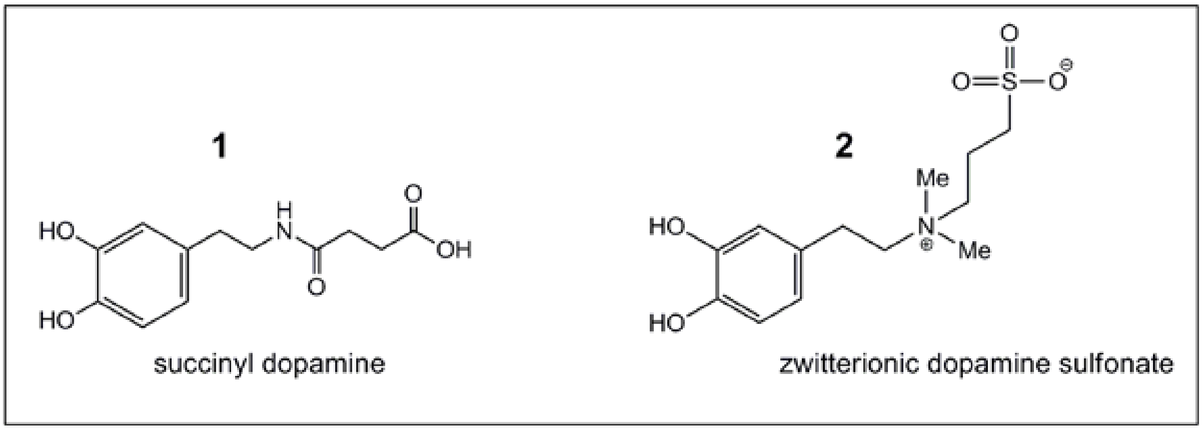


Figure 2.28. Structures of functionalised dopamines.

layer of polymer is formed after the membrane has been immersed in the dopamine-containing solution for 2 hours, while, for the zwitterionic dopamine sulfonate, only a pale beige layer is visible after 72-hours immersion. SEM analysis confirmed that the difference in colour of the two coating did reflect a difference in the thickness of the coatings. SEM micrographs of the three membranes shown in Fig. 2.29 are given in Fig. 2.30 and it can be seen clearly that a thicker polymer coating is present on the membrane coated with polydopamine. The polydopamines did not form as thick a coating on the nanofiltration membranes as they did on the microfiltration ones. However, it was clear again for the polymers studied that the polydopamine formed the most adherent coating. Inspection of the nanofiltration membranes directly on the SEM showed that the pore size had decreased slightly, but due to the resolution of the images, no real difference in the nanofiltration membrane morphology upon coating can be observed between Figure 2.30 (d) and (e).

The coating of the zwitterionic dopamine sulfonate was also characterised using EDX analysis as it contained an element not present in the base polymer. An EDX of a zwitterionic dopamine sulfonate coated membrane showed a strong signal for sulfur present in the coating. Water-contact angle measurements were carried out on the polydopamine and zwitterionic-dopamine sulfonate-coated membranes, indicating that the coatings are hydrophilic.

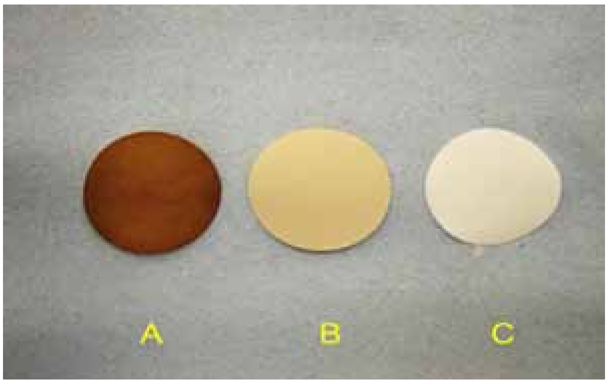


Figure 2.29. Photograph of (A) membrane coated in polydopamine (2 h in Tris-HCl buffer), (B) membrane coated in zwitterionic dopamine sulfonate (72 h in Tris-HCl Buffer), (C) unmodified membrane.

2.6.5.3 *Anti-fouling Properties of the Membranes Coated with Polydopamine*

A study was carried out to determine the optimum thickness of polydopamine needed to enable it to act as protein anti-fouling coating. Membranes were coated for a different period of time with polydopamine. The study was carried out with the model protein BSA in

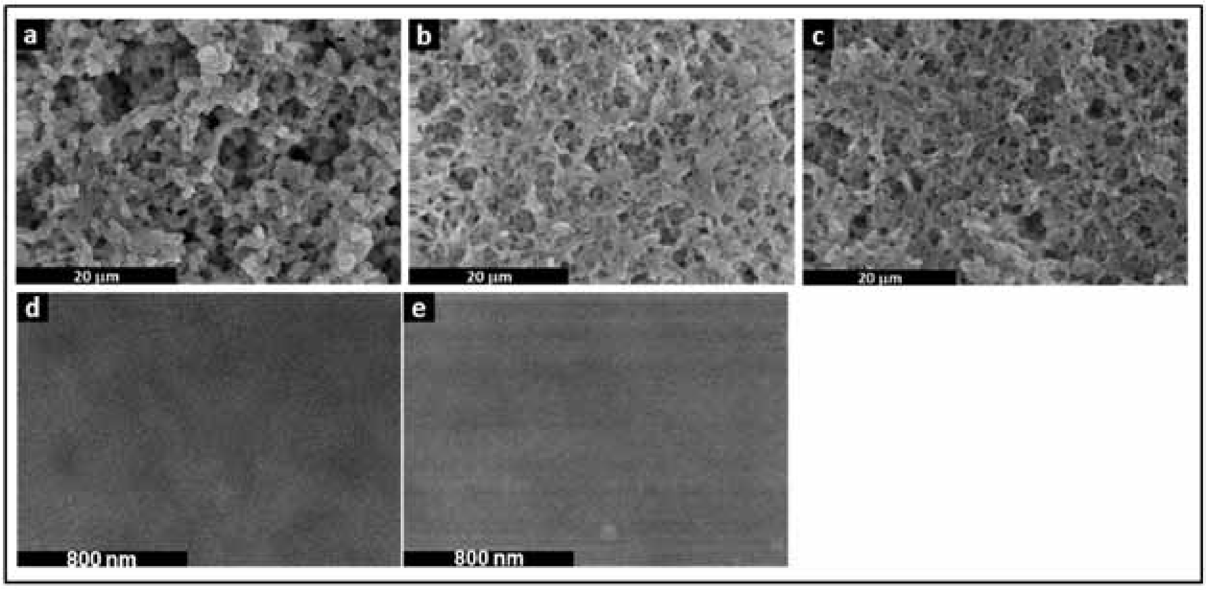


Figure 2.30. Scanning electron microscopy (SEM) micrograph of (a) unmodified membrane, (b) membrane coated in polydopamine (2 hours in Tris-HCl buffer), (c) membrane coated in zwitterionic dopamine sulfonate (72 hours in Tris-HCl buffer), (d) unmodified nanofiltration membrane, (e) nanofiltration membrane coated in polydopamine (2 hours in Tris-HCl buffer).

PBS buffer. The best performing membrane had been coated for 2 hours. The thin coatings showed poorer performance than the unmodified membrane, as did the very thick coating grown for 10 hours. A further study was carried out on the zwitterionic dopamine sulfonate-coated membrane which had been immersed in the polymerisation mixture for 72 hours. Surprisingly, the zwitterionic dopamine sulfonate coating resulted only in a small improvement of the protein anti-fouling properties of the polyamide membrane. However, as discussed in Section 2.6.5.2, this may reflect the thin nature of the coating.

3 Conclusions and Recommendations

This project involved a laboratory-scale study into the feasibility of producing novel methodologies for improving the properties of commercial water-filtration membranes with respect to the removal of metal ions such as copper and chromium from water, forming ion-selective smart membranes and the reduction of protein fouling.

A range of coated polyamide membranes using 10 different polymeric materials was produced. This involved the development of a number of new synthetic strategies for membrane modification, including the growth of conducting polymer nanofibers and zwitterionic dopamine directly on the membrane. The coated membranes were shown to remediate chromium(VI) from water under acidic conditions and copper(II) under neutral conditions. Currently, chromium(VI) in water is generally converted to the less toxic Cr(III) using chemical reductants which cannot be reused, and further treatment of the water is required to remove the resulting contaminants. Copper is commonly removed from water by precipitation using added hydroxide, and again this chemical additive cannot be reused. The combination of a conducting coated membrane and electrochemical reduction is an attractive alternative recyclable technology for the removal of chromium(VI) or copper(II) ions from water.

The possibility of utilising the membranes for the removal of nitrate from water was also investigated. However, they did not demonstrate any ability to selectively allow the transport of dissolved nitrate over chloride ions. The properties of the polymer coatings used in this study are well known to depend on the morphology of the material. However, as indicated in Section 2.2 the ion-exchange behaviour of these materials is complex, and the factors that control anion selectivity are not currently well understood. A number of the coated membranes were tested for their ability to resist fouling using the model protein BSA. Some of the coated membranes showed improved anti-fouling properties compared to unmodified polyamide.

The research conducted in this project has indicated some potential for the development of new environmentally advantageous technologies for water treatment using coated membranes. In the future, there is a need for further research and development to optimise the potential of the membranes before this technology can be transferred to commercial application. This further research must address certain challenges, including the following:

- The stability and recyclability of the membranes must be increased. The polymer membranes are unstable under the chemically acidic conditions in which they operate, so further research would be required to find membranes that can operate under near neutral pH.
- The results obtained in this project showed that the membranes behaved in a similar manner in real and deionised water samples. Further studies of the performance of the membranes with real water samples would be required in order to investigate what other species present in real water may interfere with the membranes.
- Reduction of the costs involved in growing the polymer nanofibers on the membranes. Cheaper conducting substrates such as graphite should be considered.
- Cost analysis of the removal of metal ions using coated membranes compared to current methodologies. The potential reusability of membranes offers a cost benefit over chemical additives that are used currently.

Support for research which underpins innovative technologies that deal with current water challenges is important as there are significant economic opportunities for Ireland in a growing world market in this sector. In addition this research would fall under the priority area ‘Processing Technologies and Novel Materials’ as highlighted by the Forfás Report of the Research Prioritisation Steering Group.

References

Akieh, M. N., Price, W. E., Bobacka, J., Ivaska, A., & Ralph, S. F. (2009). Ion exchange behaviour and charge compensation mechanism of polypyrrole in electrolytes containing mono-, di- and trivalent metal ions. *Synthetic Metals* **159(23–24):** 2590–8.

Akieh, M. N., Ralph, S. F., Bobacka, J., & Ivaska, A. (2010). Transport of metal ions across an electrically switchable cation exchange membrane based on polypyrrole doped with a sulfonated calix[6]arene. *Journal of Membrane Science* **354(1–2):** 162–70.

Ansari, R., & Fahim, N. K. (2007). Application of polypyrrole coated on wood sawdust for removal of Cr(VI) ion from aqueous solutions. *Reactive and Functional Polymers* **67(4):** 367–74.

Antilen, M., Guzman, D., del Valle, M. A., del Rio, R., Letelier, M. V., Lagos, G., Escudey, M., Pizarro, C. (2012). Application of polypyrrole/humic acid composite electrode for copper ion extraction from drinking water. *International Journal of Electrochemical Science* **7(7):** 5939–50.

Ariza, M. J., & Otero, T. F. (2007). Nitrate and chloride transport through a smart membrane. *Journal of Membrane Science* **290(1–2):** 241–9.

Bai, L., Zhang, L., Cheng, Z., & Zhu, X. (2012). Activators generated by electron transfer for atom transfer radical polymerization: recent advances in catalyst and polymer chemistry. *Polymer Chemistry* **3(10):** 2685–97.

Baker, C. K., Qiu, Y. J., & Reynolds, J. R. (1991). Electrochemically-induced charge and mass transport in polypyrrole/poly(styrene sulfonate) molecular composites. *Journal of Physical Chemistry* **95(11):** 4446–52.

Beeskow, T., Kroner, K. H., & Anspach, F. B. (1997). Nylon-based affinity membranes: impacts of surface modification on protein adsorption. *Journal of Colloid and Interface Science* **196(2):** 278–91.

Bhaumik, M., Maity, A., Srinivasu, V. V., & Onyango, M. S. (2011). Enhanced removal of Cr(VI) from aqueous solution using polypyrrole/Fe_3O_4 magnetic nanocomposite. *Journal of Hazardous Materials* **190(1–3):** 381–90.

Bidan, G., & Niel, M.-A. (1997). Electrode modified by sulfonated calixarenes immobilized into a polypyrrole film: a step towards new ion-sensitive layers. *Synthetic Metals* **84(1–3):** 255–6.

Bonina, F., Puglia, C., Rimoli, M. G., Melisi, D., Boatto, G., Nieddu, M., Calignano, A., La Rana, G., & De Caprariis, P. (2003). Glycosyl derivatives of dopamine and L-dopa as anti-Parkinson prodrugs: synthesis, pharmacological activity and in vitro stability studies. *Journal of Drug Targeting* **11(1):** 25–36.

Bredas, J. L., & Street, G. B. (1985). Polarons, bipolarons, and solitons in conducting polymers. *Accounts of Chemical Research* **18(10):** 309–15.

Bredas, J. L., Scott, J. C., Yakushi, K., & Street, G. B. (1984). Polarons and bipolarons in polypyrrole: Evolution of the band structure and optical spectrum upon doping. *Physical Review B: Condensed Matter* **30(2):** 1023–5.

Briefs, K. G., & Kula, M. R. (1992). Fast protein chromatography on analytical and preparative scale using modified microporous membranes. *Chemical Engineering Science* **47(1):** 141–9.

Debiemme-Chouvy, C. (2009). Template-free one-step electrochemical formation of polypyrrole nanowire array. *Electrochemistry Communications* **11(2)**: 298–301.

Ding, J., Misoska, V., Price, W. E., Ralph, S. F., Tsekouras, G., & Wallace, G. G. (2003). Gold recovery using fabrics coated with conducting polymers. *Synthetic Metals* **135–6**: 35–36.

Doyle, R., Breslin, C. B., Power, O., & Rooney, A. D. (2012). Electrochemical Characterisation of Polypyrrole Doped with *p*-Sulfonatocalix[4]arene. *Electroanalysis* **24(2)**: 293–302.

Earley, S. T., Alcock, B. E., Lowry, J. P., & Breslin, C. B. (2009). Remediation of chromium(VI) at polypyrrole-coated titanium. *Journal of Applied Electrochemistry* **39(8)**: 1251–7.

EPA (Environmental Protection Agency) (2007) *Protecting and Improving Ireland's Environment* (Vision 2020). Wexford: Environmental Protection Agency.

EPA (2013) *Strategic Plan 2013–2015*. Wexford: Environmental Protection Agency.

European Commission (2011) Communication From The Commission To The European Parliament, The Council, The European Economic And Social Committee And The Committee Of The Regions: A Resource-efficient Europe. Brussels: European Commission.

Feast, W. J., Tsibouklis, J., Pouwer, K. L., Groenendaal, L., & Meijer, E. W. (1996). Synthesis, processing and material properties of conjugated polymers. *Polymer* **37(22):** 5017–47.

Forfás (2010) Ireland's Nanotechnology Commercialisation Framework 2010–2014. Dublin: Forfás.

Guo, D.-S., Wang, K., & Liu, Y. (2008). Selective binding behaviors of *p*-sulfonatocalixarenes in aqueous solution. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* **62(1–2):** 1–21.

Guo, X., Fei, G. T., Su, H., & Li, D. Z. (2011). High-performance and reproducible polyaniline nanowire/tubes for removal of Cr(VI) in aqueous solution. *Journal of Physical Chemistry C* **115(5)**: 1608–13.

Hansson, S., Oestmark, E., Carlmark, A., & Malmstroem, E. (2009). ARGET ATRP for versatile grafting of cellulose using various monomers. *Applied Materials and Interfaces* **1(11)**: 2651–9.

Jeon, G., Yang, S. Y., Byun, J., & Kim, J. K. (2011). Electrically Actuatable Smart Nanoporous Membrane for Pulsatile Drug Release. *Nano Letters* **11(3):** 1284–8.

Jia, X., Herrera-Alonso, M., & McCarthy, T. J. (2006). Nylon surface modifcation. Part 1. Targeting the amide groups for selective introduction of reactive functionalities. *Polymer* **47(14):** 4916–24.

Jiang, J., Zhu, L., Zhu, B., & Xu, Y. (2011). Surface characteristics of a self-polymerized dopamine coating deposited on hydrophobic polymer films. *Langmuir* **27(23):** 14180–7.

Lei, Y., Qian, X., Shen, J., & An, X. (2012). Integrated reductive/adsorptive detoxification of Cr(VI)-contaminated water by polypyrrole/cellulose fiber composite. *Industrial Engineering Chemical Research* **51(31):** 10408–15.

Lewis, A. L., Tolhurst, L. A., & Stratford, P. W. (2002). Analysis of a phosphorylcholine-based polymer coating on a coronary stent pre- and post- implantation. *Biomaterials* **23(7):** 1697–706.

Li, J., Xie, H., & Li, Y. (2012). Template-free electrochemical synthesis of well-aligned polypyrrole nanofibers for electrochemical supercapacitors. In *Advanced Materials Research* (pp. 512–515), 1776–9.

Li, S., Lu, X., Li, X., Xue, Y., Zhang, C., Lei, J., and Wang, C. (2012). Preparation of bamboo-like PPy nanotubes and their application for removal of Cr(VI) ions in aqueous solution. *Journal of Colloid and Interface Science* **378(1):** 30–5.

Lin, T., Wang, L., Wang, X., & Kaynak, A. (2005). Polymerising pyrrole on polyester textiles and controlling conductivity through coating thickness. *Thin Solid Films* **479(1–2):** 77–82.

Liu, L. L., Wang, X. J., Zhu, Y. S., Hu, C. L., Wu, Y. P., & Holze, R. (2013). Polypyrrole-coated LiV_3O_8-nanocomposites with good electrochemical performance as anode material for aqueous rechargeable lithium batteries. *Journal of Power Sources* **224**: 290–4.

MacDiarmid, A. G. (2001). Nobel lecture: "Synthetic metals": a novel role for organic polymers. *Reviews of Modern Physics* **73(3)**: 701–12.

Mao, L., Chan, H. S., & Wu, J. (2012). Cetyltrimethylammonium bromide intercalated graphene/polypyrrole nanowire composites for high performance supercapacitor electrode. *RSC Advances* **2(28):** 10610–17.

McCloskey, B. D., Park, H. B., Ju, H., Rowe, B. W., Miller, D. J., & Freeman, B. D. (2012). A bioinspired fouling-resistant surface modification for water purification membranes. *Journal of Membrane Science* **413–14**: 82–90.

O'Lehane, M. and O' Leary, B. (2012) *Ireland's Environment 2012: An Assessment*. Wexford: Environmental Protection Agency.

Ostuni, E., Chapman, R. G., Holmlin, R. E., Takayama, S., & Whitesides, G. M. (2001). A survey of structure-property relationships of surface that resist the adsorption of protein. *Langmuir* **17(18):** 5605–20.

Piatnicki, C. M., Azambuja, D. S., Hasse, E. E., Castagno, K. R. L., & Guterres, S. B. (2002). Removal of Cu(II) from dilute solutions at polypyrrole modified electrodes. *Separation Science and Technology* **37(10):** 2459–76.

Pirsa, S., & Alizadeh, N. (2011). Nanoporous conducting polypyrrole gas sensor coupled to a gas chromatograph for determination of aromatic hydrocarbons using dispersive liquid-liquid microextraction method. *IEEE Sensors Journal* **11(12):** 3400–5.

Reece, D. A., Ralph, S. F., & Wallace, G. G. (2005). Metal transport studies on inherently conducting polymer membranes containing cyclodextrin dopants. *Journal of Membrane Science* **249(1–2):** 9–20.

Reynolds, J. & Skotheim, T. A. (Eds), (2007). *Handbook of Conducting Polymers, 2 Volume Set 3rd Edition.* CRC Press.

Roy, K., Mondal, P., Bayen S. P., & Chowdhury, P. (2012). Sonochemical Synthesis of Polypyrrole Salt and Study of its Cr(VI) Sorption-Desorption Properties. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* **49(11):** 931–5.

Ruegsegger, M. A., & Marchant, R. E. (2001). Reduced protein adsorption and platelet adhesion by controlled variation of oligomaltose surfactant polymer coatings. *Journal of Biomedical Materials Research* **56(2):** 159–67.

Sarry, C., & Sucker, H. (1993). Adsorption of proteins on microporous membrane filters: part II. *Pharmaceutical Technology* **17(1):** 60–70.

Shamaeli, E., & Alizadeh, N. (2012). Dye-doped nanostructure polypyrrole film for electrochemically switching solid-phase microextraction of Ni(II) and ICP-OES analysis of waste water. *Analytical Sciences* **28(2):** 153–8.

Skaarup, S., Bay, L., Vidanapathirana, K., Thybo, S., Tofte, P., & West, K. (2003). Simultaneous anion and cation mobility in polypyrrole. *Solid State Ionics* **159(1–2):** 143–7.

Syritski, V., Opik, A., & Forsen, O. (2003). Ion transport investigations of polypyrroles doped with different anions by EQCM and CER techniques. *Electrochimica Acta* **48(10):** 1409–17.

Tanaka, M., Mochizuki, A., Ishii, N., Motomura, T., & Hatakeyama, T. (2002). Study of blood compatibility with poly(2-methoxyethyl acrylate). Relationship between water structure and platelet compatibility in poly(2-methoxyethylacrylate-co-2-hydroxyethylmethacrylate). *Biomacromolecules* **3(1):** 36–41.

Tian, Y., Huang, L., Zhou, X., & Wu, C. (2012). Electroreduction of hexavalent chromium using a polypyrrole-modified electrode under potentiostatic and potentiodynamic conditions. *Journal of Hazardous Materials* **225–26:** 15–20.

Tian, Y., Wu, Y., Huang, L., & Yang, F. (2010). Comparative investigation on electroreduction of Cu(II) using polypyrrole electrode and stainless steel electrode. *Journal of Applied Electrochemistry* **40(2):** 427–33.

Toshima, N., & Hara, S. (1995). Direct synthesis of conducting polymers from simple monomers. *Progress in Polymer Science* **20(1):** 155–83.

Wang, J., Mo, X., Ge, D., Tian, Y., Wang, Z., & Wang, S. (2006). Polypyrrole nanostructures formed by electrochemical method on graphite impregnated with paraffin. *Synthetic Metals* **156(7–8):** 514–18.

Wang, J., Too, C. O., Zhou, D., & Wallace, G. G. (2005). Novel electrode substrates for rechargeable lithium/polypyrrole batteries. *Journal of Power Sources* **140(1):** 162–7.

Wang, Y., Zou, B., Gao, T., Wu, X., Lou, S., & Zhou, S., (2012). Synthesis of orange-like Fe3O4//PPy composite microspheres and their excellent Cr(VI) ion removal properties. *Journal of Materials Chemistry*, **22(18)**: 9034–40.

Wei, F., Cheng, S., Korin, Y., Reed, E. F., Gjertson, D., Ho, C., Gritsch, H. A., Veale, J. (2012). Serum creatinine detection by a conducting-polymer-based electrochemical sensor to identify allograft dysfunction. *Analytical Chemistry* **84(18):** 7933–7.

Wei, H., Insin, N., Lee, J., Han, H.-S., Cordero, J. M., Liu, W. & Bawendi, M. G. (2012). Compact zwitterion-coated iron oxide nanoparticles for biological applications. *Nano Letters* **12(1):** 22–25.

Weidlich, C., Mangold, K. M., & Juettner, K. (2005). EQCM study of the ion exchange behaviour of polypyrrole with different counterions in different electrolytes. *Electrochimica Acta* **50(7–8):** 1547–52.

Wong, S. Y., Han, L., Timachova, K., Veselinovic, J., Hyder, M. N., Ortiz, C., Klibanov, A. M., & Hammond, P. T. (2012). Drastically lowered protein adsorption on microbicidal hydrophobic/hydrophilic polyelectrolyte multilayers. *Biomacromolecules* **13(3):** 719–26.

Xu, C., Xu, K., Gu, H., Zheng, R., Liu, H., Zhang, X., Guo, Z., Xu, B. (2004). Dopamine as a robust anchor to immobilize functional molecules on the iron oxide shell of magnetic nanoparticles. *Journal of the American Chemical Society* **126(32):** 9938–9.

Xu, F. J., Zhao, J. P., Kang, E. T., Neoh, K. G., & Li, J. (2007). Functionalization of nylon membranes via surface-initiated atom-transfer radical polymerization. *Langmuir* **23(16):** 8585–92.

Yang, F., & Zhao, B. (2011). Adhesion properties of self-polymerized dopamine thin film. *The Open Surface Science Journal* **3:** 115–22.

Yang, X., & Li, L. (2010). Polypyrrole nanofibers synthesized via reactive template approach and their NH_3 gas sensitivity. *Synthetic Metals* **160(11-12):** 1365–7.

Ying, T., Yang, W., Yang, F. (2007). Removal of Cu(II) by polypyrrole deposits on stainless steel mesh. *Journal of Applied Polymer Science* **104(1):** 629–33.

Yu, Q., Zhang, Y., Wang, H., Brash, J., & Chen, H. (2011). Anti-fouling bioactive surfaces. *Acta Biomaterialia* **7(4):** 1550–7.

Zhang, F., Kang, E. T., Neoh, K. G., Wang, P., & Tan, K. L. (2001). Modification of Si(100) surface by the grafting of poly(ethylene glycol) for reduction in protein adsorption and platelet adhesion. *Journal of Biomedical Materials Research* **56(3):** 324–32.

Zhang, X., Bai, R., & Tong, Y. W. (2006). Selective adsorption behaviors of proteins on polypyrrole-based adsorbents. *Separation and Purification Technology* **52(1):** 161–9.

Acronyms and Annotations

ARGET-ATRP	Activators regenerated by electron transfer atom transfer radical polymerisation
ATRP	Atom transfer radical polymerisation
BIBB	2-bromoisobutyryl bromide
BSA	Bovine serum albumin
EIS	Electrochemical impedance spectroscopy
EQCM	Electrochemical quartz crystal microbalance
EDX	Energy dispersive X-ray
FTIR	Fourier transformation infra-red spectroscopy
HEMA	2-hydroxyethyl methacrylate
ITO	Indium tin oxide
NMR	Nuclear magnetic resonance
OCP	Open circuit potential
PEGMA	Poly(ethylene glycol) methacrylate
PSS	Polystyrene sulfonate
SCE	Saturated calomel electrode
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy

Appendix: Conference Presentations and Publications

Peer-reviewed Journals

Doyle, R., Breslin, C., Power, O., Rooney, D. (2012) Electrochemical Characterisation of Polypyrrole Doped with *p*-Sulfonatocalix[4]arene, *Electroanalysis*, **24**, 293–302.

McCarthy, C., McGuinness, N., Carolan, P., Fox, C., Alcock-Earley, B., Breslin, C., Rooney, D. (2013) Electrochemical Deposition of Hollow N- substituted Polypyrrole Microtubes from an Acoustically formed Emulsion, *Macromolecules*, **46**, 1008–16.

Conference Oral Presentations

Orla Power (2012) Remediating Hexavalent Chromium with Polymer Modified Membranes Environ 2012, University College Dublin, Dublin, 7–9 March.

Denise Rooney (2011) Electrochemical Formation of Polypyrrole Nanofibers at a Membrane Surface for the Extraction of Metal ions from Water. 13th EuCheMS International Conference on Chemistry and the Environment (ICCE). ICCE 2011. Zurich, Switzerland, 11–15 September.

Conference Posters

Catherine Fox, Denise Rooney, Carmel Breslin (2010) Polymeric Membranes for the Treatment and Purification of Water, 43rd International Union of Pure and Applied Chemistry (IUPAC) World Polymer Congress, Glasgow, July.

Orla Power, Catherine Fox, Denise Rooney, Carmel Breslin (2010) The modification of nylon membranes using conducting polymer nanowires for the remediation of heavy metals and nitrates from water., 20th Irish Environmental Researchers' Colloquium, Limerick, February.

Orla Power, Catherine Fox, Denise Rooney, Carmel Breslin (2010) The modification of nylon membranes using conducting polymer nanowires for the remediation of heavy metals and nitrates from water. EPA National Research Conference 2010 "Science into Action for a Sustainable Ireland', Dublin, June.

Orla Power, Catherine Fox, Denise Rooney, Carmel Breslin (2010) The Modification of Nylon Membranes, using Polypyrrole Nanofibers, for the Remediation of Heavy Metals or Nitrates from Water, 61st Annual Meeting of the International Society of Electrochemistry, Nice, France, September.

Orla Power, Denise Rooney, Carmel Breslin (2011) Reduction of Hexavalent Chromium at a Polypyrrole Nanofiber Modified Membrane, 63rd Irish Chemistry Colloquium, Dublin, Ireland, June.

Orla Power, Catherine Fox, Denise Rooney, Carmel Breslin (2011) Electrochemical Formation of Polypyrrole Nanofibers at a Membrane Surface for the Extraction of Metal Ions from Water, 3rd Eirelec Conference, Adare, Ireland, May.

Orla Power, Carmel Breslin, Denise Rooney (2012) Polypyrrole Nanowire Modified Membranes: Remediation of Hexavalent Chromium, Royal Society of Chemistry (RSC) Electrochemical Horizons Conference, Trinity College Dublin, Dublin, 2–4 September.

An Ghníomhaireacht um Chaomhnú Comhshaoil

Is í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) comhlachta reachtúil a chosnaíonn an comhshaol do mhuintir na tíre go léir. Rialaímid agus déanaimid maoirsiú ar ghníomhaíochtaí a d'fhéadfadh truailliú a chruthú murach sin. Cinntímid go bhfuil eolas cruinn ann ar threochtaí comhshaoil ionas go nglactar aon chéim is gá. Is iad na príomhnithe a bhfuilimid gníomhach leo ná comhshaol na hÉireann a chosaint agus cinntiú go bhfuil forbairt inbhuanaithe.

Is comhlacht poiblí neamhspleách í an Ghníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil, Pobal agus Rialtais Áitiúil.

ÁR bhFREAGRACHTAÍ

CEADÚNÚ

Bíonn ceadúnais á n-eisiúint againn i gcomhair na nithe seo a leanas chun a chinntiú nach mbíonn astuithe uathu ag cur sláinte an phobail ná an comhshaol i mbaol:

- áiseanna dramhaíola (m.sh., líonadh talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh., déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- diantalmhaíocht;
- úsáid faoi shrian agus scaoileadh smachtaithe Orgánach Géinathraithe (GMO);
- mór-áiseanna stórais peitreail;
- scardadh dramhuisce;
- dumpáil mara.

FEIDHMIÚ COMHSHAOIL NÁISIÚNTA

- Stiúradh os cionn 2,000 iniúchadh agus cigireacht de áiseanna a fuair ceadúnas ón nGníomhaireacht gach bliain
- Maoirsiú freagrachtaí cosanta comhshaoil údarás áitiúla thar sé earnáil - aer, fuaim, dramhaíl, dramhuisce agus caighdeán uisce
- Obair le húdaráis áitiúla agus leis na Gardaí chun stop a chur le gníomhaíocht mhídhleathach dramhaíola trí comhordú a dhéanamh ar líonra forfheidhmithe náisiúnta, díriú isteach ar chiontóirí, stiúradh fiosrúcháin agus maoirsiú leigheas na bhfadhbanna.
- An dlí a chur orthu siúd a bhriseann dlí comhshaoil agus a dhéanann dochar don chomhshaol mar thoradh ar a ngníomhaíochtaí.

MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOL

- Monatóireacht ar chaighdeán aeir agus caighdeáin aibhneacha, locha, uiscí taoide agus uiscí talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairisciú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntí a dhéanamh.

RIALÚ ASTUITHE GÁIS CEAPTHA TEASA NA HÉIREANN

- Cainníochtú astuithe gáis ceaptha teasa na hÉireann i gcomhthéacs ár dtiomantas Kyoto.
- Cur i bhfeidhm na Treorach um Thrádáil Astuithe, a bhfuil baint aige le hos cionn 100 cuideachta atá ina mór-ghineadóirí dé-ocsaíd charbóin in Éirinn.

TAIGHDE AGUS FORBAIRT COMHSHAOIL

- Taighde ar shaincheisteanna comhshaoil a chomhordú (cosúil le caighdéan aeir agus uisce, athrú aeráide, bithéagsúlacht, teicneolaíochtaí comhshaoil).

MEASÚNÚ STRAITÉISEACH COMHSHAOIL

- Ag déanamh measúnú ar thionchar phleananna agus chláracha ar chomhshaol na hÉireann (cosúil le pleananna bainistíochta dramhaíola agus forbartha).

PLEANÁIL, OIDEACHAS AGUS TREOIR CHOMHSHAOIL

- Treoir a thabhairt don phobal agus do thionscal ar cheisteanna comhshaoil éagsúla (m.sh., iarratais ar cheadúnais, seachaint dramhaíola agus rialacháin chomhshaoil).
- Eolas níos fearr ar an gcomhshaol a scaipeadh (trí cláracha teilifíse comhshaoil agus pacáistí acmhainne do bhunscoileanna agus do mheánscoileanna).

BAINISTÍOCHT DRAMHAÍOLA FHORGHNÍOMHACH

- Cur chun cinn seachaint agus laghdú dramhaíola trí chomhordú An Chláir Náisiúnta um Chosc Dramhaíola, lena n-áirítear cur i bhfeidhm na dTionscnamh Freagrachta Táirgeoirí.
- Cur i bhfeidhm Rialachán ar nós na treoracha maidir le Trealamh Leictreach agus Leictreonach Caite agus le Srianadh Substaintí Guaiseacha agus substaintí a dhéanann ídiú ar an gcrios ózóin.
- Plean Náisiúnta Bainistíochta um Dramhaíl Ghuaiseach a fhorbairt chun dramhaíl ghuaiseach a sheachaint agus a bhainistiú.

STRUCHTÚR NA GNÍOMHAIREACHTA

Bunaíodh an Ghníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaimseartha, ar a bhfuil Príomhstiúrthóir agus ceithre Stiúrthóir.

Tá obair na Gníomhaireachta ar siúl trí ceithre Oifig:

- An Oifig Aeráide, Ceadúnaithe agus Úsáide Acmhainní
- An Oifig um Fhorfheidhmiúchán Comhshaoil
- An Oifig um Measúnacht Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáide

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag ball air agus tagann siad le chéile cúpla uair in aghaidh na bliana le plé a dhéanamh ar cheisteanna ar ábhar imní iad agus le comhairle a thabhairt don Bhord.

Science, Technology, Research and Innovation for the Environment (STRIVE) 2007-2013

The Science, Technology, Research and Innovation for the Environment (STRIVE) programme covers the period 2007 to 2013.

The programme comprises three key measures: Sustainable Development, Cleaner Production and Environmental Technologies, and A Healthy Environment; together with two supporting measures: EPA Environmental Research Centre (ERC) and Capacity & Capability Building. The seven principal thematic areas for the programme are Climate Change; Waste, Resource Management and Chemicals; Water Quality and the Aquatic Environment; Air Quality, Atmospheric Deposition and Noise; Impacts on Biodiversity; Soils and Land-use; and Socio-economic Considerations. In addition, other emerging issues will be addressed as the need arises.

The funding for the programme (approximately €100 million) comes from the Environmental Research Sub-Programme of the National Development Plan (NDP), the Inter-Departmental Committee for the Strategy for Science, Technology and Innovation (IDC-SSTI); and EPA core funding and co-funding by economic sectors.

The EPA has a statutory role to co-ordinate environmental research in Ireland and is organising and administering the STRIVE programme on behalf of the Department of the Environment, Heritage and Local Government.

ENVIRONMENTAL PROTECTION AGENCY
PO Box 3000, Johnstown Castle Estate, Co. Wexford, Ireland
t 053 916 0600 f 053 916 0699
LoCall 1890 33 55 99
e info@epa.ie w http://www.epa.ie

Comhshaol, Pobal agus Rialtas Áitiúil
Environment, Community and Local Government