

**REJECTION MECHANISM FOR ARSENATE, CHROMATE AND PHOSPHATE
IONS VIA POLYACRYLONITRILE ULTRAFILTRATION MEMBRANE**

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DEPARTMENT OF BIOCHEMICAL ENGINEERING AND BIOTECHNOLOGY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

DECEMBER 2014

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by

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DEPARTMENT OF BIOCHEMICAL ENGINEERING AND BIOTECHNOLOGY

Submitted

in fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the



**INDIAN INSTITUTE OF TECHNOLOGY DELHI
NEW DELHI – 110016, INDIA**

DECEMBER 2014

Certificate

This is to certify that the thesis entitled “**Rejection Mechanism for Arsenate, Chromate and Phosphate Ions via Polyacrylonitrile Ultrafiltration Membrane**” being submitted by Muthumareeswaran M.R. is worthy of consideration for the award of the degree of Doctor of Philosophy. The thesis has been prepared under my supervision and guidance in conformity with the rules and regulations of Indian Institute of Technology Delhi and is a record of the original bonafide research work. The results presented in this thesis have not been submitted in part or full to any other universities or institutes for the award of any other degree or diploma.

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Acknowledgements

First of all, I sincerely thanks to my PhD supervisor, Prof. Gopal Prasad Agarwal, for making this possible. His vision, guidance, knowledge, time and input have each contributed to acquisition of the skills necessary to make this PhD possible. In addition to scientific input, I appreciate him for guiding me towards other research opportunities, such as to work in National Chemical Laboratory (NCL), Pune, India. During this stint, I had enough time to learn how to make membranes with different aspects as well as characterize it. This was a very positive experience for me and I attribute much of the success of this PhD to that visit. Dr. Ulkhas Kharul is an inspiration for me. Thank you, Kharul, for your patience and for welcoming me to the world of making membranes and I need to thank my fellow student especially Ms. Harsatha Lohokare and Mr. Kumbharkar, who gave me the guidance during my stay at NCL Pune. As part of my PhD I was fortunate to visit the Université of Paul Sabatier, France for two months. The journey was difficult, humbling and empowering, and as a result, I have grown professionally and personally. Thank Prof. Agarwal, for constantly challenging me; I am now better equipped to meet future challenges and open future doors. I would like to give a special thanks to Professors Patrice Bacchin and Christel Causserand who invited me to Laboratoire de Génie Chimique, France and gave me the proper guidance in the numerical developments of membrane processes.

My sincere thanks to Council of Scientific and Industrial Research (CSIR-HRDG) for Senior Research Fellowship (SRF) during 2009 to 2011, MHRD, Government of India, also Industrial Research and Development (IRD), IIT Delhi for the financial support as fellowships. I also thanks Embassy of France, New Delhi, Department of Biotechnology (DBT), Department of Science and Technology (DST) and European Membrane Society (EMS) for their financial supports as young scientists travel grant during my stay abroad.

I wish to express my gratitude to Prof. T.R. Sreerishnan, Prof. Sunil Nath, Prof. Subash Chand. Prof. Prasant Mishra and Dr. B. Kundu who are associated with IIT Delhi for their encouragement during the course of this thesis.

Thanks to my fellow students, past and present, for the endless support and laughs over my stay at IIT Delhi. It has been an adventure! A special thanks to Mr. Rahul keshewani, Mr. Y. Lukka Thuyavan, Dr.R.D.Karthikeyan, Dr. Z.A.Shaikh and Dr. Lawrence – who always gave motivations during my

research. I cannot imagine a better friend and colleague than Mr. Satyendra singh along with whom I have started (and ended!) this journey. A very special thanks to Mr. Sunil Kumar who also known to be as 'Party Kumar' used to ask for party for no reasons and made me laugh. Bhuvanesh, Maneesh, Premnath, Himanshu singh, Akhil Sasidharan Pillai, Arun Kumar Shukla, Deepak Tewari, Kunal Gupta, Ritesh Aggarwal: much gratitude for your smiles and support! Thanks also to Mr. Mukesh Anand, Mr. J.A. Khan and Mr. Kishan Chand for their support and help during this course of study. I express my sincere thanks to Department of Biochemical engineering and Biotechnology and IIT Delhi for their support during this course. I wish to express my gratitude to Mr. Ankit Srivastava, research scholar, School of biological science, IIT Delhi and Ms. Deepika Malpani, Anton Paar India Pvt. Ltd, for the guidance to measure the AFM images and zeta potential of membranes.

I extremely thanks to my father Mr. Ramamoorthy and mother Mrs. Muthurathinam, Brother Mr. Rajesh, Sister Mrs. Karthika for their support, guidance and encouragement for my education and social support in life. Last but not the least, I must sincerely thankful to my wife Mrs. Indra Devi and her brother Mr.Muthuramalingam, and finally my little angel Ms. Lakshmitha, without their patience and support, I couldn't have successfully completed this thesis.

Muthumareeswaran M.R.

Abstract

ABSTRACT

Development of effective and economical techniques for removal of heavy metals and inorganic pollutants from drinking water and wastewater has always been a great concern for environmental as well as process engineers. The presence of heavy metals like arsenic, chromium and large amount of phosphate in aquatic source, and eventually in potable water, is a serious health issue. Membrane separation technology is a viable and highly innovative process engineering operation which can be applied for heavy metals and inorganic pollutant removals from aquatic stream. The main advantages of membrane techniques are low energy consumption, no chemical reaction and separation in the continuous mode. Conventional membrane technologies like Reverse Osmosis and Nanofiltration require high operating pressure for water treatment as compared to Ultrafiltration membrane.

Chromium and arsenic are the sixth and twentieth most abundant element respectively in earth's crust. Generally, the heavy metals contamination in water occurs due to natural phenomena such as the presence of minerals, volcanic emissions; human activities like wood preservatives, fertilizers, industrial processes and waste treatment. On the other hand, the existence of large amount of phosphate in domestic and industrial wastewater causes the eutrophication which is a serious environmental issue in water sources. Thus, removal of arsenic, chromium and phosphate from water streams is very important from both environmental and economic points of view.

The present study is to investigate the polyacrylonitrile based UF membrane for effective and selective removal of arsenic, chromium and phosphate from water. Applicability of polyacrylonitrile (PAN) based ultrafiltration (UF) membrane for effective arsenic, chromium and phosphate removal was established, to our knowledge, for the first time. PAN based UF membrane surface was hydrolyzed by 1 N NaOH and it led to the formation of carboxylate (COO^-) groups

which reduced the pore size to improve divalent anionic rejection capability. The pore size reduction was assessed by lowering in water flux and increase in PEG and proteins rejection. The membrane structural parameters such as mean pore radius, porosity, pore size distribution and roughness were determined by atomic force microscope (AFM), whereas iso-electric point and charge density of membrane surface were measured by tangential streaming potential (TSP) measurements. Solution pH was directly correlated with the membrane structural properties like porosity, pore size distribution and these parameters were directly proportional to the volumetric flux whereas the membrane roughness was inversely proportion to the flux.

The removal of anions (arsenate, chromate and phosphate) from potable water using surface modified polyacrylonitrile ultrafiltration membranes was carried out with plate and frame module in cross-flow mode. Ultrafiltration membranes and their different coupons were subjected to anionic concentrations in the feed ranging from 250 ppb to 1000 ppm to test its efficacy. The effects of physical and engineering parameters (pressure, temperature and cross flow velocity) as well as chemical parameter (ions concentration and pH) on the rejections of anions were studied as a function of time. Variation of feed pH played a vital role on ions transport through the membrane. More than 95% rejection of arsenate, chromate and phosphate ions were achieved separately for each anions at $\text{pH} \geq 7$. The electro neutrality condition was also confirmed by counter-ion (sodium ion) rejection which was also more than 90% at $\text{pH} \geq 7$. The concentration polarization was negligible at low feed concentration (≤ 150 ppm). But concentration polarization effect was found at higher concentration of each divalent anions (≥ 200 ppm) and the rejection of arsenic, chromium, phosphate ions were found to be in the range of 45 % to 72% at high cross-flow velocity and low transmembrane pressure.

The rejection mechanism of anions was strongly dependent on Donnan exclusion principle. Generally, higher rejection % of arsenate, chromate and phosphate ions ($\geq 92\%$) were obtained with high Donnan potential value (~ 20 mV). Moreover, Donnan potential was vital at feed concentrations (1 ppm to 150 ppm) and it was negligible at very low feed concentration ($\ll 1000$ ppb) and again it became weaker at very high concentration (≥ 500 ppm).

In multicomponent system, the mixture of arsenate, chromate and phosphate ions showed more than 92% for feed concentration of 50 ppm each. However, the arsenate rejection decreased to 55–60% for 5 ppm arsenate and 50 ppm each of chromate, phosphate mixture in the feed, while chromate and phosphate rejections remained $\geq 90\%$. The change in proportion of feed concentration in multicomponent system like 50 ppm of arsenate along with 5 ppm of chromate and 5 ppm of phosphate ions resulted more than 90 % of As (V) but Cr (VI) and PO_4^{2-} rejection coefficients were reduced to 70% and 74% respectively. Moreover, the retention of anions through modified PAN UF membrane, was also dependent on hydrated radii of the solute and the rejection of anions followed the order $\text{Cr (VI)} < \text{As (V)} < \text{PO}_4^{2-}$. In addition, heavy metals (arsenate, chromate) and phosphate removal using polyacrylonitrile ultrafiltration, were effective ($\geq 97\%$) at low pressure operation compared to nanofiltration (NF) membranes.

The surface modified membrane were also subjected to high operating transmembrane pressure for the effective removal of arsenic, chromium and phosphate ions from potable water. The membrane showed more than 94% rejection efficiency of divalent anions at the transmembrane pressure of 10 bar. The surface modified polyacrylonitrile membrane was not showing any fouling and would work for a long time; gave almost 100% rejections for ppb level concentration of arsenate and ppm level of chromate, phosphate ions in the feed. However, due to concentration polarization effect on the membrane surfaces, the rejection % of arsenate, chromate

and phosphate ions were reduced to 87 %, 85% and 89% respectively at 12 bar of transmembrane pressure.

The removal of arsenate, chromate and phosphate ions through modified PAN UF membrane were also subjected to other ions (such as nitrate, sulphate, carbonate, calcium and sodium chloride) which are normally available in ground water. The rejection % of arsenate, chromate and phosphate ions were reduced to 70 % to 78% in the presence of other ions in the feed.

The Donnan steric-partitioning pore model incorporated with dielectric exclusion (DSPM-DE) model was applied to evaluate the ions transport through the membrane as a function of flux by using optimized model parameters like feed concentration, the membrane active layer thickness, the effective volumetric charge density and membrane permeability. The modified DSPM DE model was applied for theoretical calculation of flux and rejection of arsenate ions in the case of PAN membrane. The model also applied for chromate and phosphate ions rejection through the membrane. The comparison of simulated and experimental rejection data showed that DSPM-DE model fully predicted the tendencies and pattern of ionic rejection as a function of flux.

CONTENTS

	Page No.
Certificate	i
Acknowledgements	ii
Abstract	iv
Contents	viii
List of Figures	xiii
List of Tables	xviii
List of Symbols	xx
List of Abbreviations	xxiii
1. INTRODUCTION AND OBJECTIVES	1-5
1.1 Introduction	1
1.2 Scope and Outline of thesis	4
1.3 Objectives	5
2. LITERATURE REVIEW	6-63
2.0. Literature Review	6
2.1. Chemistry of Ionic Solutes	7
2.1.1. Arsenic	7
2.1.2. Chromium	9
2.1.3. Phosphate	10
2.2. Existing Methods of Removal of Divalent ions	11
2.3. Membrane Processes	13
2.3.1. Membrane Structural Classifications	14
2.3.2. Pressure Driven Membrane Processes	15
a. Reverse Osmosis (RO)	16
b. Nanofiltration (NF)	17
c. Microfiltration (MF)	17
d. Ultrafiltration (UF)	18
2.3.3. Characteristic and operating conditions	19
a. Pore size distribution	19
b. Membrane Permeability	20
c. Rejection coefficient	20
d. Cross flow velocity	21
e. Transmembrane pressure	21

	f. Temperature	21
	g. Feed concentration	22
2.4.	UF Membrane Material	23
2.5.	Membrane Configuration/Modules	24
	2.5.1. Plate and Frame Module	25
	2.5.2. Spiral Wound Module	25
	2.5.3. Tubular Module	26
	2.5.4. Hollow fiber Membranes	27
2.6.	Ultrafiltration membrane fouling	28
2.7.	Transport Processes in Ultrafiltration	29
	2.7.1. Concentration polarization (CP)	29
	2.7.2. Numerical model developments	32
	2.7.3. Modeling of Ions transport across the membranes	34
	A. Irreversible thermodynamic Models	36
	B. Mechanistic Models	38
	<i>i.</i> Steric Hindrance Pore Model (SHP)	38
	<i>ii.</i> Maxwell-Stefan (MS) Model	39
	<i>iii.</i> Space-Charge (SC) Model	40
	<i>iv.</i> Teorell–Meyer–Sievers (TMS) Model	41
	<i>v.</i> Extended Nernst-Planck Equation	42
	<i>a.</i> Donnan Steric Pore Model (DSPM)	43
	<i>b.</i> Donnan Steric Pore Model (DSPM) & dielectric exclusion (DE)	44
	<i>c.</i> Steric Electric and Dielectric Exclusion (SEDE) Model	45
2.8.	Ions separation by membranes	45
	2.8.1. Arsenic removal by membranes	45
	2.8.2. Chromium removal by membranes	50
	2.8.3. Phosphate removal by membranes	53
	2.8.4. Ions transport model via UF and NF Membrane Processes	55
3.	MATERIALS AND METHODS	64-81
3.0.	Materials and Methods	64
3.1.	Materials	64
	3.1.1. Chemicals	64
	3.1.2. Membranes	66
3.2.	Methods	
	3.2.1. Characterization of membranes	66

<i>a.</i>	Atomic absorption spectroscopy	66
<i>b.</i>	Electrokinetic analyzer	69
3.2.2.	Stock Solutions	71
3.2.3.	Experimental Set up	72
<i>a.</i>	Plate and Frame Module for Low TMP	73
<i>b.</i>	Plate and Frame Module for High TMP	73
3.2.4.	Sample analysis	75
<i>a.</i>	Atomic Absorption Spectroscopy	75
<i>b.</i>	Ion Chromatography	77
<i>i.</i>	Anionic Suppressor	78
<i>ii.</i>	Cationic Suppressor	78
<i>iii.</i>	Various wavelength detector	79
<i>c.</i>	Colorimetric method	79
3.2.5	Rejection Analysis	80
3.2.6	Material Balance of anionic solutes	80
3.2.7	Flux, Cross-flow velocity and Hydraulic Permeability	81
<i>a.</i>	Volumetric flux	81
<i>b.</i>	Cross flow velocity	81
<i>c.</i>	Hydraulic permeability	81
4.	RESULTS AND DISCUSSION	82-155
4.0.	Results and Discussion	82
4.1.	Surface properties of PAN ₂₃ UF membrane	82
4.1.1.	Surface modification	82
4.1.2.	Water flux	83
4.1.3.	Molecular weight cut-off (MWCO)	85
4.1.4.	Membrane roughness	87
4.1.5.	Pore size and its distribution	92
4.1.6.	Membrane porosity	95
4.2.	Surface charge measurements	97
4.2.1.	Zeta potential measurements	98
4.2.2.	Different pH Values	98
4.2.3.	Same salt at different feed concentration values	102
4.2.4.	Different salts at same feed concentration values	103
4.3.	Arsenic rejection	106
4.3.1.	Effect of feed concentration	106
4.3.2.	Effect of transmembrane pressure and cross-flow velocity	107
4.3.3.	Effect of feed pH	109

4.3.4.	Effect of feed temperature	112
4.3.5.	Arsenate Rejection of Modified and Unmodified PAN ₂₃ UF membrane	113
4.3.6.	Arsenate Ions rejection for longer run	117
4.3.7.	Arsenate rejection as a function of membrane structural properties	118
4.3.8.	Arsenate rejection with respect to transmembrane pressure	121
4.3.9.	Arsenate along with Sodium Ions rejection	123
4.3.10.	Arsenite Ions rejection	124
4.4.	Chromium rejection	125
4.4.1.	Effect of Feed concentration	125
4.4.2.	Effect of transmembrane pressure and cross-flow velocity	126
4.4.3.	Effect of feed pH	128
4.4.4.	Effect of membrane porosity	130
4.4.5.	Trivalent Chromium ions rejection	131
4.5.	Phosphate rejection	133
4.5.1.	Effect of feed concentration	133
4.5.2.	Effect of transmembrane pressure and cross-flow velocity	134
4.5.3.	Effect of feed pH	136
4.5.4.	Effect on feed Temperature	137
4.5.5.	Phosphate along with sodium ions rejection	138
4.5.6.	Monovalent phosphate ions rejection	139
4.6.	Multicomponent Ions rejection	140
4.6.1.	Effect of feed concentration on Multicomponent ions rejection	141
4.6.2.	Effect of Donnan potential on feed concentration	142
4.7.	Comparative Studies between modified PAN ₂₃ UF and NF membrane	144
4.7.1.	Arsenate and Phosphate ions rejection	145
4.7.2.	Chromate ions rejection	146
4.8.	High pressure data for divalent anions rejection	147
4.8.1.	Divalent anions (arsenate, chromate & phosphate) rejection	148
4.8.2.	Multicomponent ions rejection	150
4.8.3.	Effect of Donnan potential on transmembrane pressure	151
4.9.	Divalent anions rejection in the presence of other ions	153
5.	DATA SIMULATION AND ANALYSIS	156-177
5.10.	Data Simulation and Analysis	156
5.10.1.	Model Description	157
5.10.2.	Governing Equations	158
a.	Equilibrium partitioning	160

b.	Pore-Inlet	161
c.	Ions transport within the pore	162
<i>i.</i>	For charged ions	162
<i>ii.</i>	For uncharged solute	164
d.	Pore-Outlet	164
e.	Data Processing	165
5.10.3.	Model Analysis	166
5.10.4.	Model validation for Arsenate ions	167
a.	Effect of membrane surface charge density	167
b.	Effect of dielectric constant within the pores	169
c.	Effect on ratio of membrane thickness to the porosity	170
d.	Effect of temperature and pressure	171
e.	Effect of feed concentration	173
5.10.5.	Model validation for Chromate ions	175
5.10.6.	Model validation for phosphate ions	176
5.10.7.	Model validation for Multicomponent ions rejection	177
6.	CONCLUSIONS	179-182
6.1.	Conclusions	179
	REFERENCES	182-206
	APPENDICES	207-218
	RESEARCH PUBLICATION BASED ON PRESENT WORK	
	AUTHOR'S BIODATA	219-221