SEPARATION OF CHROMATE AND BORATE ANIONS BY POLYMER ENHANCED ULTRAFILTRATION FROM AQUEOUS SOLUTIONS EMPLOYING SPECIFICALLY TAILORED POLYMERS

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ABSTRACT

SEPARATION OF CHROMATE AND BORATE ANIONS BY POLYMER ENHANCED ULTRAFILTRATION FROM AQUEOUS SOLUTIONS EMPLOYING SPECIFICALLY TAILORED POLYMERS

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In this study two polychelatogens for borate and a polyelectrolyte for chromate retention (R) were designed for investigating the effect of pH and loading (g metal /g polymer) on the separation performances of the synthesized polymers using continuous polymer enhanced ultrafiltration.

Increase in pH increased the retention of borate for all of the synthesized polymers. Decrease in the loading resulted in an enhancement in boron retention with PNSM and PNSL. When COP was utilized, retentions remained almost constant after a certain loading, probably due to possible adverse effects of high polymer concentrations on polymer conformation in aqueous solutions.

Decrease in loading caused an increase in the retention of chromate until a loading of 0.01. After that a slight decrease was observed. Maximum Cr (VI) retention was obtained as 0.70 for a loading of 0.01 and a pH of 4. Effect of crowding on Cr(VI) retention was also investigated. It was observed that retention does not only depend on the loading but also on the concentrations of both Cr (VI) and PDAM. Effect of the presence of competing anions such as chloride and sulfate on the retention of chromate was investigated to see the effect of competing anion charge to the selectivity of the synthesized polyelectrolyte. Addition of both anions decreased the retention of Cr(VI) . Divalent sulfate decreased the retention more than monovalent chloride indicating that charge of the anion may be the predominant variable in the retention of chromate using PDAM.

Finally, dynamic and static light scattering measurements were performed to investigate the conformational changes in the structure of the synthesized polymers at different pH values as well as in the presence of boron in the solution.

In this study, it is shown that PEUF can be successfully applied to for boron and Cr (VI) retention with the synthesized polymers. Satisfactory retention values were obtained both for boron and Cr (VI). Even if the retention of Cr (VI) decreased with the addition of high amount of competing anions, significant Cr (VI) retentions could be obtained.

Keywords: Ultrafiltration, Membrane Separation Techniques, Anion Removal, Polychelatogen, Polyelectrolyte

ÖZ

KROMAT VE BORAT ANYONLARININ ÖZEL OLARAK SENTEZLENMİŞ POLİMERLER KULLANARAK POLİMER KOMPLEKSLEMELİ ULTRAFİLTRASYON İLE SUDAN AYIRILMASI

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Bu çalışmada, sulardan borat ve kromat anyonlarının uzaklaştırılması için özel olarak tasarlanmış polimerler sentezlenmiş ve bu polimerlerin, polimer komplekslemeli ultrafiltrasyon yöntemiyle uzaklaştırılmasına pH ve yükleme (metal/polimer) gibi parametrelerin etkisi polimer komplekslemeli ultrafiltrasyon (PKUF) kullanılarak incelenmiştir.

Bor uzaklaştırması için sentezlenen bütün polimerler için besleme çözeltisi pH'ı arttırıldığında borat anyonunun alıkonma oranı da artmıştır. PNSM ve COP'nin kullanıldığı PKUF deneylerinde, yükleme değerinin azaltılması borat anyonunun alıkonma yüzdesinde artış sağlamıştır. Şelat oluşturan polimer olarak COP'nin kullanıldığı PKUF deneylerinde alıkonma oranı yükleme değeri azaldıkça artmış ve belli bir yükleme değerinden sonra, alıkonma oranlarının sabit kaldığı belirlenmiştir.

Kromat uzaklaştırması için yapılan PKUF deneylerinde, yükleme değerindeki azalış kromat alıkonma oranını arttırmış. Ancak 0.01 yükleme değerinden daha düşük değerlerde alıkonma oranlarında hafif bir düşüş gözlenmiştir. Kromat alıkonma oranının düşük pH değerlerinde arttığı belirlenmiştir. En yüksek alıkonma, yüklemenin 0.01 ve pH değerinin 4 olduğu PKUF deneyinde 0.70 olarak bulunmuştur. Çözeltideki kalabalıklığın kromat alıkonmasine etkisinin incelendiği deneylerde, Cr(VI) alıkonma yüzdesinin sadece yüklemeye değil, Cr(VI) ve PDAM derişimlerine de bağlı olduğu belirlenmiştir. Ayrıca, anyon yükünün sentezlenen polielektrolit seçiciliğine etkisini incelemek amacı ile, sülfat ve klorür gibi yarışmalı anyonların varlığının kromat alıkonma oranına etkisi araştırılmıştır. Her iki anyonun da Cr(VI) alıkonmasinin düştüğü görülmüştür. İki değerlikli sülfatın, Cr(VI) alıkonma oranını tek değerlikli klorüre göre daha fazla düşürdüğü belirlenmiştir. Bu da sentezlenen polielektrolit ile Cr(VI) etkileşiminde değerliğin alıkonma oranında daha baskın bir etken olabileceğini göstermiştir.

Son olarak, bu çalışmada borat uzaklaştırması için sentezlenen polimerlerin sıvı ortam içerisinde pH'a gösterebileceği biçimsel değişiklikleri inceleyebilmek amacıyla dinamik ve statik ışık saçılımı yöntemiyle çeşitli analizler yapılmıştır.

Bu çalışmada, PKUF'nin bor ve Cr(VI) ayırımında sentezlenen polimerler kullanılarak başarılı bir şekilde uygulanabileceği gösterilmiş ve hem bor hem Cr(VI) için tatmin edici alıkonma yüzdeleri elde edilmiştir.

Anahtar Kelimeler: Ultrafiltrasyon, Membranlı Ayırım İşlemleri, Anyon Uzaklaştırması, Polişelatojen, Polielektrolit.

To my mom, dad and my husband

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TABLE OF CONTENTS

ABSTRACT iv

ÖZ. vi

DEDICATION viii

ACKNOWLEDGMENTS ix

TABLE OF CONTENTS x

LIST OF TABLES xiv

LIST OF FIGURES xvii

LIST OF SYMBOLS xix

CHAPTER

- 1. INTRODUCTION 1
  - 1.1 Membrane Processes. 5
    - 1.1.1 Liquid Membrane Processes 5
    - 1.1.2 Pressure Driven Membrane Processes 6
  - 1.2 Complexation-Enhanced Ultrafiltration Processes 7
  - 1.3 Polymer Enhanced Ultrafiltration (PEUF) Processes 8
  - 1.4 Aim and Scope of the Study 10
- 2 LITERATURE SURVEY 12
  - 2.1 Polymer Enhanced Ultrafiltration. 13
  - 2.2 Polymeric Materials for PEUF Processes. 14
  - 2.3 Effects of Operational Parameters on Performance of PEUF 17

2.4 Boron Removal from Aqueous Solutions by Membrane Processes. . . 21

2.4.1 Boron Chemistry. 21

2.4.2 Boron Complexation. 22

2.4.3 Membrane Processes for Boron Retention. 25

2.4.4 PEUF Technique for Boron Retention. 27

2.5 Hexavalent Chromium (Cr(VI)) Removal from Aqueous Solutions by Membrane Processes. 29

2.5.1 Chromium Chemistry. 29

2.5.2 Membrane Processes for Cr(VI) Retention. 32

2.5.3 PEUF Technique for Hexavalent Chromium Retention. 34

3. MATERIALS AND METHOD 39

3.1 Materials. 39

3.2 Polymer Synthesis for PEUF Experiments. 39

3.2.1 Synthesis of Hydroxyethylamino Glycerol Functioned Poly(glycidlmethacrylate) (PNS) for Borate Removal. 40

3.2.2 Synthesis of Poly(4-Vinyl-1,3-dioxalan-2-one-co-vinyl acetate) (COP) for Borate Removal. 41

3.2.3 Synthesis of Poly(N,N-diallylmorpholnium bromide for Cr(VI) Removal. 42

3.3 Experimental Set-up of Laboratory Scale Ultrafiltration Equipment. . . .43

3.3.1 Experimental Set-up of Laboratory Scale Continuous Mode of Ultrafiltration Equipment. 43

3.3.2 Experimental Set-up of Laboratory Scale Batch Mode of Ultrafiltration Equipment. 45

3.4 Ultrafiltration Experiments. 45

3.4.1 Preparation of Feed Solution. 45

3.4.2 Ultrafiltration Experiments. 46

3.4.3 Membrane Cleaning Procedure. 46

3.5 Analytical Methods. 47

3.5.1 Boron Determination 47

3.5.2 Total Chromium Determination. 48

3.5.3 Sulfate and Chromate Determination Using Ion Chromatography. 48

3.5.4 Dynamic and Static Light Scattering Analysis. 48

4. RESULTS AND DISCUSSION. 51

4.1 General Evaluation of PEUF Experiments 52

4.2 Boron Retention Studies Using Specifically Tailored Polychelatogens by PEUF. 54

4.2.1 Effect of Loading on The Retention of Boron and Flux Using PNSH. 54

4.2.2 Effect of pH on The Retention of Boron Using PNSH. 57

4.2.3 Effect of Loading on The Retention of Boron and Flux Using PNSL. 58

4.2.4 Effect of pH on The Retention of Boron Using PNSL 60

4.2.5 Effect of Loading on The Retention of Boron and Flux Using PNSM. 61

4.2.6 Effect of pH on The Retention of Boron Using PNSM. 63

4.2.7 Effect of Loading on The Retention of Boron and Flux Using COP. 65

4.2.8 Effect of pH on The Retention of Boron Using COP. 66

4.3 Comparison of The Boron Chelating Performances of PNS and COP. 67

4.4 Characterization of PNSM and COP by DLS/SLS Method. 70

4.5 Hexavalent Chromium Retention Studies Using Specifically Tailored Polyelectrolyte by PEUF. 74

4.5.1 Effect of Loading on the Retention of Cr(VI) and Flux using PDAM. 74

4.5.2 Effect of PDAM Concentration on the Retention of Cr(VI) . . 77

4.5.3 Effect of pH on The Retention of Cr (VI) Using PDAM 79

4.5.4 Effect of Competing Ion Concentration on the Retention of Cr (VI) using PDAM. 83

5. CONCLUSIONS. 88

REFERENCES. 92

APPENDICES

A Boron Determination by DRE-ICP-OES Analysis Method and Sample Calculations. 106

B Total Chromium Determination by Flame AAS Method 110

C Calibration Data for Sulfate and Chloride Determination. 114

D Data Tables for PEUF Experiments. 116

E Data Tables of the Graphs Given in Chapter 4. 130

F Data Tables for DLS/SLS Experiments. 135

G Determination of Viscosity Average Molecular Weight of PNS. 143

CURRICULUM VITAE 146

LIST OF TABLES

1.1 EPA Recommended Water Quality Criteria for Priority Toxic Pollutants 1

4.1 Molecular structures of the synthesized polymers. 51

4.1.1 Data obtained in a representative PEUF run for borate retention 52

4.1.2 Data obtained in a representative PEUF run for chromate retention 52

4.1.3 Data of the experiments performed for reproducibility 53

4.2.1 Effect of loading on the retention of borate using PNSH 56
4.2.5 Comparison of the boron binding performances of PNSM and PNSL 63

4.4.1 Data obtained from DLS without dilution. 71
4.4.2 Parameters extracted from Guinier plots 73
4.5.2 Retention values with respect to various PDAM and chromate concentrations. 78

4.5.3 Absorbance results for the chromium precipitation experiments 80

4.5.4a Effect of competing ion concentration on the retention of Cr(VI) at L:0.01, pH:4 84

4.5.4b Effect of pH on the retention of Cr(VI) with the presence of co-anions. 85
4.5.4.c Effect of pH on the retention of Cr(VI) with the presence of co-anions. 86

A.1 Sample Intensity Data of the Standard Solutions of Borate for Permeate 107

A.2 Sample Intensity Data of the Standard Solutions of Borate for Feed. 107
A.3 Sample Intensity Data and the Determined Concentration Values of Borate the Feed Samples. 108
A.4 Sample Intensity Data and the Determined Concentration Values Borate of the Permeate Samples. 109
B.1 Sample Intensity Data of the Standard Solutions of Cr(VI) for Permeate. 111

B.2 Sample Intensity Data of the Standard Solutions of Cr(VI) for Feed. 111

B.3 Sample Intensity Data and the Determined Concentration Values of Cr(VI) the Feed Samples. 112

B.4 Sample Intensity Data and the Determined Concentration Values of Cr(VI) of the Permeate Samples. 113

D.1 Data Tables for PEUF Experiments for Borate Retention. 116

D.2 Data Tables of PEUF Experiments for Chromate Retention 124

E.1 Effect of Loading on Boron Retention and Flux using PNSH at pH 9. 130

E.2 Effect of pH on Boron Retention using PNSH 130

E.3 Effect of Loading on Boron Retention and Flux using PNSL at pH 9 130

E.4 Effect of pH on Boron Retention using PNSL 130

E.5 Effect of Loading on Boron Retention and Flux using PNSM at pH 9 131

E.6 Effect of pH on Boron Retention using PNSM 131

E.7 Effect of Loading on Boron Retention and Flux using COP at pH 9 131

E.8 Effect of pH on Boron Retention using COP 132

E.9 Effect of Loading on Hexavalent Chromium Retention and Flux using PDAM at pH 4 132

E.10 Effect of Loading on Hexavalent Chromium Retention and Flux using PDAM at pH 5 132

E.11 Effect of Loading on Hexavalent Chromium Retention and Flux using PDAM at pH 8 132

E.12 Effect of pH on Hexavalent Chromium Retention using PDAM at L:0.01 133

E.13 Effect of PDAM Concentration on Hexavalent Chromium Retention and Flux at pH 4 and L:0.01. 133

E.14 Effect of Sulfate Concentration on Hexavalent Chromium Retention and Flux at pH 4 and L:0.01. 133

E.15 Effect of Sulfate Concentration on Hexavalent Chromium Retention at pH 4 and L:0.01 133

E.16 Comparison of Boron Retention Performances of PNSM and COP 134

F.1 Data Obtained from Guinier Plot of PNSM/Water Solution at pH 7. 135
F.2 Data Obtained from Guinier Plot of PNSM/Water Solution at pH 9. 136
F.3 Data Obtained from Guinier Plot of PNSM/Water Solution at pH 10. 137
F.4 Data Obtained from Guinier Plot of PNSM/Boron/Water Solution. 138
F.5 Data Obtained from Guinier Plot of COP/ Water Solution at pH 7. 139
F.6 Data Obtained from Guinier Plot of COP/ Water Solution at pH 9. 140
F.7 Data Obtained from Guinier Plot of COP/ Water Solution at pH 10. 141
F.8 Data Obtained from Guinier Plot of COP/Boron /Water Solution. 142
G.1 Concentration versus Relative Viscosity Data 143
G.2 Viscosity average molecular weights of PNSH, PNSM and PNSL. 145

LIST OF FIGURES

2.1.1 Schematic representation of PEUF process 13

2.4.1 Percentage of boric acid with changing pH 22

2.4.2.1 Proposed structure of boric acid and borate esters with β- and γ-diols. 23

2.4.2.2 Steric considerations in the formation of borate esters with linear polyols 24

3.2.1 Synthesis of methacrylate ester polymer with hydroxyalkyl amine functions 40

3.2.2 Synthesis of poly(4-Vinyl-1,3-dioxalan-2-one-co-vinyl acetate) 42

3.2.3 Synthesis of poly (N,N-diallyl morpholinium bromide) 43

3.3.1 Schematic diagram of Osmonics Sepa CF Membrane Cell 44

3.3.2 Schematic diagram of Amicon-Millipore Membrane Cell. 45

4.2.1 Effect of loading on the flux and retention of boron using PNSH 55

4.2.2 Effect of pH on the retention of boron using PNSH 57

4.2.3 Effect of loading on the flux and retention of boron using PNSL 59

4.2.4 Effect of pH on the retention of boron using PNSL 60

4.2.5 Effect of loading on the flux and retention of boron using PNSM. 62

4.2.6 Effect of pH on the retention of boron using PNSM 64

4.2.7a Effect of Loading on the retention of boron and flux using COP 65

4.2.7b Effect of pH and loading on the retention of boron using COP 66

4.2.8 Effect of pH on the retention of boron using COP. .67

4.3.1 Comparison of Boron Retention Performances of PNSM and COP. 70
4.5.1a Effect of loading on the retention of Cr(VI) using PDAM at pH 8 75
4.5.1b Effect of loading on the retention of Cr(VI) using PDAM at pH 5 76
4.5.1c Effect of loading on the retention of Cr(VI) using PDAM at pH 4 76
4.5.2 Effect of PDAM concentration on the flux 77
4.5.3 Effect of pH on the retention of Cr(VI) at a loading of 0.01 81
A.1 Calibration Curve with the Intensity and Concentration Relation of the Related Permeate Analysis 107
A.2 Calibration Curve with the Intensity and Concentration Relation of the Related Feed Analysis 111
B.1 Calibration Curve with the Intensity and Concentration Relation of the Related Permeate Analysis 111
B.2 Calibration Curve with the Intensity and Concentration Relation of the Related Feed Analysis 112
C.1 Calibration Curve for Chloride 114
C.2 Calibration Curve for Sulfate 115
F.1 Guinier Plot of PNSM / Water Solution at pH 7. 135
F.2 Guinier Plot of PNSM / Water Solution at pH 9. 136
F.3 Guinier Plot of PNSM / Water Solution at pH 10. 137
F.4 Guinier Plot of PNSM / Boron / Water Solution 138
F.5 Guinier Plot of COP / Water Solution at pH 7. 139
F.6 Guinier Plot of COP / Water Solution at pH 9. 140
F.7 Guinier Plot of COP / Water Solution at pH 10. 141
F.8 Guinier Plot of COP / Boron / Water Solution 142
G.1 Relative viscosity versus concentration graph for PNSH. 144
G.2 Relative viscosity versus concentration graph for PNSM. 144
G.3 Relative viscosity versus concentration graph for PNSH. 145

LIST OF SYMBOLS

A_2	Second Virial Coefficient
AAS	Atomic Absorption Spectrometry
AIBN	Azo-bis-iso-butyronitrile
CC	Continuous Concentration, ppb
C_{avg}	Average Concentration
C_f	Feed Concentration (mg/L)
C_p	Permeate Concentration (mg/L)
CF	Cross-flow
COP	poly(4-Vinyl-1,3-dioxalan-2-one-co-vinyl acetate)
Cr(VI)	Hexavalent Chromium
CEUF	Complexation Enhanced Ultrafiltration
CoUF	Colloid Enhanced Ultrafiltration
Da	Dalton
DAM	N,N-Diallylmorpholinium bromide
DLS	Dynamic Light Scattering
ELM	Emulsion Liquid Membrane
EPA	Environmental Protection Agency
F	Flux, (L/m^3.h)
GMA	Glycidyl methacrylate
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
L	Loading (g metal / g polymer)
MC	Maximum Concentration (ppb)
MEUF	Micellar Enhanced Ultrafiltration
MF	Microfiltration
MWCO	Molecular Weight Cut-Off
M_w	Weight Average Molecular Weight
M_w	Viscosity Average Molecular Weight
NF	Nanofiltration

PDADMAC	Poly(diallyldimethylammonium chloride)
PEI	Polyethylenimine
PEUF	Polymer Enhanced Ultrafiltration
PGMA	Poly(glycidylmethacrylate)
PNS	Hydroxyethylamino glycerol functioned polyglycidyl methacrylate
PVA	Poly(vinyl alcohol)
QUAT	Poly(diallyldimethyl ammonium chloride)
R	Retention
Rg	Radius of gyration, (nm)
R_H	Hydrodynamic Radius, (nm)
RF	Radio Frequency
RSD	Relative Standard Deviation
RO	Reverse Osmosis
SLM	Supported Liquid Membrane
SLS	Static Light Scattering
UF	Ultrafiltration

	Subscripts
R	Retention
p	Permeate
f	Feed
avg	Average

CHAPTER I

INTRODUCTION

Environmental contamination due to wastewater discharges containing high concentrations of heavy metals is an important environmental issue [1]. Many metals, especially heavy metals like Cr, Cd, Hg, Zn, Pb, etc., have become an ecotoxicological hazard of primary concern. The major problem with these contaminants is their toxicity against all living organisms, in particular, humans [2]. Since metals have high solubility in the aquatic environments, they can be absorbed by living organisms. Once they enter the food chain, large concentrations of these contaminants may accumulate in the human body, causing serious health disorders [3]. In Table 1.1, recommended water quality criteria published by EPA (Environmental Protection Agency), for priority toxic pollutants are given [4].

Table 1.1 EPA Recommended Water Quality Criteria for Priority Toxic Pollutants

	Fresh Water		**Salt Water**		**Human Health or Consumption of**	
	MC (ppb)	CC (ppb)	MC (ppb)	CC (ppb)	Water + Organism MC (ppb)	Organism Only MC (ppb)
As	340	150	69	36	0.018	0.14
Cod	4.3	2.2	42	9.3	-	-
Cr(VI)	16	11	1100	50	-	-
Cu	13	9.0	4.8	3.1	1300	-
Hg	1.4	0.77	1.8	0.94	0.05	0.051
Ni	470	52	74	8.2	610	4600
BP	65	2.5	210	8.1	-	-
Zn	120	120	90	81	9100	69000

Increasing regulations on natural resource usage and industrial wastewater discharge have caused an increased interest in the removal and recovery of these ions from waste streams. Besides the negative environmental and health effects, some heavy metals are non-renewable resources and production of some of these metals for commercial uses is difficult. It is, therefore, essential to remove and recover these inorganic contaminants both for diminishing the possibility of uptake by plants, animals and humans and to prevent them from contaminating surface and ground waters and also for reusing them in industrial applications [5].

Metals present as anionic forms in aqueous solutions are especially complex targets to be removed. Unlike metal cations, metal anions are coordinatively saturated and they can not form covalent bonds to ligands easily [6]. In the literature, there are several studies for metal cation removal from aqueous solutions using both conventional and novel separation techniques [2,3, 7-13]. However, studies related with the removal of anions from aqueous solutions are limited.

Boron is a naturally occurring element which is widely distributed in the environment mainly in the form of boric acid or borate salts [14]. Even if it is an important micronutrient for plants, animals and humans, the range between deficiency and excess is narrow [15]. According to world health organization boron content of drinking water should be less than 0.3 mg/L. Turkey possesses approximately 60 % of the world's boron reserves. Boron concentration can reach values as high as 30-40 mg / L in geothermal waste water and drainage water discharged from boron mines. This causes a threat of boron pollution to the receiving rivers. Therefore there is an urgent need for a separation method for effective removal of boron.

Hexavalent chromium is a strong oxidizing agent and is one of the most serious environmental problems in several countries [16]. Industrial sources of chromium include leather industries (tanning), metal-plating industries, pigments and paints, and chromium mining and milling operations [17]. In Turkey, leather industry is highly developed in many areas and there is a threat of chromium contamination in the receiving rivers near the tanning facilities. The leather tanning process is composed of several batch stages associated with the consumption of large amounts of freshwater as well as the generation of liquid and solid wastes. Although tanning can be performed according to different procedures, most of the leather is obtained with chromium salts as the tanning agent. The wastewater discharged from the tanning process contains approximately 3000-4000 mg/L hexavalent chromium which is far much higher than the permissible level. Besides Cr(VI), high amounts of sulfate and chloride are also present in the discharge of the tanning process. Therefore, it is necessary to lower the hexavalent chromium concentration in the wastewater down to 50 µg/L level.

The removal and separation of toxic and environmentally relevant ions is a challenging phenomenon. Conventional methods include precipitation, sorption on water-insoluble ion-exchange resin, coagulation-flocculation, flotation, adsorption, crystallization, evaporation, etc.

In industrial applications, chemical precipitation has been the most common technology for metal removal. Metals can be precipitated as metal oxides/hydroxides, sulphides, carbonates and phosphates [18]. Metals can not be removed completely by hydroxide precipitation. Higher degrees of removal can be achieved by sulfide precipitation, but in this case high volumes of toxic sludges which are difficult to dispose are produced [19]. One of the major drawbacks of precipitation is the fact that, it can only reduce the dissolved metal concentration to the solubility product level. This level is often out of the discharge permit standards and needs further polishing stages [20]. Although it is generally used as a stand alone method chemical precipitation, can be very appropriate as a first step of a hybrid separation process when it is systematized properly [21]. Precipitation of sparingly soluble metal compounds followed by micro- or ultrafiltration [22], bioaccumulation and microfiltration [23], and precipitation followed by polymer enhanced ultrafiltration [24] are amoung the possibilities as the second step of the hybrid processes.

After pH adjustment, the dissolved metal ions are converted to insoluble solid phase via a precipitation agent. One of the major drawbacks of precipitation is the fact that, it can only reduce the dissolved metal concentration to the solubility product level. This level is often out of the discharge permit standards and needs further polishing stages [20]. In addition, there is a disposal problem for the precipitate.

Ion exchange is also a frequently used technique for wastewater treatment containing metals. In this treatment, an insoluble substance removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent amount without any structural change of the resin [25]. After separating the loaded resin, the metal is recovered in a more concentrated form by elution with suitable reagents. However, ion exchange has some limitations in treating wastewater laden with metals. Before the ion exchange process, appropriate pretreatment is required such as the removal of suspended solids from wastewater. Moreover, suitable ion exchangers are not available for all heavy metals and the capital and operational costs are high.

Coagulation-flocculation can also be employed for metal removal. In this process colloidal particles are destabilized with the addition of a coagulant which results in sedimentation. In order to increase the particle size, coagulation is followed by the flocculation of unstable particles into bulky floccules [26]. Coagulation-flocculation has some limitations such as high operational costs due to chemical consumption, high toxic sludge discharge and disposal problems.

Sorption of metals using sorbents is one of the most popular methods that produce high-quality treated effluents. It is now recognized as an effective, efficient and economic method for water decontamination applications [27]. The adsorbents may be of mineral, organic or biological origin. Activated carbons, zeolites, clays, agricultural wastes, biomass and polymeric materials can be considered as remarkable sorbents for metal removal. Recently, numerous approaches have been studied for the development of cheaper and more effective adsorbents containing natural polymers. But limitations encountered in the use of sorbents like, slower kinetics, lower capacities due to heterogeneous reactions, and interface transfer lead researchers to search for new techniques for separating metal ions.

The other methods used for metal removal have the great disadvantage of using heterogeneous reactions or distribution of substances among different phases, which are the phenomena controlled by diffusion, requiring usually large operating times. In some other methods, final metal recovery requires additional treatments, or need for hazardous chemicals make the process more complicated [28].

The various difficulties and economical disadvantages of these methods led the researchers to perform new studies to develop easier and more economical methods. A promising way to achieve effective recovery and fractional separation of metals from aqueous solutions is membrane processes.

1.1 Membrane Processes

Membrane technologies have been one of the emerging technologies during the last 35 years. Today they are used in a large number of separation processes. They have several advantages like continuous mode of operation, low energy consumption, ease of scaling up, mild separation conditions, combination with other separation processes, and variable membrane properties [29].

A membrane can be defined as a permselective barrier between two phases. In most of the membrane processes the driving force is a pressure or a concentration difference between the phases. In water treatment several membrane processes have been used such as; pressure driven membrane processes including reverse osmosis, ultrafiltration, microfiltration, and liquid membranes [30]. Efficient separation down to ppb level for several metals is made possible by using liquid membranes [29].

1.1.1 Liquid Membrane Processes:

Liquid membrane systems contain a hydrophobic membrane phase which acts as an ion barrier between two aqueous phases. An ion carrier may be dissolved in the membrane [31]. The two phases are generally aqueous solutions, while the liquid membrane phase is an organic phase that is immiscible with water [29]. There are basically two different types of liquid membranes; emulsion liquid membranes (ELM) and supported liquid membranes (SLM).

In emulsion liquid membranes (ELM); the stability of the membranes is the major problem. If the liquid membrane breaks down easily separation efficiency is reduced, however, too stable liquid membranes cause recovery of the inner phase to be too complicated [32].

SLMs are hardly used in large-scale industrial applications due to certain problems in their performance [30]. The most serious problem is the instability of the membrane due to the dissolution of the liquid held in the micropores of the supporting membrane to the source and receiving phases [33]. Contrary to the liquid membranes, conventional pressure driven membrane processes and modules are well developed and commercially available; therefore those processes are reviewed in more detail below.

1.1.2 Pressure Driven Membrane Processes:

Pressure-driven membrane processes use the pressure difference between the feed and permeate side as the driving force to transport the solvent (usually water) through the membrane. Particles and dissolved components are partially retained based on properties such as size, shape, and charge. Pressure-driven membrane processes can be classified by several criteria: the characteristics of the membrane, like pore size, size and charge of the retained particles or molecules, and pressure exerted on the membrane. This classification distinguishes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [34]. As we go from microfiltration through ultrafiltration and nanofiltration to reverse osmosis, the size (or molecular weight) of the particles or molecules separated decreases and consequently the pore sizes in the membrane become smaller. This implies that the resistance of the membranes to mass transfer increases and hence the applied pressure (driving force) has to be increased to obtain the same flux [29].

If the dimensions of target component and non-target component differ significantly, a good separation of target component from the solution containing non-target component can be achieved. When both the target and non-target components are low molecular compounds, the selectivity of separation is generally low. All components of the solution will either be retained by the membrane (reverse osmosis) or will pass through it (diafiltration, ultrafiltration, microfiltration) [29]. Because of the size of the ions, as hydrated ions or as low molecular weight complexes, reverse osmosis seems to be the only technology which could allow a direct separation of heavy metal ions. However, from an economical point of view, this method suffers from the fact that for high fluxes of permeate high transmembrane pressure is needed, which results in high energy costs. Reverse osmosis also is not suitable for achieving selective separation of metal ions since the size difference between the metal ions is too small and in addition to metal retention all other constituents in the aqueous solution would also be more or less completely retained by the membrane and the osmotic pressure in the concentrated solution would become unacceptably high [35].

1.2 Complexation Enhanced Ultrafiltration

Ultrafiltration allows relatively high fluxes with low operating pressures but the lowest molecular weight substance that can be separated from liquid medium is approximately 500 Da, therefore, ions are poorly retained [36]. Combination of low-pressure membrane techniques and complexation is one of the most attractive propositions to improve separation. In this hybrid process, the metallic ions can be bound to macroligands so that the molecular dimension of the target component is enlarged. This constitutes the basis of complexation enhanced ultrafiltration (CEUF). In complexation enhanced ultrafiltration technique, first the target compound is bound to larger soluble macromolecules and then UF is applied to the complexes. By this way, metal and the complexation agent can be retained by the membrane while non-complexed ions and solvent pass through the membrane [37].

The complexation-ultrafiltration method has not yet been applied on industrial scale, however it has been reported that this method can be a suitable technique for the treatment of wastewaters, groundwater and seawater [38]. CEUF can be classified according to the complexation agent used [39] as; colloid enhanced ultrafiltration (CoEUF), micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF).

In CoEUF, colloids of metal hydroxides especially iron and aluminum hydroxides were used as a complexing agent to enlarge the target metal molecular size [40]. Because of low selectivity and pH limitations this technique is not widely used.

MEUF is another CEUF technique in which ionic surfactant is added to the aqueous solution containing the metal ions to be removed with the opposite charge. The surfactant forms highly charged aggregates called micelles above a certain concentration known as critical micelle concentration (CMC). The concentration of surfactant should be well above the critical micelle concentration so that micelles can be formed [41]. The micellar surface has a high charge density and electrical potential so that the ions are electrostatically adsorbed or bound to the surface. Then this mixture is passed through an UF membrane with pores small enough to block the passage of the micelles [42]. Disadvantages such as inapplicability to remove low concentrations of metals, requirement for high amount of surfactant to exceed the critical micellar concentration and inselectivity, limits the application of MEUF in industrial scale.

Both in CoEUF and MEUF techniques, two phase systems are utilized for the separation. Possibility of homogeneous aqueous phase may make CEUF more beneficial by preventing the interface mass transfer resistance. Polymer enhanced ultrafiltration is a promising technique to achieve higher efficiency and selectivity of target component in homogeneous aqueous phase [43].

1.3 Polymer Enhanced Ultrafiltration

Use of water soluble functional polymers in combination with ultrafiltration to separate ions from aqueous solutions by complexation is called polymer enhanced ultrafiltration [35]. In PEUF technique membrane is just a barrier that has to retain everything bound to the polymer and allow permeation of the unbound components.

The majority of the applications of polymer enhanced ultrafiltration are related to the removal and recovery of heavy metals from wastewaters. It was reported that metal ions, such as copper, nickel, lead, chromium, mercury and arsenic, can be selectively removed from multicomponent solutions of different origins [30, 44, 45]. It is also used to remove components from natural waters, groundwater and seawater.

The performance of PEUF process is determined by two factors, namely retention and permeates flux. Retention values (R) are calculated by the following expression:

$$R_i = 1 - \frac{C_{pi}}{C_{f\,i}} \qquad (1.1)$$

where C_{pi} is the concentration of metal ion “i” in the permeate and C_{fi} is the concentration of metal ion “i” in the feed.

The separation process will be successful if the polymer used has high affinity toward target component, inactivity towards nontarget component, high molecular size, possibility of regeneration, chemical and mechanical stability, low toxicity and low cost. There are various kinds of water-soluble polymers that can be classified into several groups according to the chemical moieties present. Many of these polymers are designed for different industrial applications, but only some functional soluble polymers are found to be suitable for PEUF processes [38].

The heart of PEUF technique is the polymer used for complexation. Therefore, it is crucial to select a suitable polymer for the target component to bind. Polymers used in PEUF studies can be classified into two categories, polyelectrolytes (non-co-ordinating polymers) and polychelatogens (co-ordinating polymers). polyelectrolytes and polychelatogens. Polyelectrolytes are polymers bearing dissociated ionic groups. They partially dissociate in the aqueous solution into polyions and small ions of opposite charge, known as counterions [33]. Polychelatogens are water soluble functional polymers containing ligands at the main or side chains that are capable of forming chelates with metal ions [34]. Binding of polyelectrolyte with metal ions is due to electrostatic interaction. However polychelatogens bind to metal ions via coordinative covalent bonds. These type of bindings are significantly more selective than electrostatic interaction.

In the literature, most of the PEUF studies, investigated the removal of cationic metals and applied PEUF in batch mode. The purpose of those studies was mainly to investigate the synthesis and UF applications of the polymeric agents and study their binding capacity. Very few studies investigated the removal of metals that are in the form of anions in aqueous solutions. Furthermore, in most of these studies, metal ion removal was carried in batch mode. Continuous PEUF systems have been less frequently studied by the researchers. However, it is important to have a continuous process in order to have an insight on the possibility of using PEUF at industrial scale by investigating the process parameters on the separation performance of the technique [39].

In earlier studies of our group, continuous PEUF was employed efficiently for the removal of mercury and cadmium from multi component solutions as the effects of the operating parameters were investigated [35, 48]. A hybrid precipitation and polymer enhanced ultrafiltration process was applied for fractional separation of heavy metals from real electroplating waste effluent. At the end of the precipitation steps, concentrations of metals in the samples were reduced down to suitable limits for PEUF. Then PEUF was employed for further removal of the target metals [49]. In all of these studies poly(ethyleneimine) (PEI) was employed as the complexing agent. PEUF was also employed for boron removal using polyvinyl alcohol [14] and a specially synthesized polymer, N-methyl-D-glucamine grafted Poly (GMA) [50]. In these studies, effect of pH, loading and polymer type on the retention of boron were investigated and it was observed that boron retention increased significantly when the specially synthesized polymer was used.

1.4 Aim and Scope of The Study

In the literature, most of PEUF studies deal with the removal of cationic metals. Very few studies investigated the removal of metals that are in the form of anions in aqueous solutions. Furthermore, in most of these studies, metal anion removal was carried in batch mode; therefore, operating parameters were not investigated. Anions like chromate and borate represent especially complex targets, as they are coordinatively saturated and cannot form covalent bonds to ligands easily. Many commercially available anion exchange resins make use of electrostatic attraction to retain anions, but such interactions do not generate selectivity in anion retention. In waste water treatment, the design of selective ligands for anions is complicated by additional factors. It is necessary to synthesize highly highly selective ligands that will bind to the target metal which is present in very low concentrations and in the presence of other anions [6].

In this study, two chelating polymers for borate and a strong cationic polyelectrolyte for chromate were synthesized for investigating the separation performance of these polymers from aqueous solutions. In order to explore the suitable conditions for the maximum retention of the target metal anion with the highest possible permeate flux a parametric study was performed utilizing continuous polymer enhanced ultrafiltration. Effect of process parameters such as pH, loading, polymer type (for borate retention), and effect of competing anion (for chromate retention) were investigated.

It is known that polyol groups are capable of forming stable complexes with borate at basic pH. In most of the previous studies polymers with sugar derivatives were used as complexing agents. However chemical stability of the sugar functions is limited. This may be a disadvantage for the regeneration of the polymer using acids. Therefore, in this study two polychelatogens, hydroxyethylamino glycerol functioned polyglycidyl methacrylate (pGMA) and a copolymer, poly (4-Vinyl-1, 3-dioxalan-2-one-co-vinyl acetate), were synthesized, which are much more stable than sugar derivatives and resistant to acid hydrolysis. Effect of process parameters such as loading, pH and polymer type on borate retention were examined using PEUF.

In the literature, there is no study that utilizes polychelatogens for chromate removal. All of the studies make use of polyelectrolytes for the retention of chromate. Especially quaternary ammonium polymers such as poly (dimethyl diallyl ammonium chloride), were found to be promising materials. Therefore, in this study a polyelectrolyte, poly (N, N-diallyl ammonium bromide), which contains quaternary ammonium groups that is fully ionized at all pH values was synthesized. Besides the effect of loading and pH on chromate retention, effect of competing anions that can be present in waste waters containing Cr(VI), such as chloride and sulfate were also investigated to see the effect of anion charge to the selectivity of the synthesized polyelectrolyte. Furthermore, to see the effect of crowding in the feed solution to the retention of chromate effect of polymer concentration at a fixed loading was investigated.

Finally, the characteristics of association between the synthesized polymers and metal anions and effect of pH on this association were investigated by performing dynamic and static light scattering measurements. Radius of gyration and hydrodynamic radius of the synthesized polymers and metal-polymer complexes were determined for different experimental conditions.

CHAPTER 2

LITERATURE SURVEY

Several methods have been applied to remove metal ions from aqueous solutions, such as; precipitation, use of water insoluble ion-exchange resins and organic solvents. But limitations encountered in these methods like, precipitate disposal problems, slow kinetics, low capacities due to heterogeneous reactions, and interface transfer lead researchers to develop new techniques for separating metal ions [48].

Use of chemically inert membranes makes it possible to achieve separations in the homogeneous aqueous phase [43]. They have several advantages like continuous mode of operation, low energy consumption, ease of scaling up, mild separation conditions, easy combination with other separation processes, and variable membrane properties [29].

Ultrafiltration (UF) processes are well known in industrial separation technology to remove and recover macromolecules and colloids from solutions with relatively high fluxes with low operating pressures. However, ordinary ultrafiltration methods are not effective in removing solutes having molecular weights less than about 500 daltons [51]. The main disadvantage of UF for treatment of effluents with heavy metals is ionic size of the dissolved metallic salts. These ions, as hydrated ions or as low molecular weight complexes, would pass easily through all membranes with the exception of reverse osmosis membranes [52].

One promising method for having a more selective metal removal, with low energy cost, and high rejection coefficient, is the use of polymers in combination with ultrafiltration. This technique is called polymer enhanced ultrafiltration (PEUF) [35].

2.1 Polymer Enhanced Ultrafiltration (PEUF)

Schematic representation of PEUF process can be seen in figure 2.1.1.

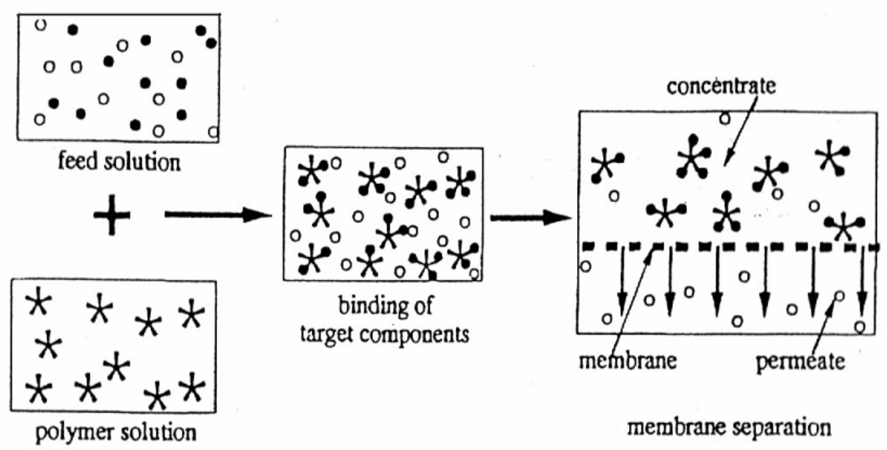


Figure 2.1.1 Schematic representation of PEUF process

There are several advantages inherent to polymer enhanced ultrafiltration compared to other conventional water treatment techniques, such as reverse osmosis and ion-exchange. One important advantage of this process is that, the complexation can be made selective for any target compound based on the knowledge of complexation chemistries. Theoretically, the same functional groups used in the preparation of insoluble resins can be incorporated to the water soluble polymers, thus diffusion limitations observed in resins can be eliminated [53]. Since PEUF employs only a single aqueous phase, the problems of multiphase separation processes like mass-transfer limitations, interphase reactions and membrane instability are not observed [32]. Furthermore, having low transmembrane pressures, UF process requires lower energy for operation which makes PEUF process a promising technique for metal ion retention.

In majority of the previous PEUF studies, batch systems were employed mostly for the retention of cations [36, 43, 54-56]. This mode shows some disadvantages like feasibility only for small scale processes and existence of dead operation times.

Since, in most of the previous studies batch mode of PEUF was employed the feed concentrations were not constant throughout the experiments, therefore the effect of operating parameters were not investigated. Even though it has significant advantages there are few studies using continuous mode of PEUF [14, 35, 39, 48, 49, 57-60].

Continuous mode of PEUF was reported to be feasible for large scale operations [71]. Besides, it enables the investigation of operating parameters and it may clarify the possibility of the handling of wastewater with PEUF in industrial scale. In one of the previous studies, separation of metals from aqueous streams by continuous PEUF was simulated in order to understand, evaluate and optimize the process feasibility. It was shown that, proposed separation process can produce good quality water at high production rates, using a convenient polymer-metal system by fixing the appropriate operating variables [58]. In study of Lorens *et al.* feasibility of a continuous PEUF process was tested for water softening process in the presence of a weakly ionized polyelectrolyte poly(acrylic acid-maleic anhydride) sodium salt) [59] and it was shown that the proposed system have the ability to continuously remove Ca^{2+} from water satisfactorily. In another study a continuous hybrid ultrafiltration process consisting of consecutive separation and regeneration units were used for the separation of Cu^{2+}, Co^{2+} and Pb^{2+} and regeneration of the polymeric binding agents like carboxymethyl cellulose, pectin and polyethylene imine (PEI) were investigated using continuous mode of PEUF [60].

In the previous studies of our research group continuous mode of polymer enhanced ultrafiltration processes were applied for boron [14, 50], mercury and cadmium [35, 48] removal from aqueous solutions and effects of operational parameters like metal/polymer ratio and pH on the performance of the process was investigated with the help of continuous mode operation.

2.2 Polymeric Materials for PEUF Studies

In PEUF studies, selection of the polymer to be used for complexation with the target metal ion plays an important role in the efficiency and the selectivity of the process. Therefore, it is crucial to find a suitable polymer to achieve complexation with target metal. PEUF technique will be successful if the polymer used has high affinity toward target component, inactivity towards non-target component, high molecular mass, possibility of regeneration, chemical and mechanical stability, low toxicity and low cost [61].

The molecular mass of the polymeric agent should be high enough to ensure efficient separation of the non-target component and complete retention of the target component according to the molecular exclusion limit of the membrane. However, if the molecular mass is too high, it results in a high viscosity solution which leads to a reduction in the size of the macromolecules [62]. This size reduction along with concentration polarization bring along polymer permeation through the membrane, which eventually reduce the permeate flux and increase the process cost [54].

Chemical and mechanical stability of the polymers are two other important parameters that should be considered in the selection of polymeric agents to be used in PEUF process [38]. Chemical instability may arise from the degradation of the polymers due to hydrolysis. In some cases mechanical instability of the polymer may be a drawback. Since the feed solution containing the polymer is pumped to the ultrfiltration unit by means of a pump, degradation of soluble polymers may arise due to mechanical shearing by pumps. Therefore, it was stated that low-shear pumps should be used to ensure mechanical stability of the polymers [54].

There are some important criteria in the selection of polymers to be used for metal ion removal using PEUF such as; sufficient solubilizing power of the constitutional repeating unit which provides water solubility of the polymer complexes, having a great number of functional groups for high capacity, and reasonably high molecular weight which allows an easy separation.

In the literature, the main concern of the majority of the previous PEUF studies was to find suitable polymers to achieve complexation with target metal ion. There are plenty of commercially available water soluble polymers that can be classified into several groups according to the chemical groups present as moiety [54]. A variety of water-soluble polymers containing carboxylic acid, sulfonic acid, amide, and phosphonic acid groups have been synthesized to be used in combination with membrane filtration. There have been several reviews dealing with water soluble polymers in combination with ultrafiltration [54, 63-66].

Water soluble functional polymers can be classified into two categories, non-co-ordinating polymers (polyelectrolytes) and co-ordinating chelating polymers (polychelatogens).

Polyelectrolytes are polymers which have many ionizable groups. They partially dissociate in the aqueous solution into polyions and small ions of opposite charge, known as counterions [46]. Polyelectrolytes can adopt numerous conformations in aqueous solutions. The charge and shape of the conformation are determined by the charge of the polymer and interactions with counterions. The polymer conformation can change from a contracted coil to an expended rod with increasing charge [17]. Retention of metal ions by polyelectrolytes is generally due to the electrostatic interaction of the positively or negatively charged sites of the polyelectrolyte with the oppositely charged metal ion. It is known that the interactions which are dominated by electrostatics are more sensitive to the presence of other ions in the solution as compared to the coordinative bonds. Polyelectrolytes can be cationic, anionic or amphoteric. There are many varieties of cationic polymers available, as has been reviewed in detail. Generally they possess quaternary ammonium groups that have a formal positive charge irrespective of pH, and are termed as strong polyelectrolytes. Weak polyelectrolytes that acquire cationic properties in acidic media are also available. These weak cationic polyelectrolytes are based on polyamines [66]. The most commonly used anionic polymers contain weakly acidic carboxylic acid groups, so the charge density depends on pH. Anionic polymers that contain strongly acidic groups, which are fully ionized at normal operating pH levels are also present. These polyelectrolytes generally possess phosphorus groups. Amphoteric polyelectrolytes contain both anionic and cationic sites on the same polymer chain. Copolymers of strongly basic cationic monomers and strongly acidic anionic monomers can be used as amphoteric polyelectrolytes [66].

In polychelatogens co-ordinate covalent bonds are formed [67]. These types of bindings are significantly more selective than ionic interactions. The complexation of water-soluble polymers with metal ions occurs in the same manner as in the case of chelating resins. The polymers that are capable of forming chelate rings usually include functional groups that comprise oxygen, nitrogen and sulfur in their structure and usually contain polyfunctional groups. Nitrogen can be present in a primary, secondary or tertiary amine, nitro, azo, amide or other groups. Oxygen is usually in the form of phenolic, carbonyl, carboxylic, hydroxyl and some other groups. Sulfur is in the form of thiol, thioether, disulphide groups *etc*. Functional polymers are of interest because the functional group has a desired property or can be used to attach some moiety with the desired property. Functional groups can be introduced into the polymer by chemical transformation of the matrix or by the synthesis of the polymer from the monomeric ligands. The insertion of suitable highly selective functional groups into the polymeric matrix makes them capable of interacting with metal ions to form chelate rings [67].

The most usual procedures for the synthesis of chelating polymers are addition polymerization, especially radical polymerization, and functionalizing of polymer backbones through polymer-analogous reactions. The macromolecules can be homo- or copolymers and may contain one or more coordinating and/or charged groups. These groups are placed at the backbone, or at the side chain, directly or through a spacer group [47].

Many researchers investigated the synthesis and UF application of several water-soluble polymers. Poly(ethyleneimine)-based reagents have been used in many studies as complexing ligand, as well as a versatile source of chelating derivatives for removing metal ions from aqueous solutions via PEUF [35, 39, 49]. Among these, poly (acrylic acid) and copolymers with acrylamides [68, 69], N-maleyl glycine [70], N-vinyl-2-pyrolidone [69], poly (2-acrylamido-2-methyl-1-propane sulfonic acid) [71], as well as mixtures of two polychelatogens [72] were investigated for their ability to bind di- and trivalent cations. The most investigated ligands present in the polychelatogens are amines, carboxylic acids, amides, alcohols, aminoacids, pyridines, thioureas, iminos, etc. Among them, polymers containing amino groups have been extensively studied by ultrafiltration, particularly the functional polyethylenimine [73].

2.3 Effects of Operational Parameters on The Performance of PEUF

Besides the selection of the functional polymer, there are some other important criteria for the process to be effective. These are pH, loading, ionic strength, and membrane type.

pH is one of the most important factors in the interaction of a metal ion with a binding polymer. By changing the pH values appropriately it is possible to have high retention values in the separation of metal ions in one extreme and to disassociate polymer-metal complexes in the other extreme. The latter will enable the recovery of the concentrated metal present in the feed and regeneration of the complexing polymer. If several metal ions form macromolecular complexes with different stability constants, it is possible to separate them by varying the pH [54].

Effect of pH, on the binding ability of polymers as well as on the performance of the PEUF operation was the subject of various studies in literature [37, 39, 74-76]. In one of the studies, polymers containing carboxylic acid, phosphoric acid and sulfonic acid groups were investigated and maximum retention capacity (MRC) of the polymers for Ag (I), Cu (II), Co (II), Ni (II) and Cr (III) were determined at different pHs. They concluded that there was an important effect of the pH on the MRC [64]. In another study, PEI was used as the chelating polymer for the removal of mercury and cadmium from binary mixtures using PEUF [35]. The influence of various operating parameters including pH, on the retention of metals was investigated and it was shown that at low pH values mercury was removed by UF operation while almost all cadmium passed through the membrane. By another group, the removal of hexavalent chromium from an aqueous solution using PEUF was investigated at different pH values and a maximum in the retention of Cr (VI) was observed at pH near 5. It was concluded that since the most active form of Cr(VI) prevails in the pH range of 4.5-5.5, the maximum binding degree hence the maximum retention was obtained at pH ~5 [77]. In another study, the removal of cadmium ions from aqueous solutions where chitosan was the chelating agent was carried out by polymer enhanced ultrafiltration (PEUF). They showed that chitosan, is able to complex Cd^{2+} at neutral pH and when pH is lowered to a value of about 4, Cd^{2+} is released and chitosan can be regenerated by alkali addition [78].

It is stated that there exists a pH value above which stable polymer-metal complex is formed depending on the polymer and metal ion type [79]. In a study, the retention of metal ions such as copper, nickel, zinc, cadmium, mercury, manganase, cobalt were investigated using PEI and its thiourea derivative by PEUF and observed that copper forms the most stable complexes with PEI at lower pH (≤ 3) while manganase is completely retained at pH greater than 8 [43]. This means that for each metal ion, complete complexation with polymer takes place at different pH values which enables selective separation of two metal ions unless the pH values of stable complex formation are not close to each other.

Loading (metal/polymer ratio) is another important but rarely studied parameter in PEUF. Decreasing the loading (increasing polymer concentration) increases the binding capacity. From this point of view it seems that the use of excess complexing agent enhances the retention of metal ion. However, when the polymer concentration is too high both retention and flux decreases. This is primarily caused by an increased viscosity of the solution and also by concentration polarization [54]. Besides, it is known that macromolecules reduce their size in concentrated polymer solutions [62]. This size reduction along with concentration polarization results in an increased polymer permeation through the membrane hence reduce the permeate flux, and decrease of complexation of target ion with active sites of the polymer.

The effect of loading on the performance of PEUF can be realistically observed in a continuous system [14, 35, 48-50]. In a study of our group, separation of mercury ions was investigated using PEI as complexing agent by continuous PEUF and effects of operating parameters including loading was studied on the retention of mercury. Constant retention values were obtained until a critical loading was exceeded and after that point the retention of mercury decreased with the increase in the loading [48]. In another study retention of cadmium ions was studied using chitosan as chelating polymer by PEUF. Similarly, they showed that with the increase in polymer concentration, retention of cadmium increased [59].

Ionic strength is another important parameter in polymer enhanced ultrafiltration, which can be expressed by the following formula [80]:

$$\mathrm{IonicStrength} = \mu = \frac{1}{2}\left([A]Z_a^2 + [B]Z_b^2 + [C]Z_c^2 + ...\right)$$

where, [A], [B], [C], represent the species molar concentrations of ions A, B, C, and Z_a, Z_b, Z_c... are their charges, respectively.

It was reported that the amount of metal ions free in solution and that of bound to polymer are strongly dependent on the ionic strength [81]. Furthermore, it also influences the stability of the metal ions-polymer complex [82]. This is attributed to a change in the value of the dissociation constant during filtration, due to screening effects, changes in the polymer conformation, and competition between monovalent and polyvalent metal ions for binding the polymer. When the ionic strength of the solution containing the polymer is high, the dissociation constant increases, which leads to a decrease in the retention ability of the polymer. Furthermore, increasing the salt concentration leads to compression of the electrical double layer and thus to reduction in the electrostatic attraction between ions and polymers [83].

Generally water-soluble polymers are sensitive to the presence of suspended particles in solution since many of these polymers have flocculent properties that will result in polymer precipitation. When the ionic strength of the solution is high, solubility of a polymer reduces and hence precipitation may occur [28].

Many researchers studied the effect of ionic strength on metal removal using different polymers or adsorbers. Biosorption of metals by marine algae [85], retention of Ni on illite [86], adsorption of metal ions on activated carbons [87], metal-ligand interactions in the Co^{2+}-citrate and Ni^{2+}-citrate systems [88] can be counted as examples of the studies investigating the effects of ionic strength on the complexation mechanism of the components present in aqueous solutions. The common conclusion derived from these studies is that, depending on the nature of interaction, increase in ionic strength may increase or decrease the adsorption or complexation of the metals.

When polyelectrolytes are used in PEUF process for binding the metal anions or cations, presence of co-anions or co-cations may significantly effect the retention of the target component by the polyelectrolyte. Since, polyelectrolyte-metal ion retention mechanism is mainly due to electrostatic interaction, co-anions or co-cations in the solution can compete with the target component for the active site of the polyelectrolyte, hence decreasing the retention of the target component [89]. This competitor effect may be reduced by chemical modification of the polymer [90]. Besides, as a secondary effect, presence of co-anions or co-cations also increases the ionic strength of the solution which in turn may change the polyelectrolyte conformation and affect the target ion retention. Therefore, it is necessary to identify whether the decrease in the retention of target component is due to competition or as a result of the change in the ionic strength of the solution in order to have an insight on the retention of metal ions via polyelectrolytes.

In the literature, most of the functional polymer based separation techniques for metal removal, deal with the removal of cationic metals. Very few studies investigated the removal of metals that are in the form of anions in aqueous solutions. Furthermore, in most of these studies, metal anion removal was carried in batch mode; therefore, operating parameters were not investigated. Therefore, in this study specially synthesized functional polymers were used to investigate the effect of operating parameters on the retention of two anions, borate and chromate, via continuous mode of polymer enhanced ultrafiltration.

2.4 Boron Removal from Aqueous Solutions by Membrane Processes

2.4.1 Boron Chemistry

When boric acid dissolves in water, it forms borate ions according to the reaction given below [91]:

$H_2O + B(OH)_3 \leftrightarrow B(OH)_4^- + H^+$ $\quad pK_a = 9.14$

Additionally boric acid can interact with hydroxide ion to form borate ion [91]:

$OH^- + B(OH)_3 \leftrightarrow B(OH)_4^-$

Another suggested reaction mechanism of boric acid dissolution is given as;

$H_3BO_3 \leftrightarrow H_2BO_3^- + H^+$ $\quad pK_{a1} = 9.14$

$H_2BO_3^- \leftrightarrow HBO_3^{2-} + H^+$ $\quad pK_{a2} = 12.74$

$HBO_3^- \leftrightarrow BO_3^{3-} + H^+$ $\quad pK_{a3} = 13.80$

In figure 2.4.1, percentage of boric acid in aqueous solution with respect to pH is given. With increasing pH, concentration of boric acid starts to decrease. There is a sharp decline in the boric acid concentration from pH 6.5 to 11.5. After that point, boric acid amount becomes insignificant [92]. As boric acid concentration decreases, borate ion concentration increases and reaches its maximum value between pH 10 and 12 which can be compared with the initial boric acid concentration.

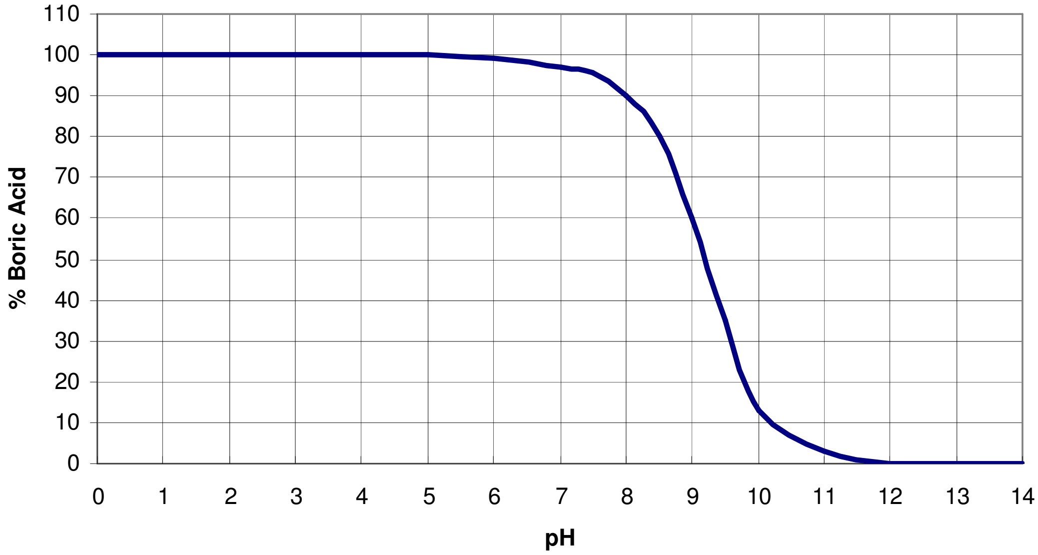


Figure 2.4.1 Percentage of boric acid with changing pH [92]

2.4.2 Boron Complexation

Boric acid is known to make complexes with polymers containing favorably oriented hydroxyl pairs. Classes of chemicals that contain suitable hydroxyl groups include polyols (compounds containing multiple hydoxyl groups), 1,2-benzenediols (catechols), α-hydroxyl carboxylic acids and dicarboxylic acids. Hydroxyl pairs can chelate both boric acid and borate as shown in figure 2.4.2 [93].

Boric acid and borate ion also react with chemical compounds containing multiple hydroxyl groups (polyols), such as mannitol, generating anionic complexes at the neutral pH of water. However regenerabilities of those materials are limited. With carbohydrates and most polyol possessing 1,2-diol systems, borate ion forms anionic mono (1:1) and bis (1:2) diol monoborate complexes [94]. As one might suspect from the equilibria shown in figure 2.4.2.1 that, the borate esters from the reaction of boric acid with diols are favored at high pH but dissociate under acidic conditions [53].

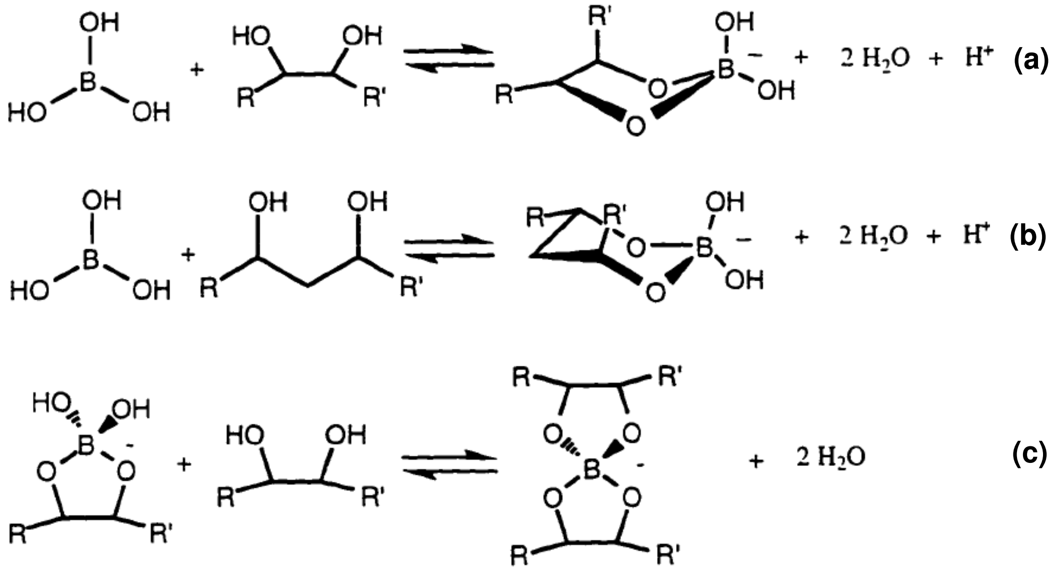
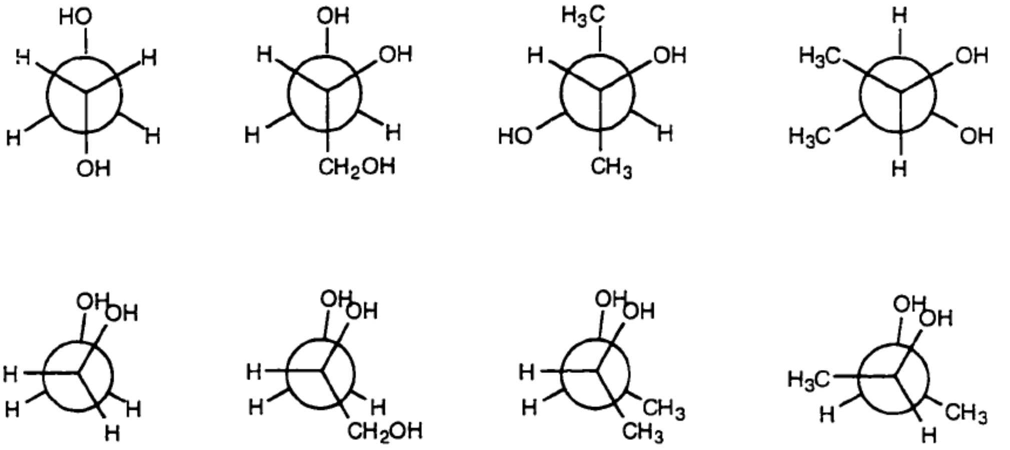


Figure 2.4.2.1 Proposed structure of boric acid and borate esters with β- and γ-diols.

The stability of borate complex formed is strongly dependent on the type of diol, namely 1,2 or 1,3-diols. If diol involves –OH groups oriented in such a way that they accurately match the structural parameters required by tetrahedrally coordinated boron, a strong complex will be formed [95].

It was proposed that glycerol was much more reactive than ethylene glycol because the steric repulsion of hydroxyl groups in ethylene glycol led to an unfavorable conformation for ester formation. The equilibrium steric configuration can be used to explain the differences in reactivity among more complex polyols like mannitol or sorbitol [96]. Figure 2.4.2.2 shows the steric considerations in the formation of borate esters with linear polyols.

In figure 2.4.2.2, the top set of figures shows the sterically favored conformations of free compounds and the bottom set shows the conformations required for formation of borate esters. If adoption of the lower conformation induces added steric hindrance the borate ester formed become less stable. In the case of longer polyols, it is expected that the terminal pair of hydroxyls would adopt conformations like the ones in 1,2-diol pair in glycerol. Whereas, the non-terminal vicinal pairs can be either threo or erythro as in the case of 2,3-butanediol.



ethylene glycol glycerol erythro-2,3-butanediol threo-2,3-butanediol

Figure 2.4.2.2 Steric considerations in the formation of borate esters with linear polyols [96]

Polymers that are selective to boron binding have most often been prepared by the attachment of sugar-like polyol ligands to polymeric backbones of both resins and soluble polymers [55]. The complexation of boron using sugar derivatives like D-glucose, D-sorbitol and D-mannitol accompanies the formation of protons that lowers the pH. Hence, the proton itself, liberated during the complexation, limits the complexation of boron. In order to overcome this drawback, it was suggested that sugars comprising amine functions, such as N-methyl-D-glucamine (MG), should be used. The role of the amine groups in the polymer structure is to capture the proton released during the complexation reaction [56].

There are several studies investigating the binding of polyol compounds with boric acid. But in most of the studies, water insoluble polymers were used to bind with boric acid. Some of the resins used in the literature include; sorbitol modified Poly(N-glycidyl styrene sulfonamide) [97], chitosan modified with galactose [98], iminodipropylene glycol functioned glycidyl methacrylate (GMA) - methyl methacrylate (MMA) – divinylbenzene (DVB) terpolymer [99] and GM modified poly(glycidyl methacrylate-co-trimethylol-propane) [100]. The common property of the mentioned polymers is obviously, the presence of hydroxyl groups in their structures.

The important points in the preparation of an efficient chelating polymer for boron removal from aqueous solutions can be summarized as follows [101];

(i) The chelating group must have two or more hydroxyl functions which are on the same or adjacent carbon atoms.
(ii) An amine function per one mole of boric acid is essential for high chelation.
(iii) The polymer should not have hydrolysable linkages to be regenarable by acid-base treatments.
(iv) Preferably, the backbone of the polymer must be as inert as possible.

2.4.3 Membrane Processes for Boron Retention

There are several physicochemical treatment processes typically used to remove boron from water and wastewater. These are adsorption with inorganic adsorbents, ion exchange and solvent extraction [102]. Unfortunately, none of these methods are capable of reducing boron content down to upper limit of permissible level. A promising method for removing boron from aqueous solutions is the use of membrane processes. Supported liquid membrane (SLM), reverse osmosis and electrodialysis are the most commonly studied membrane processes in the literature for boron retention [91, 103-105].

Supported liquid membranes containing highly selective carrier molecules was one of the membrane methods studied for boron removal from aqueous solution. In a study, SLMs mediated by 1,3-diols were used for eliminating boron from water. In the study, an experimental set-up was designed which allows the selective transport of boric acid across SLMs made of polypropylene films impregnated with dichloro benzene, using 1,3 diols as carriers. The rates of transport across SLMs containing different carriers were determined [91].

Reverse osmosis was also used for removing boron from water. In one of the studies, the influence of pH and pressure on the elimination of boron by was studied using three membranes made up of aromatic polyamide. An increase in the rejection of boron was observed at pH values of 9.5 and above. Furthermore, it was shown that higher working pressures increased elimination of boron [104]. In another study, a new RO membrane element with high boron removal performance was developed based on the concept of affinity control between the membrane surface and boron and tight function layer to enhance size exclusion performance. A three-stage system was used that consists of sea water reverse osmosis (SWRO) with the post-treatment of alkali-brackish water reverse osmosis (BWRO) and the adsorbent for the concentrate recovery which has a high boron adsorbing capacity and efficiency due to the high boron concentration of feed water. This new SWRO system provided 94-96% of boron removal from seawater [105].

Another membrane method for the recovery of boron from effluents is electodialysis. It is an electromembrane process in which ions are transported through ion permeable membranes from one solution to another under the influence of a potential gradient. Studies about boron transport through ionic membranes are limited [106, 107]. In one of these studies, electrodialysis was used to observe the boron behavior during desalination of sea and underground water and the degree of boron removal and its residual content in desalinated water with respect to boron concentration and total salt content of a solution was investigated . It was concluded that even with the optimum conditions, the boron concentration in dialyzate can not be reduced to 0.3-0.5 mg/l when the feed boron concentration is in excess of 4.5 mg/l [107].

Investigation aimed at removal of boron compounds from aqueous solution are of special importance for desalination industry because none of the conventional desalination methods (adsorption, ion exchange, reverse osmosis, electrodialysis) is capable to reduce boron content down to a permissible level even in seawater. Removal degree of boron in these processes under conventional conditions is approximately 40–70%. Ordinary biological treatment, chemical treatment using lime, iron (II) or aluminium salts are also non-effective. Therefore, an additional removal of boron from desalinated water at the finishing stage is needed [107].

2.4.4 PEUF Technique for Boron Retention

Generally, in the earlier studies, PEUF was mostly utilized on cations in batch mode in which the feed concentration keeps changing throughout the process. In very few studies, PEUF was employed for boron removal from aqueous solutions [14, 50, 93, ,107, 018]. Similar to cation retention studies, most of the previous studies for boron retention utilize batch mode PEUF [93, 108, 109]. There are a few studies using continuous mode of PEUF [14, 50].

In a study, N-methyl-D-glucamine (NMG) grafted poly(epichlorohydrin) was used as chelating polymer for boron removal using batch mode of PEUF and boron retention performance of the synthesized polymer at different pH values was investigated. It was shown that, boron is bound much more tightly to NMG in neutral or basic solutions than under acidic conditions. In fact, below about pH 3 virtually no boric acid binds to NMG [93].

In a following study of the same group, two hyperbranched chelating polymers, glucoheptonamide derivatives of dendrimeric poly(amido amine) and poly(ethylene imine) were employed in PEUF and concentration of boron from aqueous feed streams. PEUF experiments were performed in a hollow fiber system in batch mode. Boron rejection coefficients for these separations were dynamic, beginning very close to unity and dropping during the course of separation as the polymer chelating sites are filled. During the experiments some polymer was lost due to permeation and this amount dramatically increased in acidic polymer solution. Moreover, at sufficiently high boron and polymer concentrations, the solution possibly formed a crosslinked gel at the membrane surface where the polymer and boron concentrations were increased in the feed due to concentration polarization [109].

In another study, batch mode of PEUF was employed and alkyl monool, 1,2-diol, 1,2,3-triol containing PEI were used as boron binding polymer. Effect of boron concentration ranging from 100 to 5000 mg/l was investigated using 1 % constant polymer concentrations. Maximum retentions were obtained as 0.75 (pH 8.5) and 0.90 (pH 9.0) at 100 mg/L initial boron concentration using 1,2-diol and 1,2,3 triol containing PEI, respectively. Effect of NaCl was also studied with 0.1 and 0.5 M NaCl concentrations and a fixed 1 % polymer concentration. Two representative and relevant boron concentrations were chosen, 100 and 1000 mg/L, and it was observed that the percentage of retained boron decreased substantially as the salt concentration was increased [107].

In the previous investigations of our group continuous PEUF was performed for the removal of boron from water. In the first study effects of operating parameters on boron removal were investigated using continuous PEUF with a constant boron concentration of 10 mg/L, a loading (metal/polymer) and a pH range of 0.01-1 and 7-10, respectively. A commercial polymer, poly(vinyl alcohol) (PVA) was used as the chelating agent. Maximum boron retention was observed as 0.28 at a pH of 10 and a loading of 0.01 which was the minimum loading corresponding to maximum polymer concentration [14]. In that study it was shown that, PEUF can be employed satisfactorily for removal of boron from aqueous solutions and it was concluded that, in order to increase the removal performance of the process, polymers having high boron affinity consisting more active OH^- groups should be used.

In the second study of our group, effects of operating parameters on boron removal were investigated using continuous PEUF with a constant boron concentration of 10 mg/L, a loading (metal/polymer) and a pH range of 0.01-1 and 7-10, respectively. Instead of using commercial polymers, three specially synthesized water soluble functional polymers namely, N-methyl-D-glucamine grafted poly(glycidyl methacrylate) (PolyGMA), the gel form of the same polymer and iminodipropylene grafted polyGMA, were used in PEUF experiments. The common property of these polymers was the presence of high number of hydroxyl groups attached to the polymer for borate chelation. Maximum boron retention was obtained with N-methyl-D-glucamine grafted Poly(GMA) at a pH of 10 and a loading of 0.01 which was the minimum loading corresponding to maximum polymer concentration. All of the polymers had low sensitivity to pH. It would have been possible to have higher retention values if solutions having lower loadings could have been prepared. The reason for not having lower loadings was the lack of solubility of the synthesized polymer above a certain concentration. Thus, it can be concluded that besides having high selectivity towards the target metal, high solubility of the polymer in aqueous solution is also necessary for having higher retention values in PEUF.

The mentioned studies showed that the use of specially synthesized functional polymers remarkably increased the boron removal from aqueous solutions. However it is necessary to synthesize more soluble functional polymers to have lower loading values for obtaining higher boron retentions.

2.5 Hexavalent Chromium (Cr(VI)) Removal from Aqueous Solutions by Membrane Processes

2.5.1 Chromium Chemistry

It is necessary to understand the solution chemistry of hexavalent chromium in order to explain the binding mechanism of chromate by various polymeric agents. The distribution of the species is dependent on the total chromate concentration and the pH of the solution. The following equations represent the equilibria governing the distribution of Cr(VI) in aqueous solution [110].

$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^-$ $K_1=1.21$

$HCrO_4^- \leftrightarrow H^+ + CrO_4^{2-}$ $K_2= 3x10^{-7}$

$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O$ $K_3= 35.5$

$HCr_2O_7^- \leftrightarrow H^+ + Cr_2O_7^{2-}$ $K_4= 0.85$

In aqueous solutions, hexavalent chromium (Cr(VI)) exists as hydrochromate ($HCrO_4^-$), chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$) ionic species. In basic and neutral pH, the chromate form predominates. As the pH is lowered (6.0 - 6.2), the hydrochromate concentration increases. At very low pH, the dichromate species predominate [4].

Hexavalent chromium is a strong oxidizing agent and may react with organic matter or other reducing agents to form trivalent chromium (Cr(III)). The exact chemical forms of chromium in surface waters are not well defined. Although most of the soluble chromium in surface waters may be present as Cr(VI), a small amount may be present as Cr(III) organic complexes. Hexavalent chromium is the major stable form of chromium in seawater; however, Cr(VI) may be reduced to Cr(III) by organic matter present in water, and may eventually deposit in sediments. Cr(III) chromium will eventually be precipitated as $Cr_2O_3{\cdot}xH_2O$. Therefore, in surface water rich in organic content, hexavalent chromium will exhibit a much shorter lifetime [4].

In aqueous solutions chromate and dichromate anions are in a chemical equilibrium according to the reaction below:

$$2\ CrO_4^{2-} + 2H_3O^+ \leftrightarrow Cr_2O_7^{2-} + 3\ H_2O$$

This equilibrium can be pushed towards dichromate by lowering the pH or in the other direction towards chromate by raising the pH to basic.

Cr (VI) compounds are extremely irritating and toxic to human tissues. Cr(VI) in the form of chromate, complexes with molecules such as protein, nucleic acids, and hemoglobin interfering with the regulation of cellular activity. Drinking water standards have been set at 0.10 mg/L total chromium because of the toxicity of Cr (VI) and the potential of oxidation of chromium (III) to Cr (VI) [51].

Various methods have been used to remove hexavalent chromium from industrial wastewater, including conventional chemical precipitation, electrochemical reduction, sorption on different adsorbents, and ion exchange .

Chemical precipitation is a common technique for the removal of heavy metals from water. However, hexavalent chromium, existing as chromate must first be reduced to trivalent chromium then precipitated with lime, costic soda or sodium carbonate [111]. The reaction occurs rapidly at low pH; thus, large quantities of sulfuric or hydrochloric acid are required for the process. Large quantities of base are then added for neutralization and precipitation of the metal hydroxide. The costs associated with the precipitation process are high due to the large quantity of chemicals involved and the disposal of the final metal hydroxide sludge [51].

Electrochemical processes utilize iron electrodes and electrical currents to generate ferrous ions that reduce Cr(VI) to Cr(III). The resultant ferric and chromium (III) ions precipitate as hydroxides when the pH of the wastewater is maintained between 6 and 9. The primary disadvantage of this method is the additional quantity of sludge produced by iron hydroxide precipitate [112].

Various adsorbents were used for the retention of Cr(VI) from wastewater such as; activated carbon [113], xanthated chitosan [114], calcinated Mg-Al-CO_3 [115], and coal [116]. Biosorption process was also utilized for the removal of Cr(VI) using immobilized fungal biomass [117], Aeromonas caviae [118] and Termitomyces clypeatus [119].

Ion exchange is a recovery method that has been studied for Cr(VI) retention It was reported that either weak or strong-base anion exchange resins such as Amberlite IRA-94 or IRA-402 were used for selective removal of Cr(VI). Nevertheless, conventional ion exchange has several disadvantages such as high resin replacement costs, semi-batch operation, and separate sorption, elution and wash steps. Cr(VI) recovery is often lower than the desired since the process is limited by the loading capacity of the resin [120]. Therefore, there is a need for efficient and economical separation techniques which may reduce the concentration of Cr(VI) down to permissible level. Use of membrane processes for the treatment of waste water containing Cr(VI) can be a promising way to achieve this aim with low energy cost and high efficiency.

2.5.2 Membrane Processes for Cr(VI) Retention

Despite their advantages such as low energy consumption, ease of scaling up, mild separation conditions, combination with other separation processes, and variable membrane, membrane processes are not widely used in the retention of hexavalent chromium removal from wastewater. A limited number of membrane processes were performed for hexavalent chromium removal such as; supported liquid membranes, dialysis using ion exchange membranes, adsorption-microfiltration, combination of MF-RO and complexation enhanced ultrafiltration. In recent years remarkable increase in the application of liquid membranes in separation processes is observed. These membranes include bulk liquid membranes, emulsion liquid membranes and supported liquid membranes. Hexavalent chromium removal was carried by BLMs using dicyclohexane-18-crown-6 as the ion carrier [121, 122]. There are also studies on the separation and concentration of Cr(VI) using ELM process. Tertiary amines such as tri-n-dodecylamine [123] and Alamine 336 [124] were used as ion carriers. Quaternary ammonium salt was also utilized as ion carrier in ELMs [124-126]. Tertiary amines and quaternary ammonium salts are most widely used ionic carriers in the application of SLMs for Cr(VI) concentration and separation [127-129]. The common problem with SLMs is the loss of membrane solvent and/or carrier to the both aqueous phases, and as a result the SLM based processes have not been applied industrially due to their poor durability [130].

Electrodialysis, which has advantages such as modularity and profitability at small scale, is an alternative separation process that can be performed for the treatment of Cr(VI). In recent years, there are relatively low number of studies in the literature that utilize electrodialysis operation for the treatment of Cr(VI) containing wastewaters [131, 132]. In a recent study, a three compartment electrochemical membrane reactor was used which was based on electrolysis-electrodialysis principles for the separation and recovery of Cr(VI) and metal ions. In this reactor, feed solution was fed to the central compartment. Cr(VI) ions migrated through the anion exchange membrane (AEM) to the anode side where they formed chromic acid with the hydrogen ions produced by oxidative water splitting. Simultaneously metal ions passed through the cation exchange membrane (CEM) to cathode side, where they formed metal hydroxides with the hydroxyl ions formed at the cathode side of the reactor. Uncharged agents present in the actual industrial effluent were not able to cross the two ion exchange membranes. Thus, separation and recovery of both Cr(VI) and metal ions were made possible. The highest Cr(VI) recovery obtained by this process was 72 % [132].

In another study, different membrane separation techniques such as MF, NF and RO were combined with evaporation to remove Cr(VI) from wastewater and obtain high quality rinsing water suitable for plating industry. A three stage process was developed; 1) pH adjustment and removal of precipitates by MF, 2) removal of dissolved contaminants by NF and 3) Guaranteeing high quality water by final RO. During stage 1 metal hydroxide precipitates were totally removed by MF. Afterwards in stage 2, most of the dissolved contaminants were retained by a chemically robust NF membrane, which has shown good performance during 310 h of testing. Finally, at stage 3, low-pressure RO was used to ensure high quality permeate. With this method, waste water volume could be reduced by 51 % prior to evaporation. However, this combined process can only reduce the Cr(VI) content of the wastewater to 30 mg/L [133].

Although, membrane processes such as reverse osmosis and electrodialysis are generally utilized for ion removal from wastewater, it is known that reverse osmosis needs high operating pressure, and electrodialysis electrodialysis is a high energy consuming process [89].

Surfactant based separation techniques are becoming increasingly important for purposes of industrial applications. These techniques generally require much less energy than traditional methods and have the advantage that, many surfactants used are of low toxicity [42].

Micellar enhanced ultrafiltration (MEUF) has been shown to be an effective method for removing inorganic pollutants, including chromate, from the aqueous phase [89, 134-137]. The micellar surface has a high charge density and a high absolute electrical potential therefore, multivalent metal ions electrostatically adsorbed or bind onto the micellar surface. A common disadvantage of the surfactant based methods has been their lack of selectivity for the target species in the presence of similar species that are often present in large excess [138]. For example, if the target species is a metal anion, other anions may also bind to the micelle and consecuently reduce the binding capacity and separation efficiency for the target ion. To enhance the selectivity in separation, a novel surfactant based separation technique, namely ligand modified micellar enhanced ultrafiltration (LM_MEUF) have been developed. In this technique an amphiphilic ligand and a surfactant were added to water under conditions where most of the surfactant is present as micelles. The ligand has a high degree of solubilization in micelles and a tendency to selectively complex the target metal ions [139].

In the MEUF studies, generally cetyl pyridinium chloride [89, 134, 136] cetyltrimethylammonium bromide [136] and octadecylamine [135] were generally used as cationic surfactant for Cr(VI) removal. In all of these studies Cr(VI) retentions were found to be around 98%. However, besides Cr(VI) other ions were retained nearly with the same amount. Thus a selective separation of Cr(VI) can not be achieved.

A general disadvantage of MEUF is the need fo relatively large surfactant concentration for effective separation. Another drawback of MEUF is the leakage of the surfactant through UF membrane due to the possible instability of the micelles. This can add substantial expence to the separation or make the process effluent stream environmentally unacceptable [138]. Besides, MEUF techniques involve two phase systems in which there can be mass transfer limitations. Possibility of homogeneous aqueous phase may make CEUF more beneficial by preventing the interface mass transfer resistance [48]. Use of water soluble functional polymers in combination with ultrafiltration to separate ions from aqueous solutions is a promising technique to achieve higher efficiency and selectivity of target component in homogeneous aqueous phase [43].

2.5.3 PEUF Technique for Hexavalent Chromium Retention

Use of water soluble functional polymers in combination with ultrafiltration to separate Cr(VI) from aqueous solutions is a promising technique to achieve higher efficiency and selectivity of target component in homogeneous aqueous phase [43]. However, effective removal and fractional separation of Cr(VI) using PEUF have been reported in a limited number of studies [6, 51, 137-142]. In all of these studies, batch mode of PEUF was performed, thus, effect of operating parameters on the separation of Cr(VI) were not investigated. The main aim of these works was to find for suitable water soluble polymers to selectively remove Cr(VI) from aqueous solutions. In most of these studies, quaternary ammonium containing polymers were utilized for the retention of Cr(VI) such as; poly(diallyldimethyl ammonium chloride) (PDADMAC) [51,137,140]. PEI and its derivatives [6, 142] dendrimers [6], chitosan, pectin [142] and starch [141] were other polymers utilized in the PEUF studies for Cr(VI) removal. All of the mentioned polymers are cationic polyelectrolytes having ionizable groups.

In one of the studies, a mixture of a cationic polyelectrolyte, poly(diallyldimethylammonium chloride) (PDADMAC), and an anionic ligand diethylenetriaminepentaacetic acid (DTPA) were added to aqueous solution to bind simultaneously divalent cation Cu^{2+} and CrO_4^{2-}. It was shown that at pH values greater than 4, most of DTPA is attached electrostatically to the PDADMAC, so that the ligand remains in the retentate in the ultrafiltration experiments. Effects of metal ion/ligand ratio and pH were investigated for the simultaneous retention of CrO_4^{2-} and Cu^{2+}. High rejection coefficients were obtained both for CrO_4^{2-} (99 %) and Cu^{2+}(99.4 %). On the other hand, the results indicate that, the rejection of chromate increased from 99 % to 99.6 % with the addition of 1.0 mM DTPA to the solution containing PDADMAC-CrO_4^{2-}—Cu^{2+}. However, CrO_4^{2-} retention remained approximately at 96.6 % for the entire range of Cu^{2+} concentrations. Thus, although the presence of DTPA did decrease the effectiveness of the process in removing CrO_4^{2-}, the addition of various concentrations of $Cu(NO_3)_2$ did not result in further decline in the chromate retention. Therefore, it can be concluded that, PDADMAC alone or in the presence of Cu^{2+} and DTPA, is quite efficient in removing chromate from aqueous solutions. However, effect of the ionic strength and presence of other ions remain to be studied [137].

Poly(diallyldimethyl ammonium chloride) (QUAT) was used by two groups as the binding agent in batch PEUF studies. In the first study [51], the effect of QUAT/chromate ratio was studied with and without the addition of NaCl using a 400 ml stirred cell at a constant solution temperature of 30°C. The results showed that, as the feed ratio of QUAT to CrO_4^{2-} increased, the rejection also increased because of the presence of higher number of positively charged sites on the QUAT per unit volume, which enhanced the fraction of chromate bound to the polymer. Maximum retention was obtained as 99.6 % for a QUAT to chromate ratio of 20. However, the presence of NaCl decreased the chromate rejection (75 %) substantially due to the competition of Cl^- and CrO_4^{2-} for the positively charged binding sites on the polymer. In a letter study [140], again batch mode of PEUF was utilized for the retention of chromate in the presence of sulfate and nitrate to observe the effect of valence to the rejection of the target anion. It was observed that, the rejection of anions increased with increasing concentration ratio of QUAT to anion. Highest chromate retention was found as 99.8 % for a QUAT/chromate ratio of 20, which is almost the same result obtained by Sriratana et al. Rejections of sulfate and chromate were found to be similar under all conditions. However, nitrate retention was much lower than that of chromate and sulfate, conforming that charge of the anion may be the predominant variable affecting the removal of anions.

In another study PAMAM starburst dendrimers, PEI and their ligand-modified forms were investigated for the removal of anions such as; chromate, sulfate and phosphate from water using ultrafiltration. The net positive charge of the dendrimer or PEI in neutral water provides an electrostatic attraction for anion binding. The primary amine sites on both binding agents can provide either sites for anion binding or a reactive site to attach a potentially more anion-selective ligand. In the study, the primary amines of each molecule were modified with different ligands to provide three types of hydrogen bonding interactions with anions. However, increasing the amount of covalently attached ligand, often reduced the solubility of the systems in water, especially in dendrimer systems. Therefore, most of the binding studies were conducted with polymers or dendrimers with very low levels of functionalization. The maximum anion capacity of the binding agents were measured in the presence of an excess anion (1300 mg/L) by shaking the solutions for 24 h at pH 7 then applied batch mode of ultrafiltration. Total capacities were higher in each case for the PEI-derivative relative to the similarly modified dendrimer. Dendrimers had the highest selectivity for chromate, whereas the PEI derivatives had a slightly higher capacity for phosphate relative to other anions. They also studied the competition effect of chloride using chromate as target anion. At 100-fold excess of competing ion, chromate binding capacity dropped to half of its value when no chloride was present for all dendrimers. PEI derivatives showed a different trend with increasing chloride concentration. The capacity was approximately 70 % of the available chromate regardless of the competing ion concentration [6].

In one of the studies, starch was modified with 3-chloro-2-hydropropyltrimethylammonium chloride (CHPTMA) and epichlorohydryn to obtain quaternized cationic starch and used as a biodegradable polyelectrolyte to remove chromate from aqueous solution by batch mode of PEUF. In the study, chromate concentration was kept constant at 0.5 mM and cationic starch concentration was varied between 0.5-2.5 g/l As the concentration of cationic starch increased, the removal of chromate was enhanced as expected, because of the increase in the available sites for chromate binding. The highest Cr(VI) retention was obtained as 98% for a cationic starch concentration of 2.5 g/l [141].

In a recent study, semi-continuous mode of PEUF was utilized for chromium removal using different polymers such as; pectin, chitosan and PEI. Effect of pH and polymer concentration on the retention of Cr(III) and Cr(VI) were investigated and metal binding performances of the polymers were compared. It was observed that pectin showed a better performance for the separation of Cr(III) than chitosan and PEI. Whereas, PEI had the highest Cr(VI) removal ability compared to the other two polymers. Solution pH was found to be the major factor which controls the rejection of both chromium species. For Cr(III), high rejections were obtained at pH more than 7 for all polymers. Cr(VI) showed a different behavior for each type of polymer. When pectin and chitosan were used as polymeric agents in PEUF, little effect of pH was obtained for the retention of Cr(VI), which remained almost constant around a value of less than 50 %. Whereas, when PEI was used, retention of Cr(VI) approached to 100 % at low pH and sharply decreased at pH 9 and above [142].

In the literature, most of PEUF studies deal with the removal of cationic metals. Very few studies investigated the removal of metals that are in the form of anions in aqueous solutions. Removal of anions with PEUF is a new area of research. Therefore the major purpose is to find a suitable ligand as opposed to cations [6, 44, 143]. Mostly investigated anions were perchlorate, arsenate and phosohate. In those studies, most of the polymers used as ligands are specially synthesized or modified ones. Anions represent especially complex targets, as they are coordinatively saturated and cannot form covalent bonds to ligands easily. Therefore, highly highly selective ligands are needed that will bind the target anions present in very low concentrations and in the presence of much higher concentrations of other anions [6].

In this study, two chelating polymers for borate and a polyelectrolyte for chromate were synthesized for investigating the separation performance of these polymers from aqueous solutions. In order to explore the suitable conditions for the maximum retention of the target metal anion with the highest possible permeate flux a parametric study was performed utilizing continuous polymer enhanced ultrafiltration. Effect of process parameters such as pH, loading, polymer type (for borate retention), effect of competing anion (for chromate retention) were investigated.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

In the synthesis of the functional polymers, ethanolamine (Merck) was distilled before use. All the other chemicals were analytical grade commercial products; glycidyl methacrylate (Aldrich), glycidol (Aldrich), morpholine (Aldrich), allyl chloride (Aldrich), allyl bromide (Aldrich), divinyl benzene (Aldrich), 4-Vinyl-1, 3-dioxalan-2-one (Aldrich), vinyl acetate (Aldrich). They were used as purchased.

In the ultrafiltration experiments and in atomic absorption spectrometry analysis, boric acid (H_3BO_3, Merck), sodium chromate (Na_2CrO_4, Merck), sodium hydroxide (NaOH, Merck), nitric acid (HNO3, Merck), sodium sulfate anhydrous (Na_2SO_4, J.T.Baker), sodium chloride (NaCl, Merck) and ultrapure water having a specific conductance of $18.3 \mu\Omega cm^{-1}$ obtained from water purification system (Human Reverse Osmosis(RO)-UltraPure (UP) water purification systems) were used. All chemicals in this study were used without further purification. The laboratory scale ultrafiltration system used for the polymer enhanced ultrafiltration experiments has polyether sulfone membranes (Osmonics Sepa YMPTSP1905) with a molecular weight cut-off of 5 000 Da.

3.2 Polymer Synthesis for PEUF Experiments

In this study three different functional polymers were synthesized for borate and chromate retention by PEUF. For borate, three glycidyl methacrylate (GMA) based polymer with hydroxyethylamino glycerol functions (PNS) having different molecular weights (M_v) and a copolymer of 4-Vinyl-1,3-dioxalan-2-one and vinyl acetate (COP) were synthesized. For chromate separation a polyelectrolyte, poly(N,N-diallyl morpholinium bromide), which has quaternary ammonium groups, were synthesized.

3.2.1 Synthesis of Hydroxyethylamino Glycerol Functioned Poly(glycidyl methacrylate) (PNS) for Borate Removal

A water soluble glycidyl methacrylate (GMA) based polymer with hydroxyethylamino glycerol functions was synthesized, as boron selective functional polymer according to the reaction scheme given in figure 3.2.1.

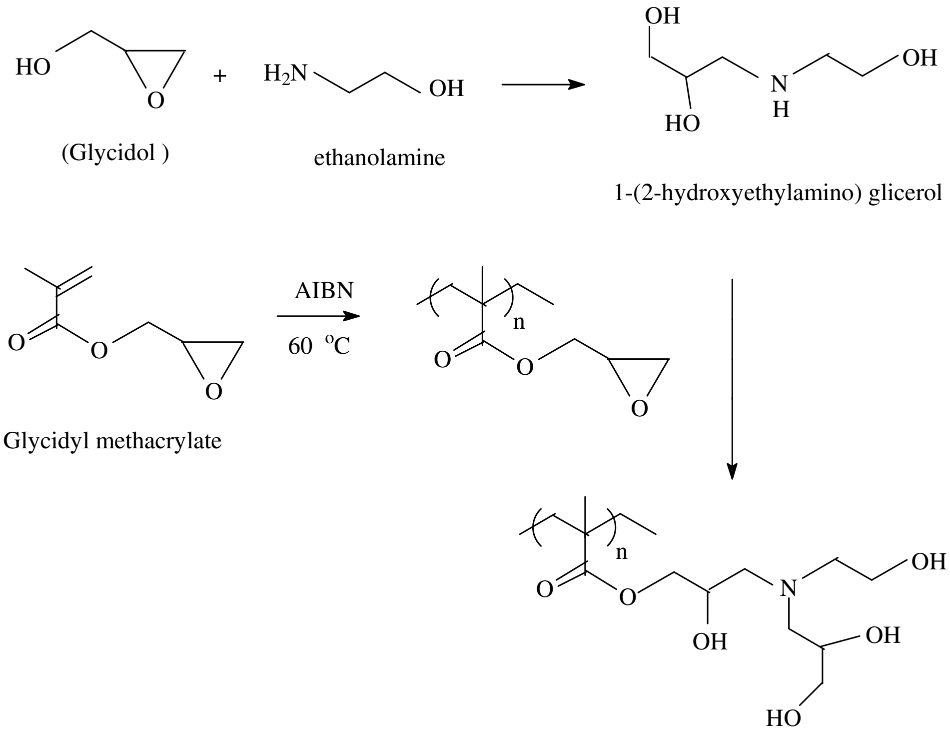


Figure 3.2.1 Synthesis of hydroxyethylamino glycerol functioned poly(glycidylmethacrylate)

In the first step; 1 mole of glycidol as added drop wise to the solution of ethanolamine (3 moles) in toluene at 0°C in 30 minutes and the mixture was heated for 30 minutes at 150°C. Toluene and the excess of ethanolamine were removed under vacuum at 150°C. The resulting pale yellow viscous liquid (1-[2-hydroxyethylamino] glycerol) (HEG) was used in the next step without any further purification.

In the second step, 7.1 g of Poly(GMA), which was prepared before, was dissolved in 75 mL of THF. This solution was added drop wise to the stirring solution of 7.5 g (0.06 mol) HEG in 50 ml THF at 55°C, by means of a pressure-equalized dropping funnel in 40 min. The resulting mixture was stirred for another 40 min at the same temperature. Then about 80 % of the solvent was distilled and the residue was precipitated in 100 mL ether. By changing the monomer/initiator ratio in poly(GMA) syntesis, different molecular weight polymers were synthesized. Calculation of the viscosity average molecular weights (M_v) of the polymers are given in Appendix G. The synthesized polymer is resistant to acid hydrolysis thus, regeneration and reusability of the polymer is possible.

3.2.2 Synthesis of Poly(4-Vinyl-1,3-dioxalan-2-one-co-vinyl acetate) (COP) for Borate Removal

Copolymerization of 4-Vinyl-1,3-dioxalan-2-one with vinyl acetate was carried out in bulk according to the reaction scheme given in figure 3.2.2. Thus, 9.6 ml 4-Vinyl-1, 3-dioxalan-2-one (0.1 mol) was mixed with 9.2 mL vinyl acetate (0.1 mol) under nitrogen atmosphere and 0.2 g AIBN was added to the mixture. The flask was mounted in a temperature controlled oil bath. The mixture was stirred until a clear solution was obtained. It was then heated to 75°C and the reaction was carried out for 3 h at constant temperature under reflux.

The product was dissolved in dimethylformamide (DMF), precipitated in 450 mL of distilled water, filtered and dried under vacuum. The co-polymer was then hydrolyzed using 70 ml 0.23 g/ml NaOH solution. The copolymer-NaOH solution was stirred overnight at room temperature to achieve complete hydrolysis of the copolymer. The resulting homogeneous solution was heated to vaporize water until 5-10 ml solution was remained. It was then precipitated in 70 ml of ethanol, filtered and dried under vacuum. The resulting polymer has two vicinal hydroxyl groups on 4-Vinyl-1,3-dioxalan-2-one, and one hydroxyl group on vinyl acetate.

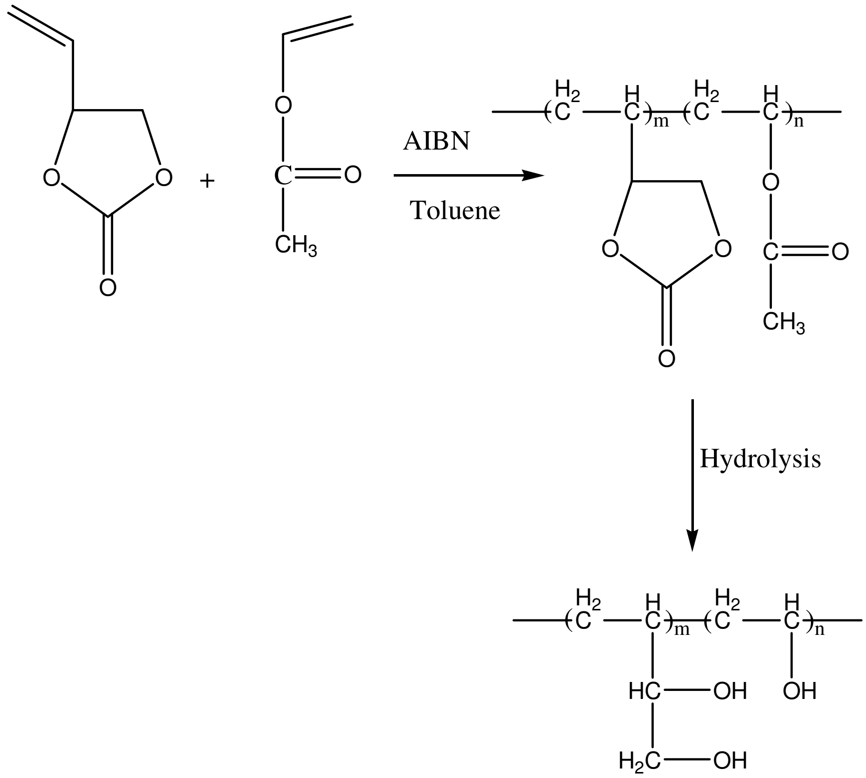


Figure 3.2.2 Synthesis of poly(4-Vinyl-1,3-dioxalan-2-one-co-vinyl acetate)

3.2.3 Synthesis of Poly(N,N-diallylmorpholinium bromide) (PDAM) for Cr(VI) Removal

A water soluble strong quaternary ammonium polyelectrolyte, poly (N,N-diallyl morpholinium bromide) was synthesized for the removal of chromate ions. Poly(DAM) is prepared starting from morpholine and allyl chloride as shown in figure 3.2.3.

The monomer, N,N-diallyl ammonium bromide (DAM) was obtained in two steps. The first step was Hofmann alkylation of morpholine with allyl chloride and the second step was the quaternization of N- allyl morpholine with ally bromide. After the monomer, DAM, was obtained, poly(DAM) was synthesized by radical polymerization of DAM using tert-butyl hydroperoxide (t-ButOOH) as initiator yielding a water soluble cyclopolymer with a molecular weight of 42 000 Da.

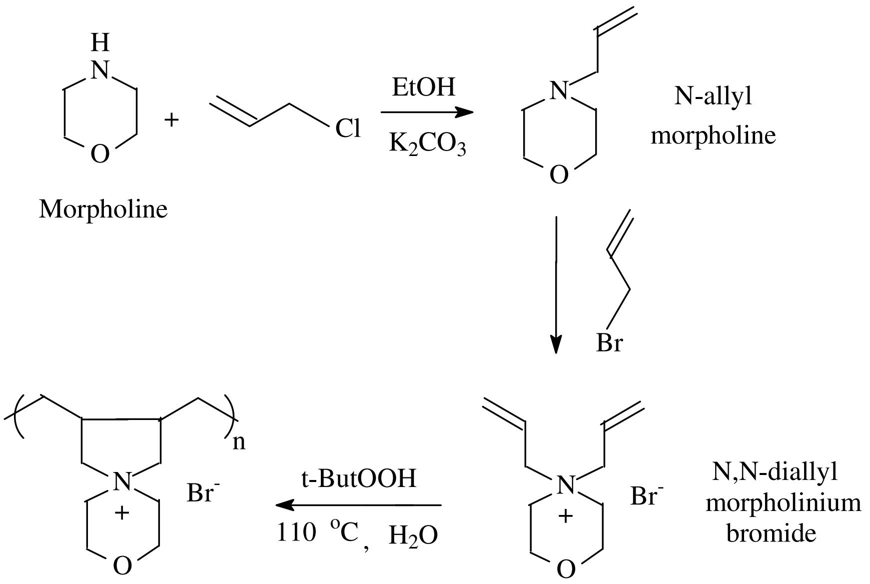


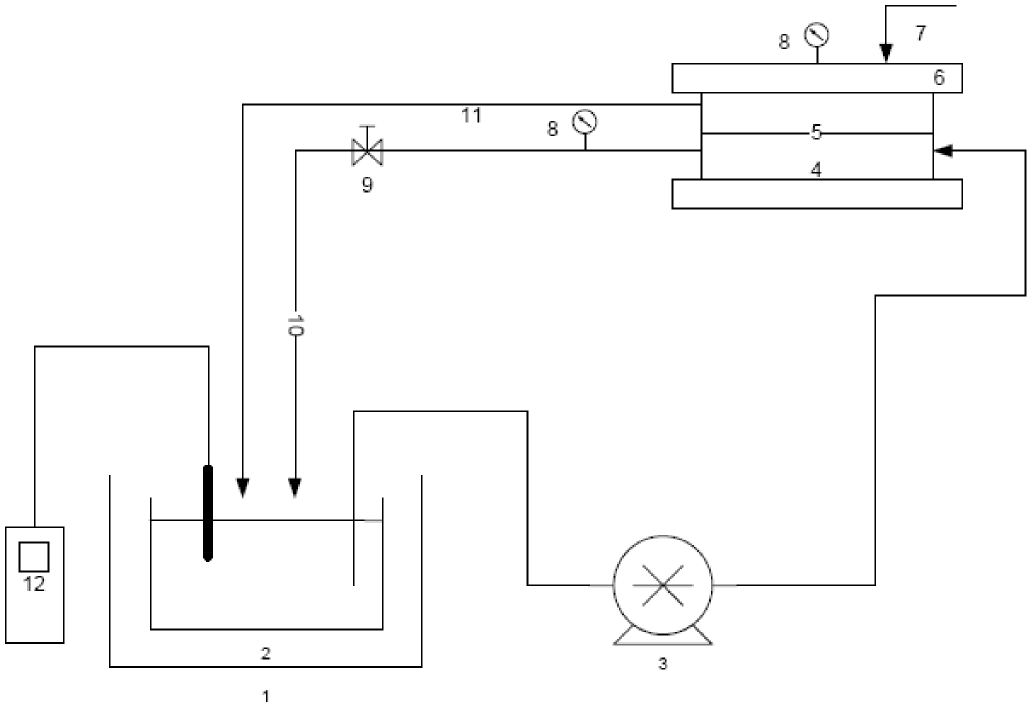
Figure 3.2.3 Synthesis of poly (N,N-diallyl morpholinium bromide)

3.3 Experimental Set-up Ultrafiltration Equipment

3.3.1 Experimental Set-up of Laboratory Scale Continuous Mode of Ultrafiltration Equipment

Experimental studies were carried out on a lab scale Osmonics Sepa CF Membrane Cell, which is shown in figure 3.3. This set-up was previously used by our research group [35, 48].

Osmonics Sepa CF Membrane Cell mainly consists of a membrane cell, a rotameter, a centrifugal pump, a water bath, valves and teflon tubings. Cell body and cell holder were the two major components of the UF cell. Membranes were mounted on the cell body. The function of the cell holder was to prevent leakages around the membrane by pressurizing the cell. Nitrogen gas was fed to the cell holder to compress the upper and lower plates of the cell. In the experiments flat sheet membranes made of poly(ether sulfone) having an effective membrane area of 155 cm^2 and a molecular weight cut off of 5000 Da were utilized. In the UF experiments UF pressure and feed flowrate were 100 kPa and 0.048 m^3/h, respectively.



1. Water Bath
2. Feed Vessel
3. Pump
4. Cell Body
5. Membrane
6. Cell Holder
7.Pressurized Air
8. Pressure Gauge
9. Back Pressure Valve
10. Permeate Stream
11. Retentate Stream
12. pH Meter

Figure 3.3.1 Schematic diagram of Osmonics Sepa CF Membrane Cell

3.3.2 Experimental Set-up of Laboratory Scale Batch Mode of Ultrafiltration Equipment

Batch mode ultrafiltration experiments were carried out on a lab-scale Model 8050 dead-end stirred membrane cell manufactured by Amicon-Millipore. Equipment has a cell capacity of 50 ml. Schematic view of the stirred cell is illustrated in Figure 3.3.2. The cell is placed on a magnetic stirrer to agitate the fluid inside the cell. Nitrogen gas cylinder is connected to the cell in order to pressurize the system. In this set-up pressure should not exceed 75psi (6.89 kPa).

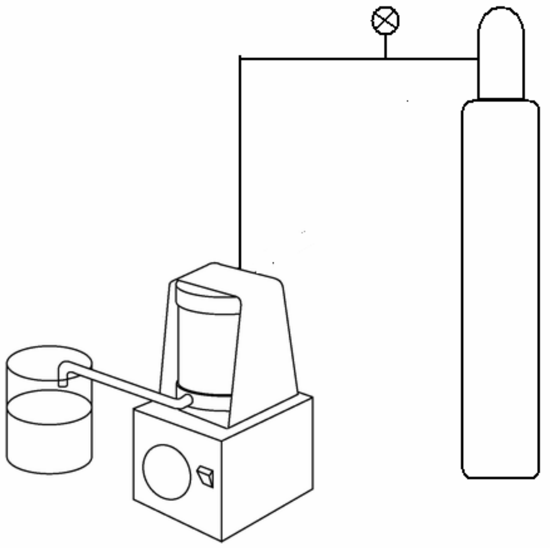


Figure 3.3.2 Schematic diagram of Amicon-Millipore Stirred Membrane Cell

3.4 Ultrafiltration Experiments

3.4.1 Preparation of Feed Solution

Feed solutions were prepared prior to ultrafiltration experiments. The desired amount of polymer was dissolved in ultrapure water then the anion salt was added to the polymer solution resulting in a target anion concentration of 10 mg/L. pH of polymer solution was adjusted by adding HNO_3 and NaOH before and after the addition of target anion salt. Then the resulting solution was stirred at 250-300 rpm for at least 3 hours to make sure that complexation equilibrium between the target anion and polymer was established. Experiments with longer mixing times showed that 3 hours was enough to achieve complexation equilibria. The pH of the solutions was controlled at the desired value during the mixing period and during the experimental run. In the preparation of competing anion containing solutions, same procedure was applied: polymer solutions were prepared and target anion salt and predetermined amount of competing anion salts were added then stirred at 250-300 rpm at the working pH value for 3 h.

3.4.2 Ultrafiltration Experiments

After complexation of the feed solutions was achieved, continuous ultrafiltration was applied to the solution. Circulation of the solution was achieved by a pump. Feed solution was first passed through the membrane, then retentate and permeate streams were returned back to the feed solution tank to keep the feed concentration constant. At certain time intervals, permeate stream flowrate was measured and small amounts of samples were collected both from the permeate and feed streams for the analysis of the target metal. All runs were carried out with the same membrane type at constant temperature of 25 ± 3°C.

3.4.3 Membrane Cleaning Procedure

All the membranes used in PEUF experiments were cleaned before and after each experimental run. Membranes were cleaned by applying a cleaning procedure, i.e., they were kept in the module while the cleaning solutions were pumped through the system for a given period while the permeate and retentate streams were discarded. Prior to ultrafiltration experiments membrane cleaning was performed by osmosized water. Upon the completion of each experimental run, firstly system was stopped, drained and flushed with osmosized water. Secondly, feed tank was filled with 0.1M NaOH solution and cleaning procedure was continued by pumping NaOH solution through the system for 15 min. During cleaning procedure, transmembrane pressure was adjusted to the same value as in the experimental run. As a third step, system was drained and flushed with osmosized water. After that, 3 ml/l HNO3 60% (v/v) solution was pumped through the system for 15min. Finally, system was drained again and flushed with osmosized water, until the pH of the permeate stream appeared to be in neutral pH range.

3.5 Analytical Methods

3.5.1 Boron Determination

For the concentration analysis of boron, Direct Reading Echelle Inductively Coupled Plasma Optical Emission Spectrometry (DRE ICP-OES) was used [Leeman Labs. Inc.]. To perform the analysis, DRE system uses an ICP source to provide excitation energy, coupled to a direct reading echelle spectrometer to separate and measure the resultant light output. The system is managed by a standard PC (Celeron 400 MHz, 128 MB RAM, Windows 98). The plasma is created with argon (Ar) gas, by the help of a radio frequency (RF) generator. This generator gives enough energy to ionize the inert Ar atom. These Ar ions, once formed in plasma, are capable of absorbing adequate energy from the RF source to preserve the temperature of the plasma at a level where further ionization keeps the plasma continuously. The intensity of the light emitted is analyzed at a certain wavelength, which will be converted to meaningful data after calibrations.

The ICP conditions were as follows:

- RF Power: 1.1 kW
- Auxiliary Flow Rate: 0.5 L/min
- Pump Rate: 1.1 mL/min
- Coolant Flow Rate: 16 L/min
- Nebulizer Pressure: 37 psi

The wavelength to be inspected for boron determination is 249.773 nm.

For calibration, standard solutions of boric acid were prepared separately for both feed and permeate. Permeate standards were prepared with boric acid and ultrapure water while feed standards had polymer with the same concentration as the feed. These standards were scanned by ICP with three replicates of each which provide the determination of the intensity data of the standards. By the help of the intensity data, calibration curves for both feed and permeate standards were obtained. Then the samples were scanned and the relative average blank corrected intensities of the samples were determined. During the feed analysis, in order to prevent clogging by polymer, system is cleaned with 0.1 M HCl. At the end of each analysis, proper calculations were performed for converting the intensity data of the samples to related concentration data for determining the retention values. Detailed data and calculations of a run are given in Appendix A.

3.5.2 Total Chromium Determination

Chromium content of the feed and permeate solutions were determined by atomic absorption spectroscopy. For chromium determination a Philips PU 9200X AAS (FAAS) with nitrous oxide-acetylene flame was used. Background correction was achieved by means of deuterium lamp. The samples were atomized by nebulizer and nitrous oxide-acetylene flame. At the beginning of each analysis, calibration of the instrument was performed by blank and standard solutions.

Detailed information about the method and typical calibration curve for chromium obtained during the analysis are depicted in appendix B.

3.5.3 Sulfate and Chloride Determination Using Ion Chromatography

Ion Chromatography analysis was performed by Dionex ICS-3000. In the analysis AS11 column was used as analytical column and AG column was used as guard column. The eluent was 9 mM Na_2CO_3 and the detector was ASRS-4mm Anion Suppressor and Conductometric detector. Dilutions were done by Milli-Q water with R≈ % 18 $M\Omega.cm^{-1}$. Calibration for the instrument was performed using four standard solutions both for chlorine and sulfate having concentrations of 0.6, 1.2, 2.5 and 5.0 mg/L. Calibration curve was given Appendix C.

3.5.4 Dynamic and Static Light Scattering Analysis

Stock solutions containing predetermined amounts of polymer were prepared using Milli-Q water with R≈ % 18 $M\Omega.cm^{-1}$. The pH of all solutions was adjusted by adding a corresponding amount of a 0.1M HNO_3 solution or a 0.2M NaOH solution. Prior to analysis, depending on the desired concentration for dynamic and static light scattering (DLS/SLS) experiments, samples were diluted and then centrifuged, in sample cells. Static and dynamic light scattering measurements were performed by ALV/CGS-3 Compact Goniometer System simultaneously. An argon ion laser operating at a 633 nm wavelength and 35-mW output power was used as a light source. The measurements were done at 13 different angles in the range of 30°≤ q ≤ 150° and at 25°C. For each angle three different measurements were performed and subsequently averaged. For every sample three dilutions were made and the same procedure was applied on each diluted solution. The data were normalized to absolute scale by using toluene as a reference material. Two different data file systems were used in ALV5000 and 60X0 software. Data obtained during the DLS and SLS experiments were stored in two different files. The correlation function and count rate trace data together with all relevant sample parameters can be stored as ASCII values, and the angular concentration dependent normalized mean values of the scattering intensity as well as diffusion coefficients derived by Cumulant analysis of the correlation functions are stored in DILS file format. An analysis of DLS/SLS data stored in DILS file format can easily be performed using the ALV/Static and Dynamic Fit and Plot program by creating Zimm, Guinier and Berry plots, plots of diffusion coefficients versus q^2 (square of scattering vector) and form factor plots. The average molecular weight, radius of gyration, hydrodynamic radius and second virial coefficient of the samples are calculated via Guinier plot where (q^2 +Kc) is plotted versus ln (Kc/R) according to the following equation.

$$\ln\left(\frac{Kc}{R}\right) = \ln\left[\frac{1}{M_w \exp\left(-\frac{1}{3}R_g^2 q^2\right)^2} + 2A_2c\right]$$

where R: Rayleigh ratio, K: optical constant, c: concentration, A_2: second virial coefficient, R_g: Radius of gyration

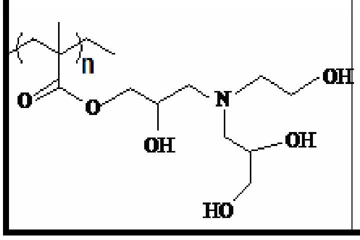
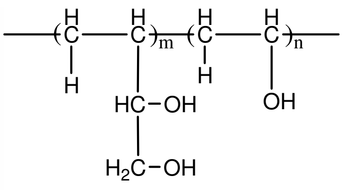
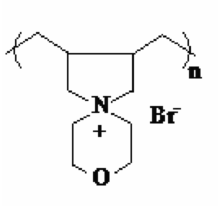
Each fit at constant angle data is extrapolated to zero concentration, and each fit at constant concentration is extrapolated to zero angle, obtaining two lines. The average molecular weight (M_w) is calculated from the intercept of each extrapolated line with the vertical-axis. Radius of gyration (R_g) is calculated from the slope of the extrapolated line at zero concentration while the second virial coefficient (A_2) is calculated using the slope of the extrapolated line at zero angle.

CHAPTER 4

RESULTS AND DISCUSSION

The aim of this study is to separate anions like chromate and borate from aqueous solutions using specifically synthesized polymers by the help of PEUF process. Thus, two chelating polymers for borate removal and a polyelectrolyte for chromate removal were synthesized for the separating borate and hexavalent chromium from aqueous solutions and observing the effect of operating parameters on the retention of these target anions. The molecular structures of the synthesized polymers are given in Table 4.1.

Table 4.1 Molecular structures of the synthesized polymers

PNS	COP	PDAM
		

Our experimental parameters are pH and loading (g metal/g polymer) for borate, and pH, loading and competing anion concentration (sulfate and chloride) for chromate. The purpose of studying the effect of various parameters is to explore the suitable conditions for the maximum retention of metal with the highest possible permeate flux. The reason for investigating the effect of sulfate and chloride concentration is to observe the influence of competing anion charge to the selectivity of the polymer. Additionally, effect of molecular weight of PNS on boron retention was also studied using three different molecular weights of the same polymer. The synthesized polymers have viscosity average molecular weights of 281,842 (PNSH), 110,480 (PNSM), 49,733 (PNSL).

4.1 General Evaluation of PEUF Experiments

The experimental data obtained in representative UF experiments are presented in Table 4.1.1 and Table 4.1.2. The rest of the data obtained in PEUF experiments are given in Appendix C, Table D1 and Table D2. Presented data include feed and permeate target anion concentrations, flux, retention (R), pH and temperature with respect to time.

Table 4.1.1 Data obtained in a representative PEUF run for borate retention

Polymer Type: PNSL, **Target Anion:** Borate (10 mg/L), **Loading:** 0.01, **pH:** 9					
t (min)	**0**	**60**	**120**	**240**	**% RSD**
F_p (L/m^{2}h)		47.4	47.3	47.4	0.158
pH	9.00	9.02	9.03	9.02	0.064
T (°C)	24.0	24.0	24.4	24.8	1.570
C_f	10.8	10.9	10.9	10.8	0.53
C_p		6.6	6.6	6.6	0.00
R		0.394	0.394	0.389	1.012
	$F_{p,avg}$= 47.4	**$C_{f,avg}$= 10.85**	**$C_{p,avg}$= 6.6**	**R_{avg}= 0.392**	

Table 4.1.2 Data obtained in a representative PEUF run for chromate retention

Polymer Type: PDAM, **Target Anion:** Cr(VI) (10mg/L), **Loading:** 0.01, **pH:** 4					
t (min)	**0**	**60**	**120**	**240**	**% (RSD)**
F_p (L/m^{2}h)		81.0	81.0	81.0	0.000
pH	4.00	4.00	4.01	4.00	0.144
T (°C)	25.6	25.6	25.8	26.0	0.777
C_f	10.2	10.1	10.1	10.1	0.000
C_p		2.6	2.6	2.6	0.000
R		0.740	0.740	0.740	0.000
	$F_{p,avg}$= 81.0	**$C_{f,avg}$= 10.1**	**$C_{p,avg}$= 2.6**	**R_{avg}= 0.743**	

In the experiments, after the determination of target anion concentration at the specified time intervals, averaged values of both feed and permeate target anion concentration were used in the calculation of retention values. The results showed that within the runs there were small fluctuations in the concentration, retention and flux values. Table 4.1.1 and Table 4.1.2 also show that steady state has been established within one hour and the values remained almost constant throughout the runs. The most important property of a continuous system is the constant feed concentration during the experiments. By using a continuous system, effect of operating parameters at constant feed concentration on the retention of target anions can be investigated efficiently. The relative standard deviations (%RSD) for permeate and feed concentrations, permeate flux and retention are small enough to accept that the set-up, methodology and the analysis are reliable.

Reproducibility of the PEUF operation is an important concept to comment on the methodology and performance of the system. In order to check the reproducibility of PEUF operation, some selected runs were repeated at the same conditions of pH, loading and polymer type. The results were compared and % RSD values are calculated and tabulated in Table 4.1.3.

Table 4.1.3 Data of the experiments performed for reproducibility
(Anion Concentration: 10mg/l, MWCO: 5 000 Da, ΔP:100 kPa, Flowrate: 0.048 m^3/h)

	Polymer	**L (g metal / g polymer)**	**pH**	**R**	**% RSD**	**Flux**	**% RSD**
1st Run	PNS L	0.05	9.00	0.24	4.84 (n:2)	46.5	1.21 (n:2)
2nd Run				0.25		47.3	
1st Run	COP	0.001	9.00	0.43	2.74 (n:2)	41.0	0.00 (n:2)
2nd Run				0.45		41.0	
1st Run	PDAM	0.01	4.00	0.70	1.02 (n:2)	81.0	0.88 (n:2)
2nd Run				0.69		80.0	

When the results presented in table 4.1.3 are inspected, it is seen that the % RSD values of the 1st and 2nd trials were very small. Therefore, it can be concluded that, the UF system can reproducibly show the same performance. These results proved that reasonable separation of the target anions can be reproducibly achieved by continuous PEUF method.

4.2 Boron Retention Studies Using Specifically Tailored Polychelatogens by PEUF

PEUF experiments for boron retention were performed using two different specifically tailored polymers, namely, hydroxyethylamino glycerol functioned polyglycidyl methacrylate (PNS) and a copolymer, poly (4-Vinyl-1, 3-dioxalan-2-one-co-vinyl acetate) (COP) in order to compare the boron retention performances of the synthesized polymers. Additionally, PNS was synthesized in three different molecular weights (M_v = 281,842, 110,480, 49,733) to examine the effect of molecular weight on the binding capacities of the polymers.

PEUF experiments were performed to observe the effect of operating parameters such as, pH and loading on boron retention using the synthesized polymers. The pH range was selected as 7-10, since boron is present in the anionic form (borate) in neutral and basic pHs. Another reason to select this pH range is to increase the boron binding capability of the hydroxyl groups in the structure of the polymers. The allowable upper limit of pH that can be applied to the membranes used in PEUF studies is 11. Thus, the maximum pH in the experiments was decided to be 10. The membrane used for boron retention studies has a molecular weight cut off (MWCO) of 20 000 Da in the experiments that utilize PNSH. For other polymers, membranes having MWCO of 5000 Da were used. Different loading ranges were investigated for the synthesized polymers according to their solubilities in aqueous solutions.

4.2.1 Effect of Loading on the Retention of Boron and Flux Using PNSH

In the UF experiments where PNSH was used as the chelating agent, different loadings varying from 0.05-0.5 were used to find out the binding capacity of PNSH. During the experiments, the permeate flux of the UF system was also measured in different operating conditions to see the influence of these parameters on the UF performance. In UF operation, the consistency of the permeate flux is one of the important factors effecting the UF efficiency. At a constant operation pressure if the permeate flux is decreasing; this may be a sign of gel layer formation on the membrane that may eventually plug the membrane pores. In figure 4.2.1, flux values obtained at different polymer concentrations are presented.

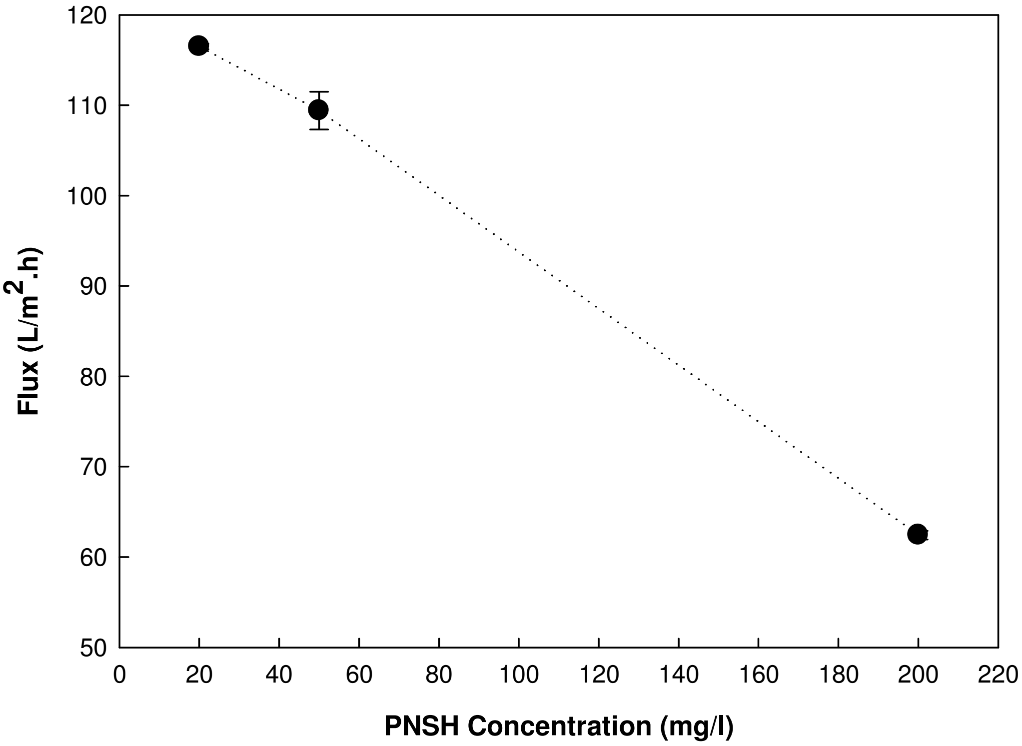


Figure 4.2.1 Effect of loading on the flux and retention of boron using PNSH (Boron: 10 mg/l, pH:9, MWCO: 20 000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

As depicted in figure 4.2.1, the increase in polymer concentration leads to a decrease in the permeate flux. This behavior may suggest that, there might be a gel layer formation in the studied polymer concentration range. Additionally, PNSH which is used as the chelating polymer has a very high molecular weight and it is known that if the molecular weight of the polymer is high, it results in a higher viscosity (1.32 cp) solution due to higher interactions between the polymer chains, thus resulting in a more compact polymer structure [62]. This size reduction along with gel layer formation may result in a decrease in the permeate flux.

Table 4.2.1 Effect of loading on the retention of borate using PNSH
(Boron: 10 mg/l, pH:9, MWCO: 20 000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

Loading	Retention	% RSD
0.050	0.079	1.47 (n:4)
0.20	0.32	0.91 (n:4)
0.50	0.30	3.44 (n:4)

Table 4.2.1 represents percent retention values of borate at different loadings. Generally decreasing the loading (increasing the polymer concentration) increases the binding capacity, hence the target anion retention. It is observed from the results that when the loading of the feed solution decreases from 0.5 to 0.2, the retention of borate increases. However, this increase is not high enough to ensure reasonable separation of boron. The same behavior was observed in the previous studies of our group in which commercial PVA [14] and iminodipropylene glycol grafted Polyglycidyl Methacrylate [50] were employed as boron binding polymers. In the mentioned studies, although loading was decreased significantly, the increase in the retention was not high enough for a reasonable boron retention. This result was attributed to unsuitable chain conformation of the polymer chains for the binding of borate and also to the insufficient dissolution of polymer in microscopic level.

In Table 4.2.1, it is also noticed that decreasing the loading further to 0.05, decreases the retention to 1/4 of the value obtained for a loading of 0.2. In the structure of PNS there are amine group which can interact with the hydroyxl groups of the other polymer chains by hydrogen bonding. Therefore, the decrease in the retention at loadings lower than 0.2 (PNS concentrations higher than 50 mg/l) may be attributed to the interaction between the amine and hydroxyl groups of the polymer chains as a result of crowding effect which may lead to an elimination of possible binding sites of borate hence decreasing the retention. The effect of crowding in PNS solution were investigated by dynamic and static light scattering (DLS-SLS) measurements and the results confirmed that PNS chains reduce their radius of gyration in concentrated solutions. The details of DLS-SLS results are given in section 4.4.

4.2.2 Effect of pH on The Retention of Boron Using PNSH

It is known that pH is one of the most important factors in the interaction of a metal ion with a binding polymer, thus the retention of the ion. By changing the pH values appropriately it is possible to separate metal ions in one extreme and to disassociate polymer-metal complexes in the other extreme. For that reason, besides loading experiments pH studies were also performed.

The results given in figure 4.2.2 depict the effect of pH on retention of boron at two different loadings with PNSH as the chelating polymer.

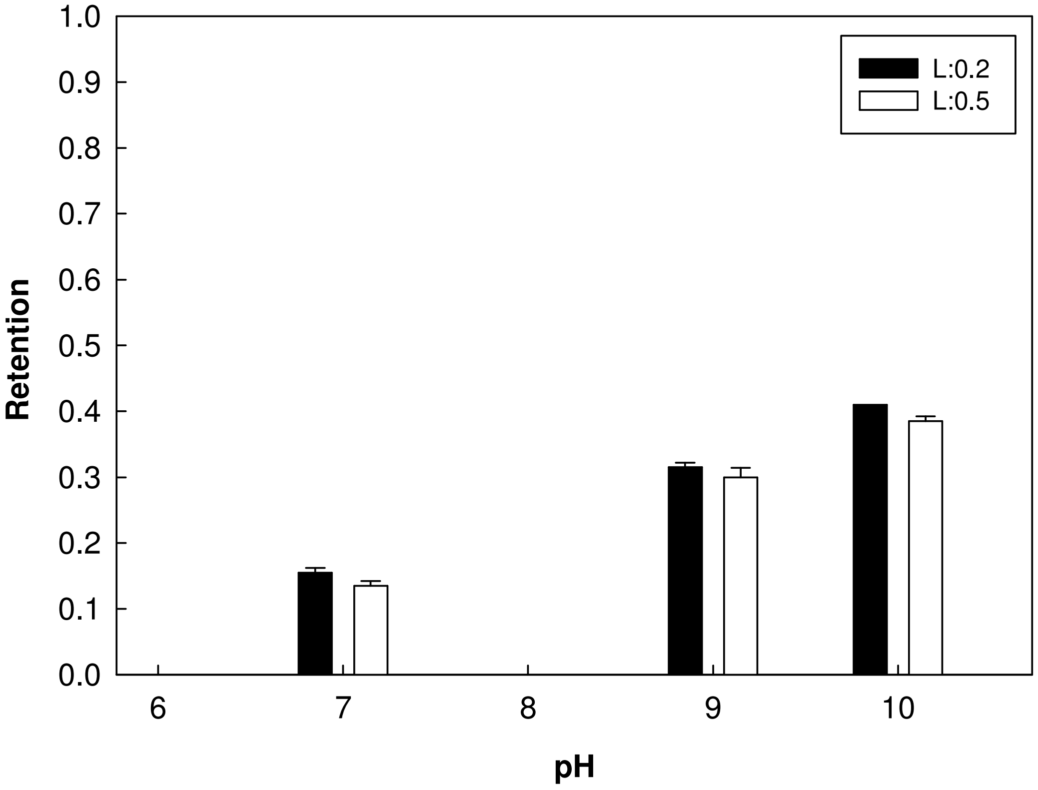


Figure 4.2.2 Effect of pH on the retention of boron using PNSH
(Boron: 10 mg/l, pH:9, MWCO: 20 000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

From figure 4.2.2 it is observed that when pH of the medium is increasing and the system is getting away from neutrality, retention values increase. At both loadings, when pH was increased from 7 to 9, retention values were doubled. As the pH of the solution was further increased to 10 a 1.3 fold increase in retention values was observed. This is an expected behavior, because in the previous two studies of our group, boron retentions were found to be increasing with the increase in pH values at various loadings [14, 50]. This phenomenon may be explained by the reaction mechanism of boric acid dissolution. When boric acid dissolves in water, borate ion concentration reaches its maximum value between pH 10 and 12. Since PNS contains hydroxyl groups in its structure that are capable of interacting borate anions and production of borate ion is enhanced in the basic medium, chelation of borate with the functional groups of the synthesized polymer is favored at higher pH values, thus, ensuring an enhanced retention of boron. Furthermore, enhancement in the retention of boron at high pH range can be attributed to the conformational changes in the polymer with respect to the changes in the pH of the solution which may result in a more suitable state for the hydroxyl groups of the polymer to make complex with borate ion. DLS/SLS measurements confirmed that, hydrodynamic radius of PNS increases as pH increases so that, there may be more available sites for boron binding.

4.2.3 Effect of Loading on The Retention of Boron and Flux Using PNSL

PEUF experiments using PNSH showed that at higher polymer concentrations (lower loadings) retention of boron decreased significantly. This behavior can be explained by the entanglement of PNSH due to the interaction of the polymer chains as the polymer concentration of the feed was increased. This may eventually decrease the possible binding sited of borate anions. Therefore, to overcome this problem, same polymer having a lower molecular weight was synthesized and the effect of loading on the retention of borate was investigated at pH 9.

In the experiments, different metal to polymer ratios between 0.05 (PNSL: 0.2 g/L) and 0.001 (PNSL: 10 g/l) were prepared and PEUF was performed for the retention of boron. Effect of loading on the permeate flux and boron retention was demonstrated in figure 4.2.3.It can be seen from the figure that, when loading was decreased, retention values increased as expected. A decrease in loading means an increase in relative polymer concentration. As the concentration of the polymer increases, the binding sites for borate complexation also increase, which leads to an enhancement in the retention values. Furthermore, since a lower molecular weight PNS was used, the changes in the stereochemistry of the polymer chains may disrupt the ability to form interchain hydrogen bonds even if the PNSL concentration was increased significantly. Therefore an increase in the amount of free hydroxyl groups on the polymer would allow more binding sites for borate complexation, resulting in an enhanced borate retention. Since lower loading values were able to be studied with PNSL, higher retention values were able to be achieved compared to PNSH.

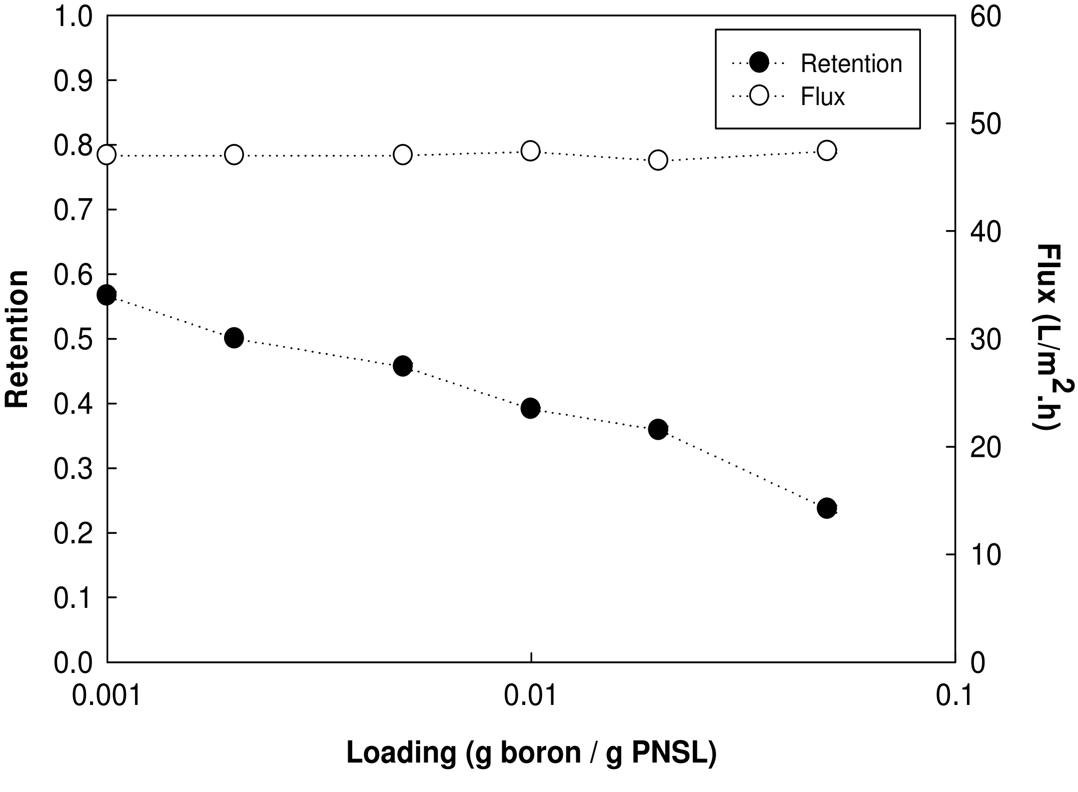


Figure 4.2.3 Effect of loading on the flux and retention of boron using PNSL (Boron: 10 mg/l, pH:9, MWCO: 5 000 Da, ∆P:100 kPa, Feed Flowrate: 0.048 m^3/h)

4.2.4 Effect of pH on The Retention of Boron Using PNSL

In order to investigate the extent of binding of boron by PNSL with respect to pH, PEUF experiments were performed at a pH range of 7-10 and at two different loadings, 0.001 and 0.005. Figure 4.2.4 demonstrates the retention values of boron for different pH and loadings.

Retention of boron obtained at pH 10 was found to be considerably superior to that at pH 7. When we go from pH 7 to 9, a two fold increase in the retention was observed for both loadings. As the pH was further increased to 10, boron retention also increased but in a less amount. Aside from the fact that borate ion concentration increases with the increase in pH, enhancement in the retention of boron can be attributed to the conformational changes in the polymer with respect to the changes in the pH of the solution which may result in a more suitable state for the hydroxyl groups of the polymer to make complex with borate ion.

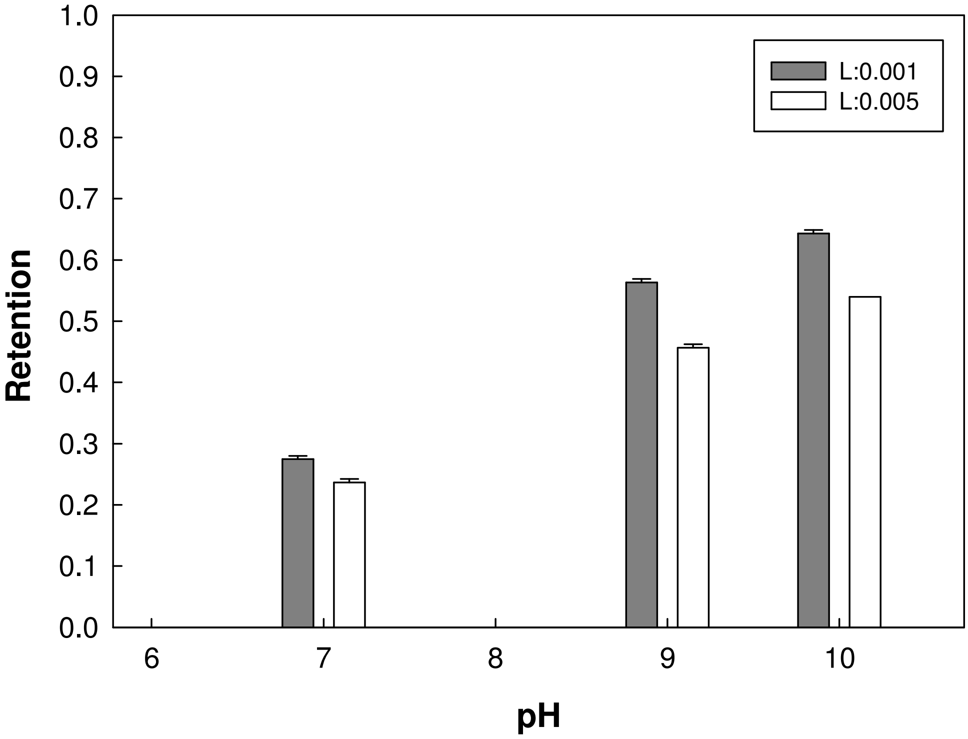


Figure 4.2.4 Effect of pH on the retention of boron using PNSL

(Boron: 10mg/l, MWCO: 5 000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

In the literature, there are a few studies that elaborately investigate the effect of pH on boron retention. In one of those studies, mannitol which is a sugar alcohol having 6 hydroxyl groups, was used in combination with nanofiltration to retain boron from aqueous solutions. Similar to this study, it was observed that, as the pH of the solution increased from 7 to 9 boron retention doubled. However, further increase in the pH did not result in that much enhancement in boron retention. In that study, the influence of pH on boron retention was attributed to the ionization of boron in water [144].

In a previous study of our group, similar behavior was obtained in the retention of borate with the change in the pH of the feed solution when PVA was used as the chelating polymer [14]. However, in that study, the highest retention of boron that can be obtained was 0.28 , which is less than the half of the value obtained with PNSL. In this study, the highest retention achieved by PNSL was 0.64 for a loading of 0.001 and a pH of 10. Since the borate retention capacity of the synthesized PNSL is higher, it will be useful for the design of a separation process which may include a few number of cascades where higher retentions will be obtained.

4.2.5 Effect of Loading on the Retention of Boron and Flux Using PNSM

When the retention values for boron with PNSH and PNSL were compared, it was observed that higher retentions were obtained when lower molecular weight PNSL was used as the chelating polymer. In order to investigate the effect of molecular weight of the polymer on the retention of boron, same polymer with a molecular weight in between PNSH and PNSL was synthesized (PNSM) and effect of pH (7-10) and loading (0.0005-0.05) on boron retention was investigated with the medium molecular weight polymer. Figure 4.2.5 demonstrates the effect of loading on the permeate flux and retention of boron in a semi-logarithmic graph using PNSM as the chelating polymer in PEUF experiments.

As it can be seen from Figure 4.2.5, for the studied range of polymer concentration, permeate flux was slightly reduced by the increase in polymer concentration. However, those flux changes are relatively insignificant compared to the ones obtained with PNSH and no significant change was observed in the viscosity (1.18 cP) of the polymer solution. Thus, it can be concluded that there is no problem gel formation for the ranges of the polymer concentration and experimental parameters (ΔP and feed flow rate) used. As depicted in figure 4.2.5, similar to the PEUF experiments with PNSL, it is seen that, as the loading decreases, enhancement in boron retention is observed.

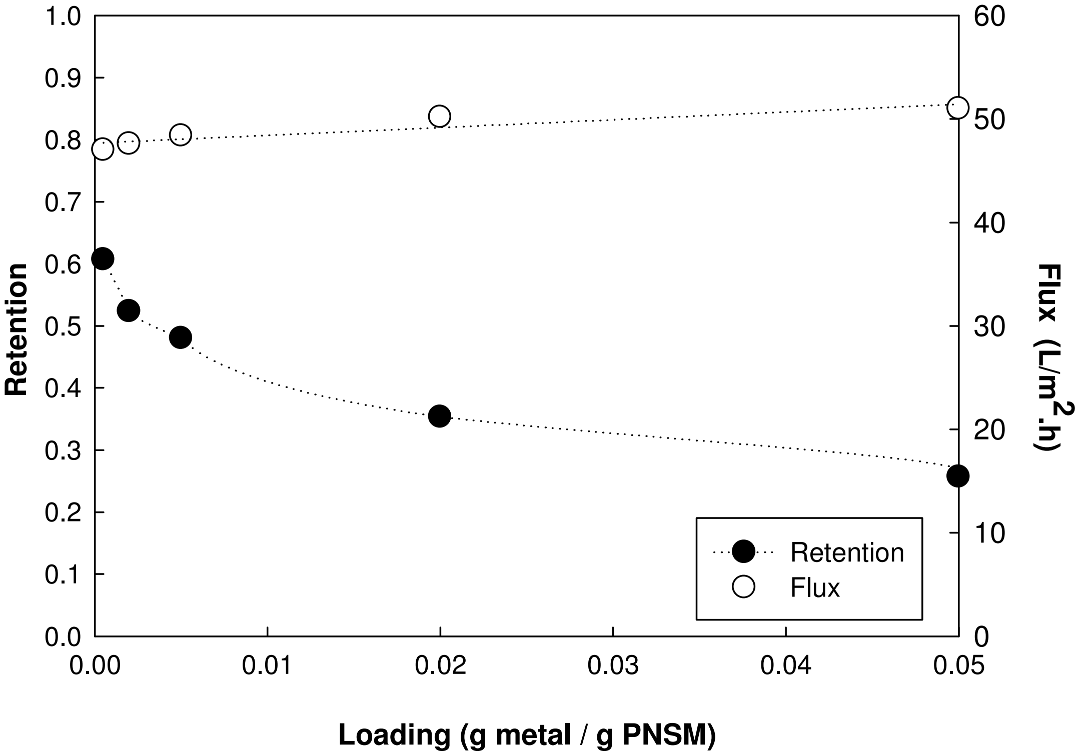


Figure 4.2.5 Effect of loading on the flux and retention of boron using PNSM (Boron: 10mg/l, pH:9, MWCO: 5 000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

In order to compare the boron binding performances of PNSM and PNSL, a set of PEUF experiments were performed at the same loadings and at pH 9 using both polymers. Table 4.2.5 summarizes the results obtained in these experiments.

Standard deviation and percent relative standard deviation values of the retentions with PNSL and PNSM were found to be small for all loadings. This small deviations between the retentions imply that, molecular weight of PNS may not be effective on the complexation and rejection of boron. Therefore the separation may not be dependent on the molecular weight of PNS in the molecular weight range between PNSL (M_v= 110,480) and PNSM (M_v= 49,733). It may rather depend on the functionalization of the polymer, that is, the available active site concentration present in the structure of the polymer capable of interacting with borate. In the previous study of our group, PVA having different molecular weight and degree of hydrolysis values were used as chelating agent in PEUF studies. Experimental results showed that, retention of boron was not significantly affected by the molecular weight of the polymer, it was rather affected by the degree of hydrolysis (concentration of active sites) [14].

Table 4.2.5 Comparison of the boron binding performances of PNSM and PNSL (Boron: 10mg/l, pH:9, MWCO: 5 000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

Loading (g boron /g PNS)	R with PNSM	R with PNSL	STD	% RSD
0.002	0.52	0.50	± 1.41	2.77 (n:4)
0.005	0.48	0.45	± 1.70	3.63 (n:4)
0.02	0.35	0.35	± 0.28	0.80 (n:4)
0.05	0.26	0.24	± 1.41	5.66 (n:4)

4.2.6 Effect of pH on The Retention of Boron Using PNSM

After investigating the influence of loading on boron retention, a set of experiments were performed to investigate the effect of pH on the retention of boron utilizing PNSM as chelating polymer at pH 9 and 10 with two different loadings. Figure 4.2.6 demonstrates the retention values of boron for different pH and loadings.

Similar to the results obtained with PNSL, the increase in pH resulted in an enhancement in the retention of boron for both loadings. Retentions as high as 68 % can be obtained with PNSM at pH 10 with a loading of 0.0005 which was the highest loading and pH achieved for boron retention in this study.

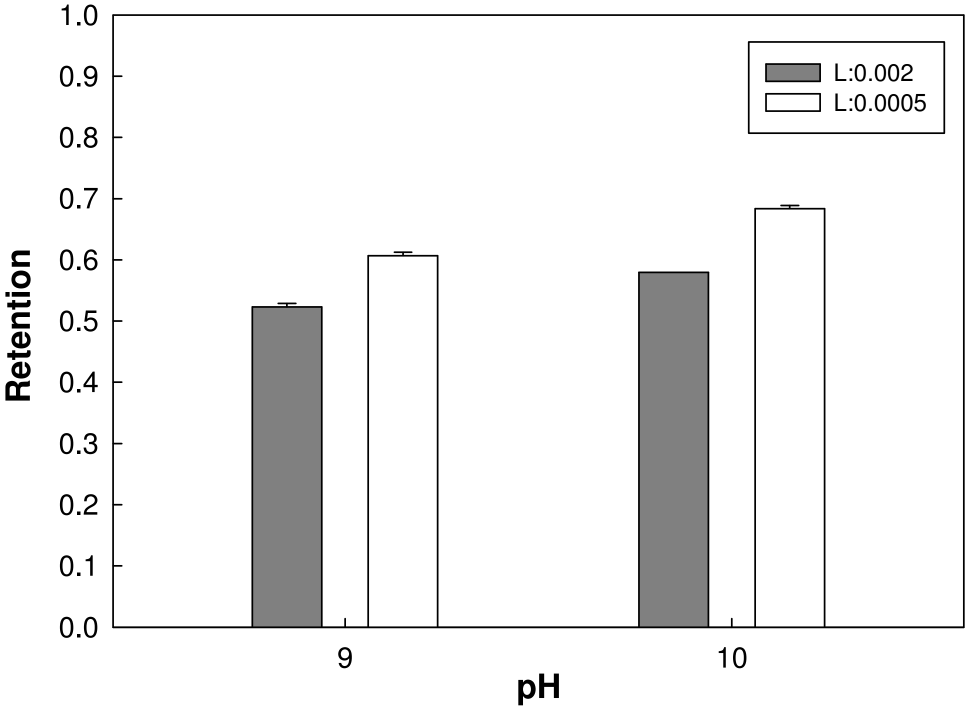


Figure 4.2.6 Effect of pH on the retention of boron using PNSM
(Boron: 10mg/l, MWCO: 5 000 Da, ΔP:100 kPa, Flowrate: 0.048 m^3/h)

Unlike the current study, in the former study of our group, in which N-methyl-D-glucamine grafted Poly (GMA) was used as chelating polymer, effect of pH was not that pronounced in the retention of boron [50]. As a matter of fact, there was only a 20 % increase in the retention of boron when the pH was increased from 7 to 10.

It must be noted that, there exists a pH value above which stable polymer-metal complex is formed depending on the polymer and metal ion type [79]. By changing the pH values appropriately it is possible to have high retention values in the separation of metal ions in one extreme (high pH) and to disassociate polymer-metal complexes in the other extreme (low pH). The latter will enable the recovery of the concentrated metal present in the feed and regeneration of the complexing polymer. If several metal ions form macromolecular complexes with different stability constants, it is possible to separate them by varying the pH. Since the pH has a strong effect on the retention of boron with all of the synthesized polymers, it will be possible to regenerate PNS and to recover boron by decreasing the pH to an appropriate value.

4.2.7 Effect of Loading on The Retention of Boron and Flux Using COP

In order to investigate the effect of polymer structure in the binding ability with boron and subsequently, to observe the effect of operating parameters like loading and pH on the removal of boron, another water soluble functional polymer, a co-polymer of 4-Vinyl-1, 3-dioxalan-2-one and vinyl acetate (COP), was synthesized and its separation performance was examined using PEUF. The experiments were carried out in a loading range of 0.05-0.005.

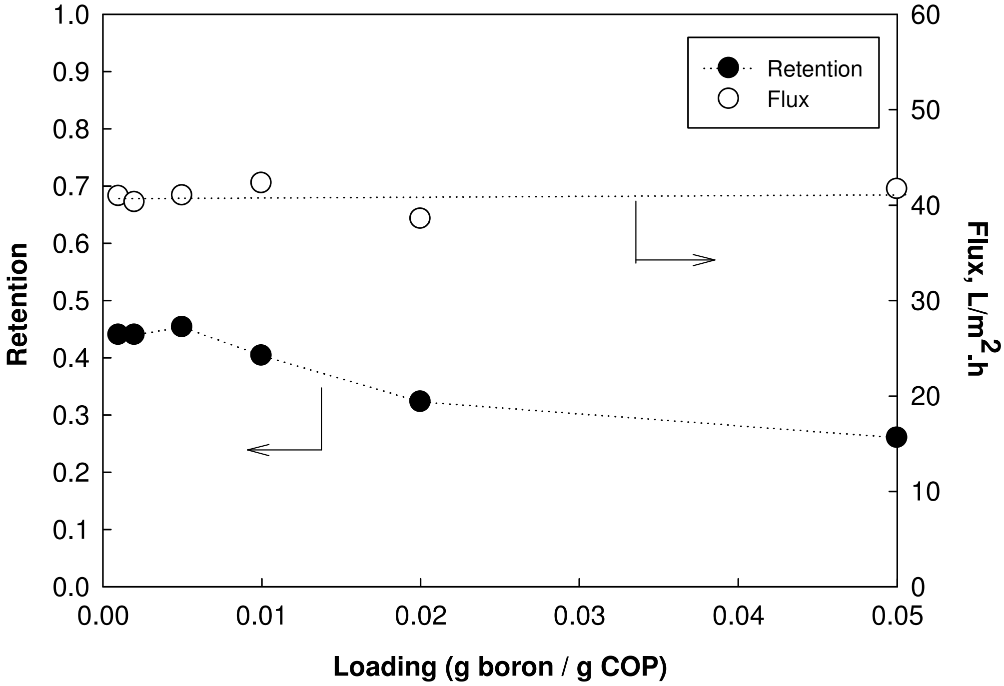


Figure 4.2.7 Effect of Loading on the retention of boron and flux using COP (Boron: 10mg/l, pH:9, MWCO: 5 000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

Figure 4.2.7 depicts the effect of loading on boron retention using COP as the chelating polymer. It is observed that, as the loading (g boron/gCOP) decreases while keeping boron concentration constant, boron retention increases up to loading of 0.005 after this loading it remains almost constant. It must be emphasized that macromolecules may reduce their sizes in concentrated polymer solutions [62]. If the polymer concentration in the feed solution is high, it may lead to a higher interaction between the polymer chains, thus resulting in a more compact polymer structure. In other words, as the polymer concentration increases and polymer chains get closer to eachother, suitable chain conformation for boron binding may not be obtained due to the entanglement of COP chains.

4.2.8 Effect of pH on The Retention of Boron Using COP

Figure 4.2.7.a shows the effect of pH on the retention of boron for different loadings. For both of the pH values studied, retention of boron remained almost constant after a loading of 0.005. Similar to the PEUF experiments in which PNS was used as the chelating polymer, as the pH of the solution increases to 10, boron retention also increases.

In order to complete the parametric study of the performance of PEUF in retaining boron with COP as chelating polymer, effect of pH was also investigated in the range of 7-10. In figure 4.2.8.b, retention values with respect to pH are presented at a loading of 0.005 which was found to be the loading resulting in the highest retention at pH 9. Similar to the results obtained with all three molecular weight PNS, the increase in pH leads to an increase in the retention of boron. When figure 4.2.8 is compared with figure 4.2.2 and figure 4.2.4, it is observed that the effect of pH is not that pronounced when COP was used in PEUF experiments instead of PNS. This may indicate that, conformational changes in COP are less sensitive to the alterations in the pH of the solution than that of PNS. In DLS-SLS measurements of the two polymers, it was observed that, as the pH of the solution increases the hydrodynamic radius of both polymers increase. However, the increment in the hydrodynamic radius of COP with respect to pH is lower than that obtained with PNS.

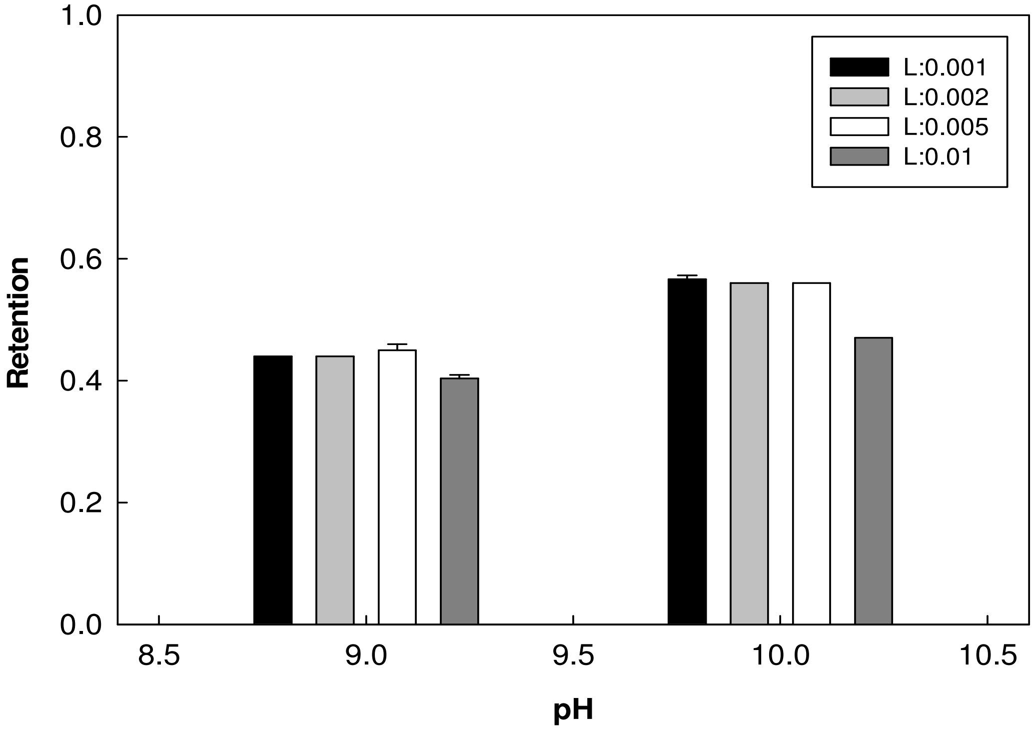


Figure 4.2.8.a Effect of pH and loading on the retention of boron using COP (Boron: 10 mg/l, MWCO: 5000 Da, Feed Flowrate: 0.048 m^3/h)

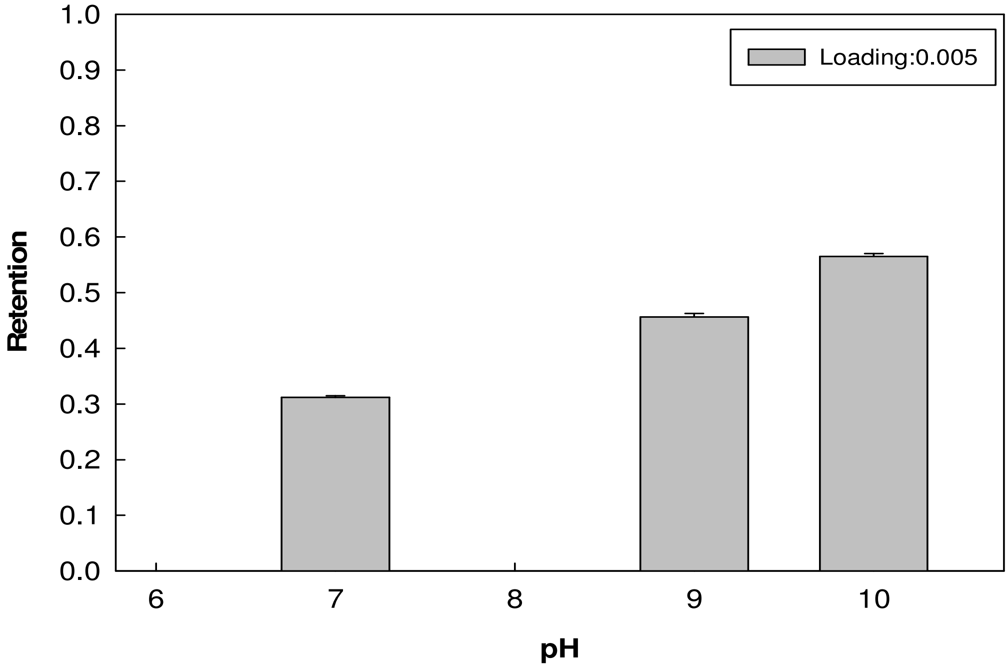


Figure 4.2.8.b Effect of pH on the retention of boron using COP

(Boron: 10mg/l, MWCO: 5 000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

Since for both of the polymers, pH range and boron concentrations are the same, it is expected to have similar boric acid dissociation behavior, hence similar borate anion concentration for both of the feed solutions. Therefore, the difference in borate anion retentions may be attributed to the differences in the conformational states of the polymers rather than the increase in boric acid dissociation at high pH values.

4.3 Comparison of The Boron Chelating Performances of PNS and COP

In the literature, it was reported that polymer bound sugar derivatives such as N-methyl D-glucamine, sorbitol and mannitol have been employed successfully in removal of trace boron. However regenerabilities of those materials are limited due to acid hydrolysis [147]. Therefore, in this study two boron selective functional polychelatogens containing polyol groups, which are much more stable than sugar derivatives, were synthesized and effect of operating parameters of PEUF process on the retention of borate was investigated using these selective polymers.

In one of the studies, polymers possessing more hydroxyl groups around the amine nitrogen were shown to be better boron chelators. It was demonstrated that, high amounts of boron can be removed from dilute boric acid solution by the polymers with triol chelating units on each amine group [15]. Therefore, in this study, one of the polymers is hydroxyethylamino glycerol functioned polyglycidyl methacrylate (PNS) having three hydroxyl groups around the amine and another hydroxyl group on the vicinal carbon to ensure the solubility of the polymer even complexed with borate. In the synthesis of PNS the functional group, hydroxyethyl amino glycerol, were formed by ring opening of the oxirane functions present in glycidol (see figure 3.2.1). It was stated that, the resulting vic-diols (hydroxyl groups placed on the adjacent carbon atoms) created on polymeric supports should be trans- to each other [148]. Some authors suggest that hydroxyl functions in cis-diol position are needed for obtaining more reactivity in forming boron esters and tetravalent borates [149]. However, both isomers (cis-diol and trans-diol) may form boron complexes, but the cis-isomer is expected to form a more stable complex. In this configuration 1:1 boron ester formation seems to be favorable (see figure 2.4.2.1, a) [148].

The second polymer used in boron retention studies is a copolymer which was obtained by random copolymerization of 4-Vinyl-1,3-dioxalan-2-one and vinyl acetate. The copolymer was hydrolyzed to result in two vicinal hydroxyl groups on 4-Vinyl-1,3-dioxalan-2-one for boron chelation, and one hydroxyl group on vinyl acetate for ensuring high solubility of the polymer when complexed with boron. The resulting polymer (COP) is also resistant to acid hydrolysis. Therefore, regeneration and reusability of the polymer is possible by acid hydrolysis. In the synthesis of COP, hydroxyl groups formed on the adjacent carbon atoms after the hydrolysis of the sythesized copolymer. Since random polymerization was carried out, the ratio of two monomers in the structure of the random copolymer depends on the relative amounts and reactivities of the monomers. The polyol/monoborate complexes formed with this polymer might be with 1:1 or 1:2 stoichiometry (see figure 2.4.2.1, a, b).

In order to compare the boron retention performances of the synthesized polymers PEUF experiments were performed with both of the polymers at the same loading and pH values. Figure 4.3.1 shows the effect of different loadings on the retention of boron using PNSL and COP. It is seen that at higher loadings (lower polymer concentrations) retention of boron is almost the same for COP and PNSM. However, as the loading is decreased, considerable increase is observed in the boron retention performance of PNSM, whereas that of COP remained nearly the same at 0.44 .

The reason for this behavior may result from the difference in the structures of COP and PNSM. In the structure of PNSM, there is a tertiary amine function in every repeating unit. The role of the tertiary-amine function is to capture the proton formed due to the formation of diol-borate complex. If tertiary-amine function is not present the neutralization of proton can not be achieved, which eventually decrease the formation of borate from boric acid. Thus, efficiency of boron-diol complex formation is reduced if the pH of the solution is not adjusted externally. In fact, it was observed that in the PEUF experiments, when COP was used as the chelating agent, pH of the feed solution tends to decrease continuously. So, it was necessary to continuously adjust the pH of the solution using NaOH and HNO_3. On the other hand, when PNSM was used as the chelating agent, once the pH of the solution was adjusted to the desired value in the beginning of the experiment, the pH of the feed solution remained almost constant. Thus, less amount of NaOH and HNO_3 addition was needed. This may suggest that since tertiary amine function is not present in the structure of COP, the proton brought about by the formation of borate-diol complex can not be neutralized. Besides, since pH of the feed solution needs to be adjusted continuously, the addition of high amount of NaOH and HNO_3 may increase the ionic strength of the solution which may limit the complexation of COP with borate. Another reason for not having higher retention values with further decrease in the loading may be solubility problem of COP in molecular level.

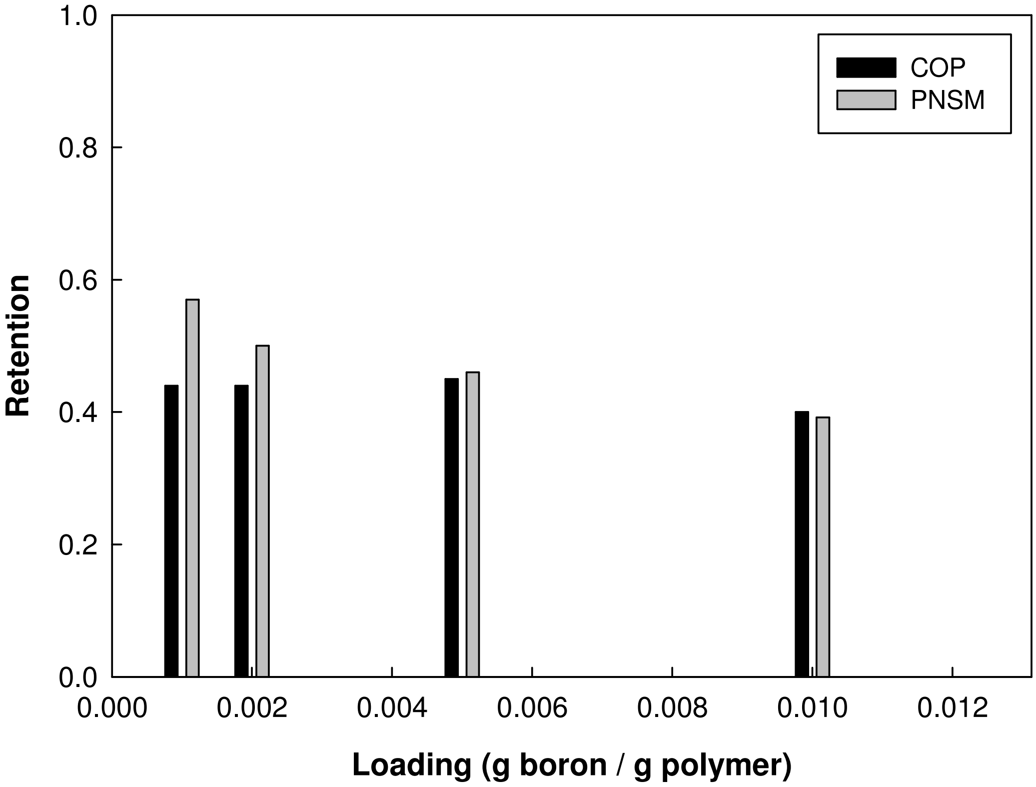


Figure 4.3.1 Comparison of Boron Retention Performances of PNSM and COP (Boron: 10mg/l, pH:9, MWCO: 20 000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

4.4 Characterization of PNSM and COP by DLS/SLS Method

In this study, to gain an insight about the conformational changes in the structure of PNSM and COP due to the pH alternations in solution, dynamic and static light scattering experiments were performed.

The data obtained by static and dynamic light scattering measurements were processed by utilizing the governing equations of Guinier method. The typical Guinier plots of the PNSM and COP solutions, calculated by ALV-5000 & 60X0 software are given in Appendix E and data obtained from light scattering experiments when there is no dilution in the samples is given in Table 4.4.1. Data obtained from Guinier plots is shown in Table 4.4.2.

As depicted in table 4.4.1, PNSM and COP polymers were analyzed at different solution pH values as well as in the presence of boron in the solution. Three different hydrodynamic radii mean that the polymer aggregate in solution exists in three size distributions. The first one has the highest intensity and corresponds to the hydrodynamic radius of the polymer aggregates and the other two may be aggregates of lower molecular weight parts of the polymer or monomer. Thus, it is convenient to compare the first hydrodynamic radii values.

Table 4.4.1 Data obtained by DLS without dilution

PNSM					**COP**				
Conc. (g/dm^3)	**pH**	**Rh (nm)**			**Conc. (g/dm^3)**	**pH**	**Rh (nm)**		
1.0	7.0	69.5	12.5	661.5	3.3	7.0	179.5	4.4	28.4
1.0	9.0	115.3	25.6	6.6	3.3	9.0	202.5	4.7	26.2
1.0	10.0	146.5	31.3	0.0	3.3	10.0	371.5	4.6	34.4
PNSM-Boron Complex					**COP-Boron Complex**				
Conc. (g/dm^3)	**pH**	**Rh (nm)**			**Conc. (g/dm^3)**	**pH**	**Rh (nm)**		
1.0	8.2	384.1	60.5	14.0	3.3	9.3	426.0	9.1	37.8

In order to comment on the impacts of the parameters obtained by light scattering measurements, their physical meanings should be considered. Radius of gyration (R_g) describes the overall spread of the molecule and is defined as the root mean square distance of the collection of atoms from their common centre of gravity. Hydrodynamic radius (R_h) is defined as the radius of a hard sphere that diffuses at the same rate as the polymer. It includes hydration and shape effects. A high hydration causes an enhancement in R_h [150].

As the data obtained for PNSM when there is no dilution in the samples are compared, it is observed that when the pH of the solution increases hydrodynamic radius of the polymers increases. This may indicate that as the pH of the solution increases, polymer chain interactions are lowered thus, the polymer becomes more widened. This result is consistent with the data obtained by PEUF experiments. In PEUF of borate using PNSM as the chelating agent it was observed that the increase in pH increased the retention of borate ion. This can be associated with the increase in the borate ion concentration with the increase in pH as well as the alteration in the conformation of PNSM with pH.

Similar behavior was obtained in the DLS measurements with the COP samples. That is, the increase in the pH of the solution leads to an increase in the hydrodynamic radius. When the R_h values of COP was compared with that of PNSM, it was noticed that, for all of the pH values studied, the hydrodynamic radius of COP is grater than that of PNSM. This is most probably due to the difference in the molecular structure of the polymers. In the structure of PNSM there is tertiary amine group bound to every repeating unit of the polymer. It is known that amine groups are capable of interacting with hydroxyl groups. This may result in an interaction between the polymer chains which eventually may lead to a lower hydrodynamic radius.

In order to gain an insight about the conformational changes in the structure of the synthesized polymers with the addition of borate, DLS measurements were also performed with the samples having both polymer and boron (10 mg/L). As depicted in table 4.5.1, the hydrodynamic radius of both PNSM and COP increased significantly with the addition of boron. In the case of PNSM the R_h is almost doubled. This may imply that, with the addition of boron, hence the complexation of boron with the polymer, the polymer chains become stretched, therefore their hydrodynamic radii increase.

In the Static Light Scattering method the aim is to reach Kc/R (where K is an optical parameter, c: concentration and R: Rayleigh ratio of the sample). After obtaining Kc/R value, by using Guinier method radius of gyration can be estimated. In order to have an accurate calculation of R_g, SLS measurements are carried out at four different concentrations. Each fit at constant angle data is extrapolated to zero concentration, and each fit at constant concentration is extrapolated to zero angle, obtaining two lines. Apparent radius of gyration (R_g) is calculated from the slope of the extrapolated line at zero concentration.

Table 4.4.2 demonstrates the data extracted from Guinier plots obtained by SLS measurements. Guinier plots are given in appendix F.

Table 4.4.2 Parameters extracted from Guinier plots

PNSM pH 7		**COP pH 7**	
Conc. (g/dm^3)	**Rg**	**Conc. (g/dm^3)**	**Rg**
0.0	255.6	0.0	319.4
1.0	132.6	3.3	157.5
0.8	165.6	2.9	158.1
0.5	205.3	2.3	191.9
0.2	235.1	1.7	219.7
PNSM pH 9		**COP pH 9**	
Conc. (g/dm^3)	**Rg**	**Conc. (g/dm^3)**	**Rg**
0.0	231.9	0.0	282.9
1.0	116.6	3.3	156.5
0.8	146.6	2.9	179.5
0.5	192.7	2.3	188.9
0.2	210.0	1.7	231.0
PNSM pH 10		**COP pH 10**	
Conc. (g/dm^3)	**Rg**	**Conc. (g/dm^3)**	**Rg**
0.0	192.6	0.0	229.9
1.0	135.7	3.3	182.6
0.8	135.6	2.9	224.5
0.5	150.0	2.3	219.5
0.2	186.7	1.7	200.1
PNSM-Bor		**COP-Bor**	
Conc. (g/dm^3)	**Rg**	**Conc. (g/dm^3)**	**Rg**
0.0	211.5	0.0	251.1
1.0	136.1	3.3	174.2
0.8	174.8	2.9	185.6
0.5	169.9	2.3	187.5
0.2	202.8	1.7	216.1

The radius of gyration value corresponding to zero concentration is the apparent R_g. When the radius of gyration values of different concentrations are compared, it is observed that the decrease in the solution concentration results in an increase in the radius of gyration of both COP and PNSM at all pH values. This may imply that as the solutions become less crowded, interactions between the polymer chains decrease which results in an increase in the radius of gyration of the polymer. Similar to the hydrodynamic radius results, radius of gyration of COP is higher than that of PNSM at every concentration and pH value. On the other hand opposite to the R_h results, it was observed that as the pH of the solution increases, radius of gyration of the polymers decreases. Similar to the R_h results, addition of boron increases R_g values for both of the polymers.

4.5 Hexavalent Chromium Retention Studies Using Specifically Tailored Polyelectrolyte by PEUF

PEUF experiments for hexavalent chromium retention were performed using a specifically tailored polyelectrolyte, namely, poly (N, N-diallylmorpholinium bromide) (PDAM) in order to investigate the effect of loading and pH on the separation of Cr(VI) from aqueous solutions. The synthesized PDAM is a strong polyelectrolyte, that is fully ionized at all pH values. Since the synthesized polymer is a polyelectrolyte, effect of competing-ion concentration on the retention of Cr (VI) was also examined to observe the effect of competing ion charge on the retention of the target anion. The membrane used in the PEUF experiments had a molecular weight cut off (MWCO) of 5 000 Da.

4.5.1 Effect of Loading on The Retention of Cr(VI) and Flux Using PDAM

In the study, various loading values were examined for chromate retention at different pH values using continuous PEUF. Since Cr (VI) exists in the form of chromate (CrO_4^{2-}) in basic and neutral pH, as a starting point, pH of the solution was selected as 8 and the effect of loading was investigated using continuous PEUF. Loading profiles of Cr (VI) obtained in PEUF experiments for different pHs are given in Figure 4.5.1a, 4.5.1b and 4.5.1c.

Permeate flux remained almost constant regardless of the loading of the feed solution for all of the pH values examined in PEUF experiments. Independence of flux from loading proved that in the UF system there is no gel formation for the ranges of the polymer concentration used.

PDAM is a polyelectrolyte having an ionizable quaternary ammonium group. Thus, the possible mechanism for the retention of chromate is due to electrostatic interaction. In general, a decrease in loading (increase in polymer concentration) leads to an increase in retention. However, figure 4.5.1a, 4.5.1b, 4.5.1c showed that, decreasing loading lower than 0.01 caused a slight decrease in the retentions for all of the pH values studied. This behavior suggests that, at high polymer concentrations either suitable chain conformation for polymer-Cr(VI) interaction may not be achieved due to the crowding of the solution or, counter-ion bromine in the structure of the polyelectrolyte may repel the chromate anions causing the retention to decrease [17].

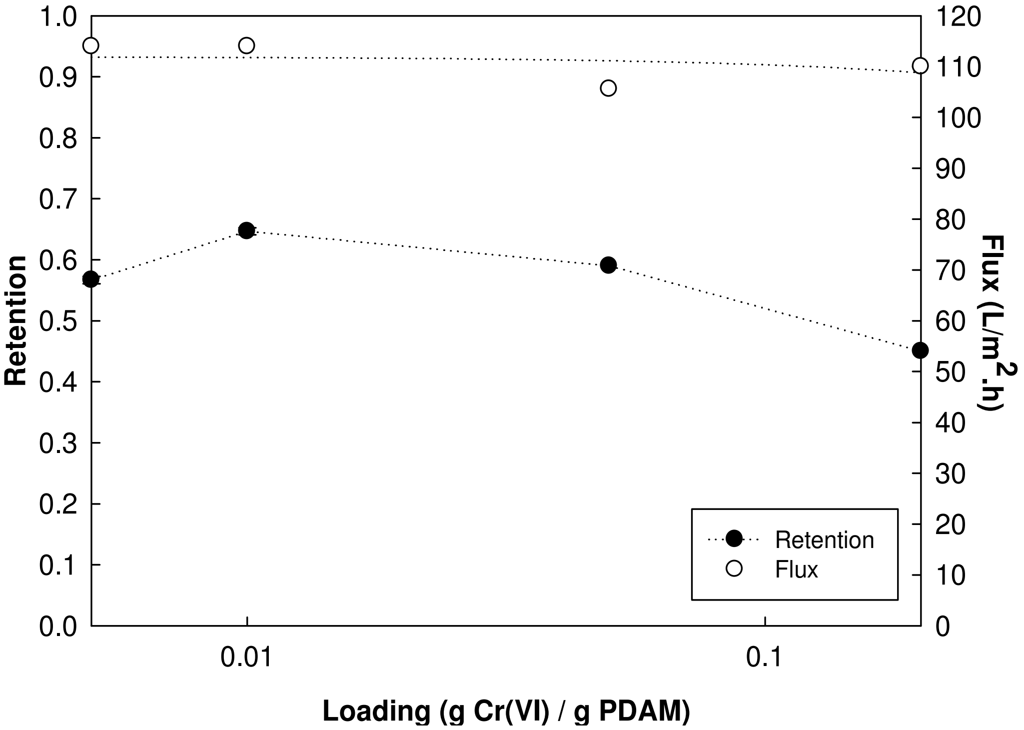


Figure 4.5.1a Effect of loading on the retention of Cr (VI) using PDAM at pH 8 (Cr(VI): 10 mg/l, MWCO: 5000 Da, pH: 8, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

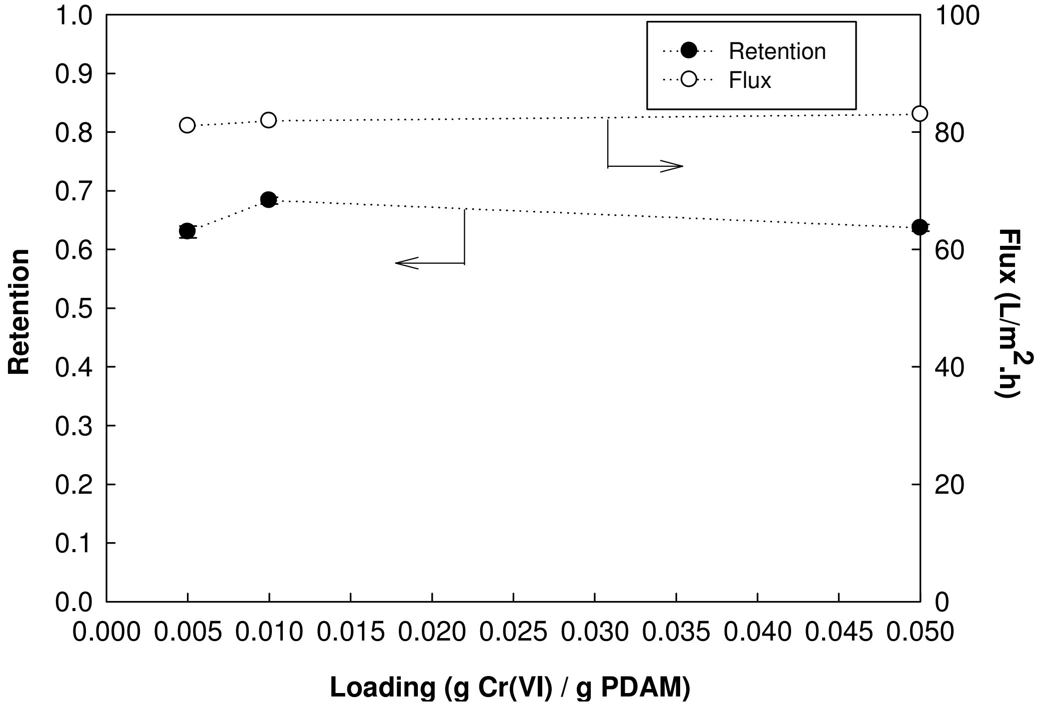


Figure 4.5.1b Effect of loading on the retention of Cr (VI) using PDAM at pH 5 (Cr(VI): 10 mg/l, MWCO: 5000 Da, pH: 5, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

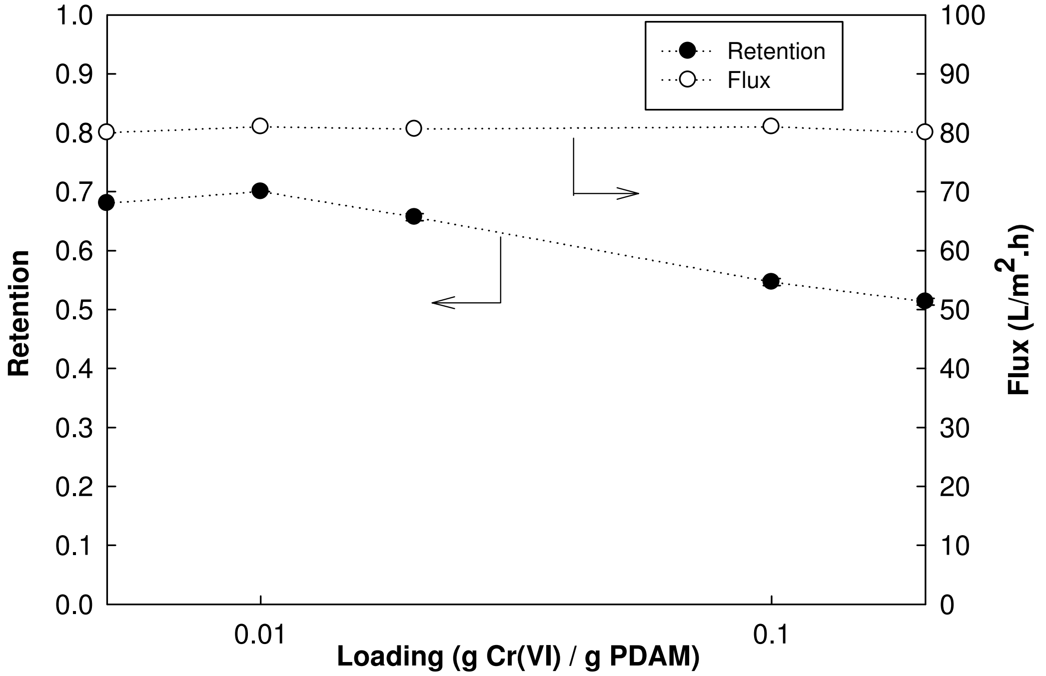


Figure 4.5.1c Effect of loading on the retention of Cr (VI) using PDAM at pH:4 (Cr(VI): 10 mg/l, MWCO: 5000 Da, pH: 4, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

In the literature, all of the studies for chromate removal employed batch mode of PEUF operation. Similar to this study, it was observed that increase in the polymer concentration resulted in a higher Cr (VI) retentions. However, since continuous PEUF has not been used, the effect of operating parameters such as loading and pH on the retention of Cr (VI) could not be investigated elaborately. In most of the studies, high Cr (VI) retentions were obtained (~0.99), but the effect of competing ion on Cr (VI) retention were not examined. Moreover, in very few studies that investigate the effect of competing ion on Cr(VI) retention, it was found that besides chromate, other anions were also retained nearly with the same extend. Therefore, selective separation could not be achieved [140].

4.5.2 Effect of PDAM Concentration on The Retention of Cr(VI)

In order to see the effect of crowding in the feed solution to the retention of chromate, PEUF experiments were carried out at a fixed loading of 0.01, and both polymer and chromate concentrations were varied to obtain the same loading value.

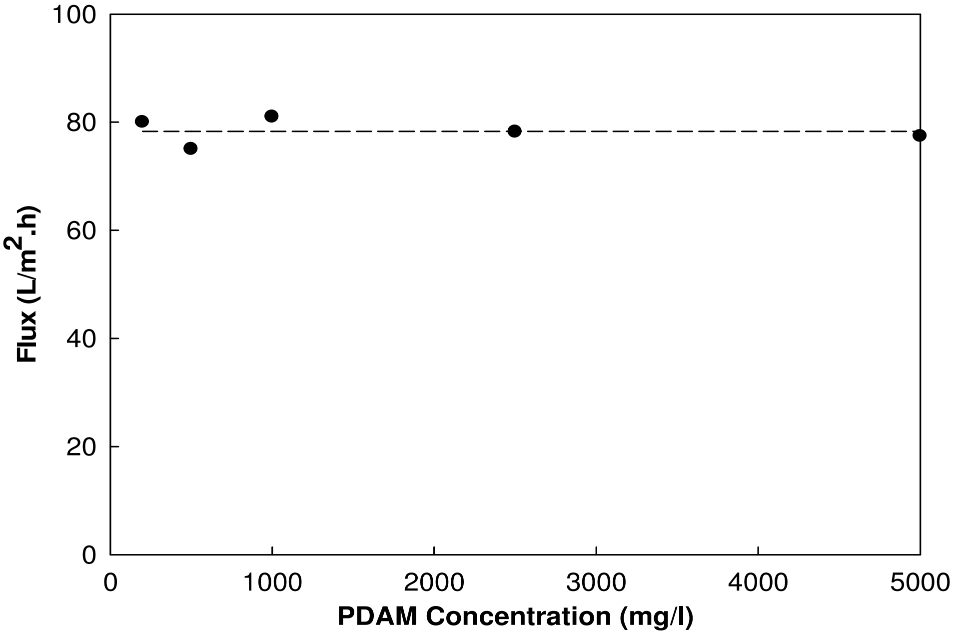


Figure 4.5.2 Effect of PDAM concentration on the permeate flux at pH 4 (Cr(VI):10 mg/L, L:0.01, MWCO: 5000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

Figure 4.5.2 depicts the flux and table 4.5.2 demonstrates the retention values obtained from the PEUF experiments with respect to various PDAM and chromate concentrations.

It is seen from figure 4.5.2 that permeate flux values remained nearly the same for the whole concentration range of PDAM indicating that gel formation does not exist in the studied experimental conditions.

Table 4.5.2 Retention values with respect to various PDAM and chromate concentrations

Loading	pH	Polymer Concentration (mg/L)	Chromate Concentration (mg/L)	Retention	% RSD of Retention
0.01	4.0	200.0	2.0	0.67	1.49 (n:4)
0.01	4.0	500.0	5.0	0.70	1.64 (n:4)
0.01	4.0	1000.0	10.0	0.69	0.00 (n:4)
0.01	4.0	2500.0	25.0	0.59	0.00 (n:4)
0.01	4.0	5000.0	50.0	0.53	1.10 (n:4)

(Cr(VI): 10 mg/l, MWCO: 5000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

In Table 4.5.2, the order is in the direction of increasing crowdedness of the feed solution. It can be observed that, before a PDAM concentration of 1000 mg/L, retention of Cr (VI) is almost constant. Although the loading of the feed solution is constant, it is seen that as the feed solution gets crowded, after a PDAM concentration of 1000 mg/l, retention decreases significantly .

In a previous study of our group, effect of loading was investigated on the retention of mercury using PEI via PEUF. In that study, when both mercury ion and PEI concentrations were increased, keeping L constant, no change occurred in the retention values of mercury. It was concluded that retention of mercury was dependent on the loading value rather than the concentration of polymer in the feed solution [48]. In this study it is observed that retention does not only depend on the loading but also on the concentrations of both Cr(VI) and PDAM. Results obtained from the PEUF experiments may imply that, after a certain polymer concentration, due to the crowding effect, suitable chain conformation of the polymer may not be achieved in order the polymer chains to interact with chromate anions. It is known that polymeric substances may change their conformation and reduce their sizes in the concentrated, crowded solutions, thus decreasing the possibility of interaction between the polymeric chains and target substances. This phenomena will eventually cause a decrease in the retention of the related substance. Therefore, it can be concluded that Cr(VI) separation will be efficient in a less crowded solution having the optimum amount of polymeric agent.

4.5.3 Effect of pH on The Retention of Cr(VI) Using PDAM

In aqueous solution, hexavalent chromium exists as hydrochromate ($HCrO_4^-$), chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$) ionic species depending on the pH of the solution. In basic and neutral pH, the chromate form predominates. Since Cr(VI) can be found in different forms at different pH values in aqueous solutions, before proceeding to the PEUF experiments, pH range was selected.

The limiting factor in the determination of the lowest pH value to be studied in the PEUF experiments was the membrane tolerance to acidic medium. In the literature, the pH range of the membrane used in this study was reported to be 2-10. Therefore, to be on the safe side, the lowest pH for Cr(VI) retention experiments was selected as 4.

In order to determine the highest pH value, it is necessary to check if there is any precipitation or colloid formation that can be retained by the membrane after a certain pH within the membrane tolerance range. Therefore, to check the possibility of precipitation or colloid formation, feed solutions containing 10 mg/l Cr(VI) were prepared. While preparing the feed solutions, polymer was not added in order to determine if membrane alone can also retain some amount of Cr(VI). Before the UF process, the pH of the solution was adjusted to the desired value between 3 and 9, then batch UF was performed. The membrane used in batch UF experiments was the same membrane as the one used in PEUF experiments (MWCO: 5000 Da).

Before performing batch mode of UF, absorbance of the feed solution was measured using UV-Vis spectrophotometer at a wavelength of 375 nm. This wavelength was selected based on the highest absorbance of Cr(VI) solution obtained in the wavelength range of 190-800 nm.

In batch UF experiments feed solution is placed in a stirred UF cell (see figure 3.3.2) and dead-end filtration is applied to the feed solution containing only 10 mg/l Cr(VI). Permeate is collected in a separate beaker until 4-5 ml of feed solution is left in the cell. The absorbance of permeate was also measured at a wavelength of 375 nm. Results obtained in the UV-Vis spectrophotometer analysis are given in table 4.3.3.

Table 4.5.3 Absorbance results for the chromium precipitation experiments (Cr(VI): 10 mg/l, MWCO: 5000 Da, batch UF system)

	Absorbance		
pH	**Feed**	**Permeate**	**Difference (%)**
3	0.202	0.197	0.5
4	0.202	0.198	0.4
5	0.358	0.356	0.2
6	0.442	0.440	0.2
7	0.675	0.674	0.1
8	0.856	0.820	3.6
9	0.880	0.778	10.2

As it is seen from table 4.5.3, after a pH of 8, the difference between the absorbance values of feed and permeate solutions becomes significant, implying that there may be chromium precipitation or colloid formation above this pH. These colloids or precipitates may be retained by the UF membrane resulting in a decrease in the absorbance of the permeate solution. This means that, when the pH is adjusted to values higher than 8 in PEUF experiments, there may also be Cr(VI) retention due to the colloid formation as well as polymer-Cr(VI) interaction. Therefore, to eliminate the possibility of precipitation and colloid formation, the upper limit of pH was selected as 8. After specifying the pH range for Cr(VI) retention studies, PEUF experiments were performed at various pH values at a loading of 0.01 which was found to be the loading at which highest Cr(VI) was obtained. The retention profile obtained by PEUF experiments are given in figure 4.5.3. Retention of Cr(VI) was found to increase as the pH of the solution was decreased. The maximum retention was obtained as 0.74 at a pH of 4.

In the literature, similar results were obtained where quaternary ammonium compounds were used as extractants to remove Cr(VI) from aqueous solutions . In these studies [145] highest Cr(VI) recovery was obtained at a pH of 3. At pH values higher than 5, Cr(VI) recovery dropped sharply. Therefore, it was concluded that Cr(VI) removal was favored at acidic pH values. In another study [146], in which chitosan membrane was used in Cr(VI) retention, pH values of the solutions were varied from 3 to 5.6 and they obtained a significant dependence of Cr(VI) retention to the pH of the solution. In that study it was observed that the lower the pH the higher the Cr(VI) retention.

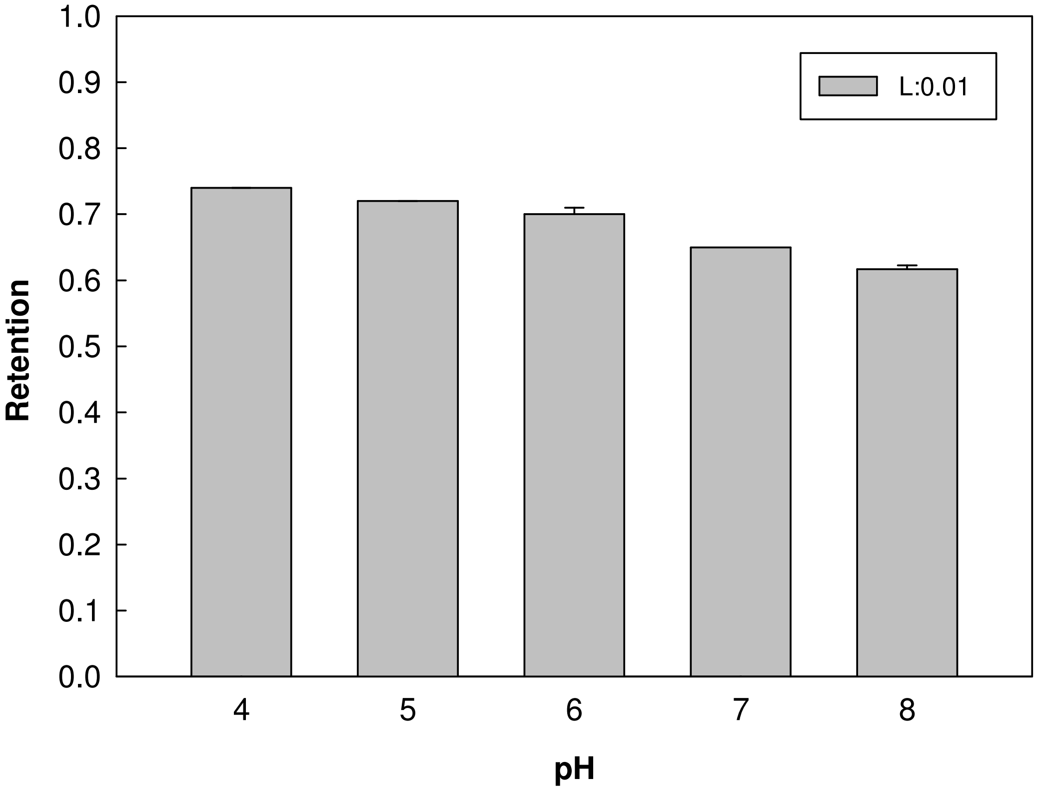
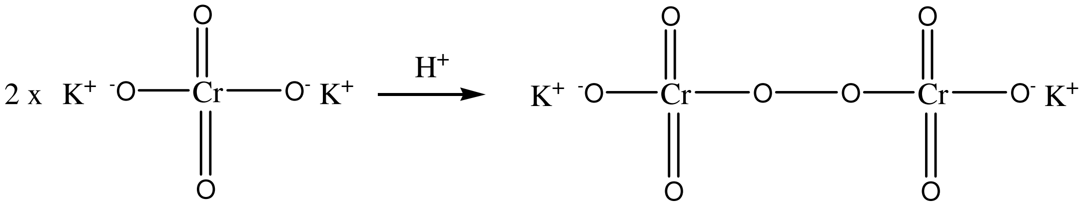


Figure 4.5.3 Effect of pH on the retention of Cr(VI) at a loading of 0.01 (Cr(VI): 10 mg/l, MWCO: 5000 Da, ΔP:100 kPa, Feed Flowrate: 0.048m^3/h)

In one of the studies, it was reported that pH is the key parameter for efficient separation of Cr(VI) using quaternary ammonium compounds. Moreover, it was stated that the pH of the solution should be kept below pH 4.5 for a sufficient separation of Cr(VI). In that study, the decrease in the efficiency of Cr(VI) separation above pH 5 was related to the speciation of Cr(VI) and especially to a decrease in the fraction of $HCrO_4^-$ and $Cr_2O_7^{2-}$ with the increase in pH [90].

In aqueous solutions chromate and dichromate anions are in a chemical equilibrium according to the reaction scheme below:



This equilibrium can be pushed towards dichromate by lowering the pH or in the other direction towards chromate by raising the pH to basic values. Therefore, as the pH of the solution was lowered, chromate anions become dichromate. Positively charged quaternary amine groups interact with dichromate. Therefore, for every quaternary amine group two chromate anions are retained at low pH values. This results in an increase in Cr(VI) retention with the decrease in pH.

This behavior may also be explained by the binding mechanism of Cr(VI) and PDAM. Binding of PDAM with Cr(VI) is due to electrostatic interaction between the positively charged quaternary amine groups of the synthesized polymer and negatively charged Cr(VI). In neutral and basic media amount of hydroxyl ions are higher that that in the acidic medium. This may cause the competition of OH^- ions with Cr(VI) and decrease the retention of the target anion.

4.5.4 Effect of Competing Ion Concentration on The Retention of Cr(VI) Using PDAM

In experiments which were performed in order to observe the effect of competing ion concentration on Cr(VI) retention, it was decided to use two different salts; NaCl, having monovalent anionic group and Na_2SO_4, having divalent anionic group that can be present in the waste waters containing Cr(VI). The aim was to observe the effect of competing ion charge in addition to the effects of competing ion concentration on Cr(VI) retention.

The experiments were performed at a chromate loading of 0.01 and a pH of 4 in the presence of Na_2SO_4 or NaCl. Sulfate and chloride concentrations in the feed and permeate were determined by ion chromatography and retention values were calculated according to equation 1.1.

In the PEUF experiments containing both Cr(VI) and competing anion, permeate flux remained constant around 80 $L/m^2.h$ regardless of the competing ion type and concentration. This may imply that the presence of high concentrations of competing ions did not result in gel formation or precipitation within the conditions used in the PEUF experiments.

Table 4.5.4.a demonstrates the effect of competing ion concentration on the retention of Cr(VI) at a loading of 0.01 and a pH of 4. As it is seen from table 4.5.4a, addition of a competing ion to the feed solution decreased the Cr(VI) retention. It was observed that after a competing ion concentration of approximately 10 mg/L, there was a drastic decrease in the retention of target anion.

In a similar study [140], PDADMAC, a quaternary ammonium containing polymer, was used for removing Cr(VI) via batch PEUF and the effect of the presence of sulfate and nitrate in the retention of Cr(VI) was investigated. It was found that, the retention of chromate and sulfate were approximately the same in the feed solutions having equal amounts of chromate and sulfate. However, nitrate retention was found to be much lower than that of chromate and sulfate, conforming that charge of the anion may be the predominant variable affecting the removal of anions.

Table 4.5.4.a Effect of competing ion concentration on the retention of Cr(VI) (Cr(VI):10 mg/l, L:0.01, MWCO: 5000 Da, pH: 4, ∆P:100 kPa)

Co-anion Type	Cr(VI) Retention	Co-anion Concentration (Feed) (mg/L)	Co-anion Concentration (Permeate) (mg/L)	Co-anion Retention
no co-anion	0.70	0.0	0.0	0.0
sulfate	0.51	11.1	9.3	0.16
sulfate	0.30	101.0	72.8	0.28
sulfate	0.22	528.3	352.3	0.33
chloride	0.59	9.5	8.9	0.05
chloride	0.48	97.5	85.7	0.12
chloride	0.39	436.7	354.1	0.19

As the data in table 4.5.4.a was considered it was observed that, divalent sulfate having the same charge as Cr(VI) decreased the retention more than that of monovalent chloride. Consequently, divalent sulfate anions were retained more than monovalent chloride ions by PDAM.

In the literature, it was reported that the retention of metal ions are strongly dependent on the presence of other ions in the solution [81]. It is known that the interactions which are dominated by electrostatics are more sensitive to the existence of competing ions as compared to the coordinative bonds [144]. In studies with polyethylene imine or polyacrylic acid as the complexing polymer, loss of metal retention was observed when the competing ion concentration was increased.

In a study of our group, effect of ionic strength on the efficiency of heavy metal removal via continuous PEUF was examined and similar results were obtained [38]. Dynamic and static light scattering experiments were performed to gain an insight about the conformational changes in PEI structure due to the pH and ionic strength alternations in solution. It was found that, the increase in ionic strength reduces the size of the macromolecules which may eliminate the possible active sites of the polymer for interacting with the target metal.

In order to identify whether the decrease in the retention of target component is due to competition or as a result of the change in the ionic strength of the solution, conductivities of the feed and permeate samples of PEUF experiments at different competing ion concentrations were measured and tabulated in Table 4.3.4.b.

Table 4.3.4.b Conductivity values of the feed and permeate solutions obtained in PEUF experiments in the presence of competing anions at pH 4
(Cr(VI): 10 mg/l, MWCO: 5000 Da, pH: 4, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

Feed			**Permeate**			**Retention**	
Cr(VI) (mg/l)	**Cl$^-$ (mg/l)**	**Cond. (mS/m)**	**Cr(VI) (mg/l)**	**Cl$^-$ (mg/l)**	**Cond. (mS/m)**	**Cr(VI)**	**Cl$^-$**
10.1	0	0.23	3.0	0	0.18	0.70	0.0
10.1	9.5	0.25	4.1	8.9	0.21	0.59	0.50
10.0	97.5	0.52	5.2	85.7	0.44	0.48	0.12
9.6	436.7	1.39	5.9	354.1	1.11	0.39	0.19
Cr(VI) (mg/l)	**SO_4^{2-} (mg/l)**	**Cond. (mS/m)**	**Cr(VI) (mg/l)**	**SO_4^{2-} (mg/l)**	**Cond. (mS/m)**	**Cr(VI)**	**SO_4^{2-}**
10.1	0	0.23	3	0	0.18	0.70	0.0
10.1	11.1	0.28	4.9	9.3	0.22	0.51	0.16
10.5	101.1	0.58	7.4	72.8	0.44	0.30	0.28
10.7	528.3	1.415	8.3	352.3	1.20	0.22	0.33

As the conductivities for different concentrations of competing ions are compared, it is seen that as the competing ion concentration increases, conductivities of feed solutions increase. This is an expected result, since in the high ion containing solutions conductivities are also high. Conductivities in permeate samples were found to be slightly lower than that of the feed solution because of binding of ions by polymer in the feed side.

In one of the previous study of our group, effect of ionic strength was investigated on the binding performance of PEI with Cd^{2+}, Ni^{2+} and Zn^{2+} using $NaNO_3$ and Na_2SO_4 With the addition of both $NaNO_3$ and Na_2SO_4, depending on the salt concentration (0.1N-1N), 100-500 times increase was recorded in conductivities. The retention of target metals were found to decrease with the addition of salt to the feed solution.

Since the binding of PEI and metal cations is due to co-ordinate covalent bond formation, the main reason for the decrease in the retention was attributed to the increase in the ionic strength of the solution [38].

It must be noted that, in this study, even as the concentration of competing ions were increased 10-50 fold, conductivities did not change as drastically as in the study mentioned above. However, retention of both chloride and sulfate increased, leading to a decrease in chromate retention. This may imply that, the predominant variable in the decrease in the retention of chromate is competition. Increase in the ionic strength of the solution may have a secondary effect on the decrease in retention by changing the conformation of PDAM to an undesirable position or due to the screening effect of the presence of other ions in the solution. It must also be emphasized that even in the presence of high concentrations of competing anions, significant retentions of Cr(VI) by PDAM were obtained.

In order to see the effect of pH on the retention of Cr(VI) in the presence of competing anions, PEUF experiments were performed at different pH. In these experiments both Cr(VI) and competing anion concentrations were 10 mg/l.

Table 4.5.4.c Effect of pH on the retention of Cr(VI) with the presence of co-anions (Cr(VI): 10 mg/l, MWCO: 5000 Da, ΔP:100 kPa, Feed Flowrate: 0.048 m^3/h)

Co-anion Type	pH	Cr(VI) Retention	Co-anion Concentration (Feed)	Co-anion Concentration (Permeate)	Co-anion Retention
no co-anion	4.00	0.69	0.0	0.0	0.0
sulfate	4.00	0.51	11.1	9.3	0.16
chloride	4.00	0.59	9.5	8.9	0.05
no co-anion	5.50	0.66	0.0	0.0	0.0
sulfate	5.50	0.49	10.2	8.4	0.18
chloride	5.50	0.56	10.4	9.5	0.09
no co-anion	7.00	0.65	0.0	0.0	0.0
sulfate	7.00	0.47	11.0	5.8	0.47
chloride	7.00	0.53	16.3	12.1	0.26

Table 4.5.4.c depicts the effect of pH on Cr(VI) retention with the presence of 10 mg/L co-anion. The data showed that at all pH values, chromate retention decreased with the addition of co-anion. The decrease in Cr(VI) retention was higher with the addition of sulfate than that of chloride, hence the retention of sulfate was higher than the retention of chloride. However, it must be noted that as the pH was adjusted to 7, sulfate retention was found to be the same as Cr(VI) retention and chloride retention was significantly higher than those obtained at pH 4.0 and 5.5. The reason for this behavior might be the precipitation of sulfate and chloride at higher pH values which may cause an increase in their retention values.

CHAPTER 5

CONCLUSIONS

In this study, two chelating polymers for borate removal and a polyelectrolyte for chromate removal were synthesized for investigating the separation performance of these polymers utilizing continuous polymer enhanced ultrafiltration to explore the suitable conditions for the maximum retention of the target anion with the highest possible permeate flux. Effect of PEUF operating parameters like pH and loading were investigated on chromate and borate retention. For chromate, besides these parameters effect of competing ion concentration was also examined to see the effect of valency to the selectivity of the synthesized polyelectrolyte. Furthermore, to understand the effect of conformational changes of PNSM and COP on the complexation ability, characterization tests of boron chelating polymers were performed by dynamic and static light scattering analysis methods.

Following conclusions were drawn in the light of the experimental results obtained in this study:

1. Within the runs there were small fluctuations, which may be considered insignificant, in the concentration, retention and flux values. The relative standard deviations (%RSD) for permeate and feed concentrations, permeate flux and retention values are small enough to accept that the set-up, methodology and the analysis are reliable.

2. In the UF experiments where PNSH was used as the chelating agent, the decrease in the loading (increase in polymer concentration) while keepimg boron concentration constant at 10 mg/L leads to a decrease in the permeate flux. This behavior may suggest that, there might be a gel formation problem in the studied polymer concentration range. Decreasing the loading to 0.05, decreased the retention to 1/4 of the value obtained for a

loading of 0.2. This result may be attributed to unsuitable chain conformation of the polymer chains for the binding of borate and also to the insufficient dissolution of polymer in microscopic level.

3. In order to overcome the dissolution problem, same polymer having a lower molecular weight was synthesized and the effect of loading on the retention of borate was investigated at pH 9. Flux values remained almost constant with the increase in PNSL concentration. Higher retention values were able to be achieved with PNSL, compared to PNSH, since lower loading values could be studied.

4. In order to investigate the effect of molecular weight of the polymer on the retention of boron, same polymer with a molecular weight in between PNSH and PNSL was synthesized (PNSM). Similar to the PEUF experiments with PNSL, a linear relationship between the logarithm of loading and retention of boron was obtained when PNSM was used as chelating polymer. As the loading decreases, enhancement in boron retention was observed.

5. When the boron retention performances of PNSL and PNSM were compared small deviations between the retentions were obtained implying that, molecular weight of PNS may not be effective on the complexation and rejection of boron. Therefore the separation may not be dependent on the molecular weight of PNS. It may rather depend on the amount of the active sites present in the structure of the polymer that is capable of interacting with borate anion.

6. Besides PNS, a co-polymer of 4-Vinyl-1,3-dioxalan-2-one and vinyl acetate (COP), was synthesized and its separation performance was examined using PEUF, in order to investigate the effect of polymer structure in the binding ability with boron and subsequently, to observe the effect of operating parameters like loading and pH on the removal of boron. Data obtained from PEUF experiments showed that decrease in the loading of the feed solution, when borate concentration was kept constant, increased the retention of borate until a certain loading. After this loading retention values remained almost constant with the further decrease in the loading. This may

be a sign of a solubility problem of COP like in the case of PNSH or together with insufficient dissolution of COP or coiling of polymer (see light scattering experiments) at high polymer concentrations may be hindering the exposure of borate ions to the active site of the polymer.

7. Increase in pH was found to increase the retention of borate for all of the synthesized polymers. However, effect of pH was more significant when PNS was used as the chelating agent compared to COP, implying that conformational changes in COP might be less sensitive to alterations in the pH of the solution then that pf PNS.

8. Hexavalent chromium retention experiments were performed using a specifically tailored polyelectrolyte, PDAM. In the experiments, permeate flux remained almost constant regardless of the loading of the feed solution for all of the pH values examined. Decreasing loading down from 0.01, keeping Cr(VI) concentration constant, caused a slight decrease in the retention of Cr(VI) for all of the pH values studied, suggesting that, at high polymer concentrations either suitable chain conformation for polymer-Cr(VI) interaction may not be achieved due to the crowding of the solution or, counter-ion bromine in the structure of the polyelectrolyte may repel the chromate anions causing the retention to decrease.

9. In order to see the effect of crowding in the feed solution to the retention of chromate, PEUF experiments were carried out at a fixed loading of 0.01, and both polymer and chromate concentrations were varied to obtain the same loading value. It is observed that increase in the crowdedness of the feed solution decreased Cr(VI) retention. Therefore, it is concluded that Cr(VI) retention does not only depend on the loading but also on the concentrations of both Cr(VI) and PDAM.

10. Unlike borate experiments, higher chromate retentions were obtained at low pH values. Effect of the presence of competing anions such as chloride and sulfate on the retention of chromate was also investigated to see the effect of valency to the selectivity of the synthesized polyelectrolyte. Decrease in the retention was observed with the addition of both chloride and sulfate for all of

the pH values studied. However, divalent sulfate decreased the retention more than monovalent chloride indicating that charge may be the predominant variable in the retention of chromate using PDAM.

11. Dynamic and static light scattering experiments showed that both PNSM and COP reduced their sizes in the concentrated solutions, but this reduction was higher for PNSM. This behavior may be explained by the presence of tertiary amine group in the structure of PNSM. The interaction between the amine and hydroxyl groups of the polymer chains may cause a decrease in the size of PNSM as the solution is getting crowded. Increase in pH increased the hydrodynamic radius and decreased the radius of gyration of both PNSM and COP. Additionally, both R_h and R_g were found to increase with the addition of boron implying that the polymer chains became stretched as complexed with borate.

REFERENCES

[1] Agrawal A., Sahu K.K., Pandey B.D. , "Removal of zinc from aqueous solutions using sea nodule residue", Colloids and Surfaces A: Physicochem. Eng. Aspects 237 (2004) 133–140.

[2] Fisher R.J., Pang D., Beatty S.T., Rosenberg E., "Silica–Polyamine Composite Materials for Heavy Metal Ion Removal, Recovery, and Recycling. II. Metal Ion Separations from Mine Wastewater and Soft Metal Ion Extraction Efficiency", Separation Science and Technology 34 (1999) 3125–3137.

[3] Kurniawan A.T., Chan G.Y.S., Lo W., Babel S., "Physico-chemical treatment techniques for wastewater laden with heavy metals", Chemical Engineering Journal, 118 (2006) 83-98.

[4] EPA. National Recommended Water Quality Criteria; EPA 822-Z-99 001. Technical report, U.S. Environmental Protection Agency, Washington, DC, 1999.

[5] McLaughlin M.J., Zarcinas B.A., Stevens D.P., and Cook N. "Soil testing for heavy metals". Commun. Soil Sci. Plant Anal., 31 (2000) 1661-1700.

[6] Birnbaum E.R., Rau K. C., Sauer N.N., "Selective Anion Binding from Water Using Soluble Polymers", 38 (2003) 389- 404.

[7] Karabulut S., Karabakan A., Denizli A., and Yurum Y, "Batch Removal of Cu (II) and Zn (II) from aqueous solutions with low-rank Turkish coals" Sep. Purif.Tech., 18 (2000) 177–184.

[8] Bereket G., Aroguz A.Z., and Ozel M.Z., "Removal of Pb(II), Cd(II), Cu(II) and Zn(II) from aqueous solutions by adsorption on bentonite", J. Colloid Interface Sci., 187 (1997) 338–343.

[9] Davila J.S., Matos C.M., and Cavalcanti M.R. "Heavy metals removal from wastewater by using activated peat", Water Sci.Technol., 26 (1992) 2309-2312.

[10] Gao Y.M., Sengupta A.K., and Simpson D., "A new hybrid inorganic sorbent for heavy metals removal", Water Res., 29 (1995) 2195–2205.

[11] Korus I., Bodzek M., and Loska K., “Removal of zinc and nickel ions from aqueous solutions by means of the hybrid complexation-ultrafiltration process”, Sep. Purif. Technol., 17 (1999) 111–116.

[12] Barron-Zambrano J., Laborie S., Viers Ph., “Rakib M., and Durand G. Mercury removal from aqueous solutions by complexation ultrafiltration” Desalination, 144 (2002) 201–206.

[13] Yurlova L., Kryvoruchko A., and Kornilovich B., “Purification of water containing heavy metals by chelating-enhanced ultrafiltration”, Desalination, 144 (2002) 243–248.

[14] C. Dilek, H.Ö. Özbelge, N. Bicak, L. Yilmaz, Removal of Boron from Aqueous Solutions by Continuous Polymer Enhanced Ultrafiltration using Polyvinyl Alcohol, Separation Science and Technology, 37 (2002) 1257-1271.

[15] Smith B.F., Robison T.W., Carlson B.J., Labouriau A.,1 K. Khalsa G.R., Schroeder N.C., Jarvinen G.D., Lubeck C.R., Folkert S.L., Aguino D.I. “Boric Acid Recovery Using Polymer Filtration: Studies with Alkyl Monool, Diol, and Triol Containing Polyethylenimines”, Journal of Applied Polymer Science, 97 (2005) 1590-1604.

[16] Gang D., Banerji S.K., Clevenger T.E:, “Factors Affecting Chromium (VI) Removal be Modified Poly(4-Vinylpyridine) Coated Silica Gel”, Prac.Period.Hazard.Tox.Radioac.Waste Manag., April 2001, 58-65.

[17] C.S., Christian S.D, Tucker E.E., Scamehorn J.F., “Study of the Binding of Anions by a Cationic Polyelectrolyte Using Equilibrium Dialysis. 1. Chromate Anions”, Langmuir 14 (1998) 1002-1012.

[18] Andrus M.E., “A review of metal precipitation chemicals for metal-finishing applications”. Met. Finish., 11 (2000) 20-23.

[19] Peters, R.W., Ku, Y., AIChE Symposium Series 9, “Separation of heavy metals and other trace contaminants”, 1985.

[20] Brown P.A., Gill S.A., Allen S.J., “Metal removal from waste water using peat”, Water Resources, 34 (2000) 3907-3916.

[21] Islamoglu S., Yilmaz L., Ozbelge H.O., “Development of a Precipitation Based Separation Scheme for Selective Removal and Recovery of Heavy Metals from Cadmium Rich Electroplating Industry Effluents”, Separation Science and Technology, 41 (2006) 3367–3385.

[22] Fabiani C., “Recovery of metal ions from waters and sludges”, Raport RT/AMB/92/32 ENEA Ente per le Nuove Technologie l’Energia e l’Ambiente, 1992, Rome.

[23] Brady D., Rose P.C., Duncan J.R., “The use of hollow-fiber cross-flow microfiltration in bioaccumulation and continuous removal of heavy metals from solution by saccharomyces-cerevisiave”, Biotechnology Bioengineering, 44 (1994) 1362-1368.

[24] Islamoglu S., “Removal and recovery of heavy metals from industrial effluents by polymer enhanced ultrafiltration” Master Thesis, Middle East Technical University, Ankara,Turkey, 2002.

[25] Rengaraj S., Yeon K.H., Moon S.H., “Removal of chromium from water and wastewater by ion exchange resin, Journal of Hazardous Materials, 87 (2001) 273-287.

[26] Semerjian L., Ayoub G.M., “High pH magnesium coagulation-floculation in wastewater treatment”, Adv. Environ.Res., 7 (2003) 389-403.

[27] Crini G., “Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment”, Prog. Polym. Sci., 30 (2005) 38–70.

[28] Canizares P., Perez A., Camarillo R., “Recovery of heavy metals by means of ultrafiltration with water-soluble polymers: calculation of design parameters”, Desalination 144 (2002) 279-285.

[29] Mulder M., “Basic Principles of Membrane Technology”, 2nd Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 2000.

[30] Strathmann H., “Membrane Separation Processes: Current Relevence and Future Opportunities, AIChE Journal, 47 (2001) 1077-1087.

[31] Izatt R.M., Clark G.A., Bradshaw J.S., Lamb J.D., Cristensen J.J., “Macrocycle- Facilitated Transport of Ions in Liquid Membrane Systems”, Separation and Purification Methods, 15 (1986) 21.

[32] Tavlarides L.L., Bae J.H., Lee C.K., “ Solvent Extraction, Membranes, and Ion Exchange in Hyrometallurgical Dilute Metal Separation”, Separation Science and Technology, 22 (1987) 561.

[33] Teramoto M., Tohno N., Ohnishi N., Matsuyama H., “ Development of a Spiral-Type Flowing Liquid Membrane Module with High Stability and Its Applications to the Recovery of Cadmium and Zinc”, 24 (1989) 981.

[34] Van der Bruggen B., Vandecasteele C., Van Gestel T., Doyenb W., Leysenb R., “A review of Pressure Driven Membrane Processes in Wastewater

Treatment and Drinking Water Production, Environmental Progress, 22 (2003) 46-56.

[35] Müslehiddinoğlu, J., Uludağ Y., Özbelge H.Ö., Yılmaz L., “Effect of operating parameters on selective removal of heavy metals from binary mixtures via polymer enhaced ulrafiltration”, Journal of Membrane Science, 140 (1998) 251-266.

[36] Mundkur S.D., Watters J.C., “Polyelectrolyte Enhanced Ultrafiltration of Copper from waste stream”, Separation Science and Technology, 28 (1993),1157-1162.

[37] Bodzek M., Korus I., and Loska K. Application of the hybrid complexationultrafiltration process for removal of metal ions from galvanic wastewater. Desalination, 121 (1999) 117–121.

[38] İslamoğlu S., “Effect of Ionic Strength on The Performance of Polymer Enhanced Ultrafiltration in Heavy Metal Removal From Aqueous Solutions”, PhD Thesis, Middle East Technical University, Ankara, Turkey, 2007.

[39] Uludag Y., “Removal and recovery of heavy metals from waste streams via polymer enhanced ultrafiltration”, M.Sc.Thesis, Middle East Technical University, Turkey, 1995.

[40] Zhou R., Palmer V.,Geckeler K.E., “Removal of inorganic ions by polymer-based-colloid enhanced membrane filtration in aqueous solution”, Water Resources, 28 (1994) 1257-1268.

[41] Cheryan M., “Ultrafiltration and Microfiltration Handbook”, Technomic Publishing Co.Inc., Pennsylvania, (1998).

[42] Schamehorn, J.F., Cristian, S.D., El-Sayed, D.A., Uchiyama, H., “Removal of Divalent Metal Cations and Their Mixtures from Aqueous Streams Using Micellar-Enhanced Ultrafiltration”, Separation Science and Technology, 29(7), 809-830.

[43] Geckeler K.E., Bayer E., “Liquid-Phase Polymer Based Retention, A New Method for Separation and Preconcentration of Elements”, Analytica Chimica Acta, 189 (1986) 285-292.

[44] Legault A., Volchek K., Tremblay A., and Whittaker H. “Removal of Arsenic from groundwater using reagent binding/membrane separation” In Proceedings, Miami, Florida, November 1-6 1992. AIChE Annual Meeting.

[45] Migalati E., Naschetnikova O., and Pushkarev V. Forth national conference on membrane methods. In Proceedings, volume 4, pages 38–41, Moscow, May 1987.

[46] Nicholson J.W., “Polymer Materials- Reflections on a Highly Charged Topic, Chem.Soc. Rev., 23 (1994) 53-58.

[47] Rivas B.L., Pereira E., “Water-Soluble Polymeric Materials with the Ability to Bind Metal Ions”, Macromol.Symp., 193 (2003) 237-250.

[48] Uludağ Y., Özbelge H.Ö., Yilmaz L., “Removal of mercury from aqueous solutions via polymer-enhanced ultrafiltration”, J.Membrane Sci., 129 (1997) 93-99.

[49] İslamoğlu S., 2002, “Removal of Heavy Metals from Industrial Wastewaters by means of Hybrid Precipitation and Polymer Enhanced Ultrafiltration Process”, M.S. Thesis, Chemical Eng. Dept., Middle East Technical University, Ankara, Turkey.

[50] Yürüm A., “Development and Evaluation of Performance of New Ligands for Removal of Boron by Polymer Enhanced”, M.S Thesis, Chemical Eng. Dept., Middle East Technical University, 2003.

[51] Sriratana S., Schameron J.F., Christian S.D., Tucker E.E., “Use of Polyelectrolyte Enhanced Ultrafiltration to Remove Chromate from Water”, Separation Science and Technology, 31 (1996) 2493-2504.

[52] Canizares P., Perez A., Camarillo R., and Linares J.J. “A semi-continuous laboratory-scale polymer enhanced ultrafiltration process for the recovery of cadmium and lead from aqueous effluents”, J. Membr. Sci., 240 (2004) 197–209.

[53] Smith B.M., “Reversible Polymer Complexation for Boron Removal and Concentration with Polymer Assisted Ultrafiltration”, PhD thesis, University of Cololado, USA, 1997.

[54] Geckeler K.E, Volchek K., “Removal of Hazardous Substances from Water Using Ultrafiltration in Conjuction with Soluble Polymers”, Environmental Science & Technology, 30 (1996) 725-734.

[55] Simonnot M., Castel C., Nicolai M., Rosin C., Sardin M., Jauffret H., “Boron Removal from Drinking Water with a Boron Selective Resin: Is the Treatment Really Selective. Wat. Res. 34 (2000) 109–116.

[56] Yoshimura K., Miyazaki Y., Matsuoka O.S., Sakahita H., J. Chem. Soc., Faraday Trans. 94 (1998) 857.

[57] Guadix A., Sorensen E. "Optimal design and operation of continuous ultrafiltration plants", J. Membr. Sci., 235 (2004) 131–138.

[58] Sabate J., Pujola M., and Llorens J. "Simulation of a continuous metal separation process by polymer enhanced ultrafiltration", J. Membr. Sci., 268 (2006) 37–47.

[59] Lorens J., Sabate J., and Pujola M. "Viability of the use of polymer assisted ultrafiltration for continuous water softening", Sep. Sci. Technol., 38 (2003) 295– 322.

[60] Schlichter B., Mavrov V., Erwe T., and Chmiel H. "Regeneration of bonding agents loaded with heavy metals by electrodialysis with bipolar membranes", J. Membr. Sci., 232 (2004) 99–105.

[61] Geckeler K., Lange G., Eberhardt H., and Bayer E. "Preparation and application of water soluble polymer-metal complexes", Pure Appl. Chem., 52 (1980) 1883 -1905.

[62] Shkinev V.M., Vorobeva G.A., Spivakov B.Y., Geckeler K.E., and Bayer E. Enrichment of Arsenic and its separation from other elements by liquid-phase polymer based retention. Sep.Sci.Technol., 22 (1987) 2165–2174.

[63] Rivas B.L. and Pooley S.A. "Water-soluble amine and imine polymers with the ability to bind metal ions in conjuction with membrane filtration", J.App.Polym.Sci., 96 (2005) 222–231.

[64] Rivas B.L., Pereira E.D., Paola G., Geckeler K.E., "Water soluble Acidic Polyelectrolytes with Metal-removing Ability", Polym. Adv.Technol., 13 (2002) 1000-1005.

[65] Rivas B.L., Martinez E., Pereira E.D., Geckeler K.E., "Synthesis, characterization and polychelatogenic properties of poly(2-acrylamido-2-methyl-1-propane sulfonic acid-co-methacrylic acid)", Polymer International, 50 (2001) 456-462.

[66] Bolto B.A., "Soluble Polymers in Water Purification", Prog.Polym.Sci. 20 (1995) 987-1041.

[67] Kantipuly C., Katragadda S., Chow A., Gesser H.D., "Chelating Polymers and Related Supports for Separation and Preconcentration of Trace Metals", Talanta, 37 (1990) 491-517.

[68] Rivas B.L., Pooley S.A., Soto M., Maturana H.A., Geckeler K.E., "Poly (N,N*-dimethylacrylamide-co-acrylicacid) : Synthesis, Characterization, and

Application for the Removal and Separation of Inorganic Ions in Aqueous Solution", J.Appl.Polym.Sci., 67 (1998) 93-100.

[69] Rivas B.L., Pooley S.A., Soto M., Geckeler K.E., "Synthesis, Characterization, and Polychelatogenic Properties of Poly (acrylic acid-co-acrylamide)", J.Polym.Sci. Part A: Polym.Chem., 67 (1998) 2461-2467.

[70] Pizarro G., Marambio O.G., Rivas B.L., Geckeler K.E, "Interactions of the Water-Soluble Poly(N-Maleyl Glycine-*co*-Acrylic Acid) as Polychelatogen with Metal Ions in Aqueous Solution", J.Macromol.Sci.Pure Appl.Chem. A34 (1997) 1483-1491.

[71] Rivas B.L., Villoslada I.M., "Binding of Cd2+ and Na+ Ions by Poly(sodium 4-styrenesulfonate) Analyzed by Ultrafiltration and Its Relation with the Counterion Condensation Theory", J.Phys.Chem., 102 (1998) 6994-6999.

[72] Rivas B.L., Villoslada I.M., "Chelation properties of polymer complexes of poly(acrylic acid) with poly(acrylamide), and poly(acrylic acid) with poly(*N,N*dimethylacrylamide)", Macromol.Chem.Phys., 199 (1998) 1153-1160.

[73] Rivas B.L., Geckeler K.E., "Synthesis and metal complexation of poly(ethylenimine) and derivatives", Adv.Polym.Sci, 1992 (102) 171–88.

[74] Molinari R., Argurio P., and Poerio T. Ultrafiltration of polymer-metal complexes for metal ion removal from wastewaters. Macromol. Symp., 235 (2006) 206–214.

[75] Alpatova A., Verbych S., and et.al. Ultrafiltration of water containing natural organic matter: heavy metal removing in the hybrid complexationultrafiltration process. Sep. Purif.Technol., 40 (2004) 155–162.

[76] Pastor M.R., Samper-Vidal E., and et.al. Analysis of the variation in the permeate flux and of the efficiency of the recovery of mercury by polyelectrolyte enhanced ultrafiltration (PE-UF). Desalination, 151 (2002) 247–251.

[77] Renualt N., Aulas F., Rumeau M., Chem.Eng. 23 (1983) 137-143.

[78] Lorens J., Pujolà M., Sabaté J., "Separation of cadmium from aqueous streams by polymer enhanced ultrafiltration: a two-phase model for complexation binding", J.Membrane Sci., 239 (2004) 173-181.

[79] Rumeau M., Persin F., Sciers V., Persin M., Sarrazin J., "Separation by Coupling Ultrafiltration and Complexation of Metallic Species with Industrial

Water Soluble Polymers, Application for Removal or concentration of metallic cations”, J.Membrane Sci., 73 (1992) 73-81.

[80] Skoog D.A., West D.M., and Holler F.J. Fundamentals of Analytical Chemistry, chapter 8, page 150. Saunders College Publishing, Orlando, 7edition, 1996.

[81] Villoslada I.M. and Rivas B.L., “Retention of metal ions in ultrafiltration of mixtures of divalent metal ions and water-soluble polymers at constant ionic strength based on Freundlich and Langmuir isotherms” *J. Membr. Sci.*, 215 (2003)195–202.

[82] Rivas, B.L., Pereira, E., and Moreno-Villoslada, I. “Water-Soluble Polymer-Metal Ion Interactions”, Prog. Polym. Sci., 28 (2003) 173–208.

[83] Juang R.-S., Chiou C.-H., “Ultrafiltration rejection of dissolved ions using various weakly basic water-soluble polymers”, Journal of Membrane Science 177 (2000) 207–214.

[71] Bouyer F., Robben A., Yu W.L., and Borkovec M. “Aggregation of colloidal particles in the presence of oppositely charged polyelectrolytes: Effect of surface charge heterogeneities” Langmuir, 17 (2001) 5225–5231.

[85] Schiewer S. and Wong M.H. “Ionic strength effects in biosorption of metals by marine algae” Chemosphere, 41 (2000) 271–282.

[86] Echeverria J., Indurain J., Churio E., and Garrido J., “Simultaneous effect of pH, temperature, ionic strength, and initial concentration on the retention of Ni on illite” Colloids Surf., A: Physicochem. Eng. Aspects, 218 (2003) 175–187.

[87] Lopez-Ramon V., Moreno-Castilla C., Rivera-Utrilla J., and Radovic L.R. “Ionic strength effects in aqueous phase adsorption of metal ions on activated carbons” Carbon, 41 (2002) 2009– 2025.

[88] Borkowski M., Choppin G.R., Moore R.C., and Free S. J., “Thermodynamic modeling of metal-ligand interactions in high ionic strength nacl solutions:The Co(II)-citrate and Ni(II)-citrate systems” Inorg. Chim. Acta, 298 (2000) 141–145.

[89] Baek K., Yang J.-W, “Micellar enhanced ultrafiltration of chromate and nitrate: binding competition between chromate and nitrate”, Desalination 167 (2004) 111-118.

[90] Guibal E., “ Interactions of Metal Ions with Chitosan Based Sorbents: a review”, Separation Science and Technology, 38 (2004) 43-74.

[91] Bachelier N., Chappey C., Langevin D., Metayer M., Verchere J.-F., “Facilitated transport of boric acid by 1,3-diols through supported liquid membranes”, J. Membrane Sci., 119 (1996) 285–294.

[92] Pastor M.R., Ruiz A.F., Chillon M.F., Rico D.R., “Influence of pH in the elimination of boron by means of reverse osmosis”, Desalination, 140 (2001) 145-152.

[93] Smith, B.M.; Todd, P.; Bowman, C.N. Boron Removal by Polymer-Assisted Ultrafiltration. Sep. Sci. Technol. 30 (1995) 3849–3859.

[94] Chapelle S., Srella J.-F., Verchere A., “^{11}B and ^{13}C NMR determination of the structure of borate complexes of pentoses and related sugars”, Tetrahedron, 44 (1988) 4469-4481.

[95] Power P.P., Woods W.,G., “The chemistry of boron and its specialization in plants”, Plant Soil 193 (1997) 1-13.

[96] Böeseken J., “The use of boric acid for the determination of the configuration of carbohydrates”, Adv.Carbohydrate Chem., 4 (1949) 189-210.

[97] Bıçak N., Şenkal B.F., “Sorbitol-Modified Poly(N-glycidyl styrene sulfonamide) for removal of boron”, J.Appl.Polym.Sci., 68 (1998) 2113-2119.

[98] Matsumoto M., Matsui T., Kondo K., “Adsorption mechanism of boric acid on chitosan resin modified by saccharides”, J.Chem.Eng Japan, 32 (1999) 190-196.

[99] Bicak N., Şenkal B.F., “Polymer supported iminidipropylene glycol functions for removal of boron”, Reac.Func.Polym., 55 (2003) 27-33.

[100] Qi T., Sonoda A., Makita Y., Kanoh H., Ooi K., Hirotsu T., “Synthesis and borate uptake of two novel chelating resins”, Ind.Eng.Chem.Res., 41 (2002) 133-138.

[101] Biçak N., Bulutçu N., Şenkal B.F., Gazi M., “ Modification of crosslinked glycidyl methacrylate-based polymers for boron-specific column extraction”, Reac.Func.Polym., 47 (2001) 175-184.

[102] Badruk M., Kabay N., Demircioğlu M., Mordoğan H., İpekoğlu U., “Removal of Boron from Wastewater of Geothermal Power Plant by Selective Ion Exchange Resins. II.Column Sorption-Elution Studies”, Separation Science and Technology, 34 (1999) 2981-2995.

[103] Hyung H., Kim J.-H., “A mechanistic study on boron rejection by sea water reverse osmosis membranes”, Journal of Membrane Science 286 (2006) 269–278.

[104] Prats D., Chillon-Arias M.F., Rodriguez-Pastor M., “Analysis of the influence of pH on the elimination of boron in reverse osmosis”, Desal., 128 (2000) 269-273.

[105] Taniguchi M., Fusaoka Y., Nishikawa T., Kurihara M., “Boron removal in RO seawater desalination” Desalination, 167 (2004) 419-426.

[106] Perie M., Perie J., Chemla M., Camp J.J., “Equilibrium and transport properties of boron species”, 365 (1994) 107-118.

[107] Melnik L., Vysotskaya O., Kornilovich B., “Boron behavior during desalination of sea and underground water by electrodialysis”, Desalination, 124 (1999) 125-130.

[108] Smith B.F., Robison T.W., Carlson B.J., Labouriau A.,1 K. Khalsa G.R., Schroeder N.C., Jarvinen G.D., Lubeck C.R., Folkert S.L., Aguino D.I. “Boric Acid Recovery Using Polymer Filtration: Studies with Alkyl Monool, Diol, and Triol Containing Polyethylenimines”, Journal of Applied Polymer Science, 97 (2005) 1590-1604.

[109] Smith, B.M.; Todd, P.; Bowman, C.N. “Hyperbranched Chelating Polymers for the Polymer-Assisted Ultrafiltration of Boric Acid”, Sep. Sci. Technol. 34 (1999) 1925–1945.

[110] Cabatingan J.K., Agapay R.C., Rakels J.L.L., Ottens M., Vander Wielen L.A.M., “Potential of Biosorption for the Recovery of Chromate in Industrial Wastewaters”, Ind. Eng. Chem. Res., 40 (2001) 2302-2309.

[111] Minbagheri S.A., Hosseini S.N., “Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse”, Desalination 171 (2004) 85-93.

[112] Beszedits S., “Chromium in the Natural and Human Environments”, Nriagu J.O., Nieboer E., Eds., John Wiley & Sons, New York, 1988, Chapter 9, p.231.

[113] El-Sikaily A., El Nemr A., Khaled A., Abdelwehab O., “Removal of toxic chromium from wastewater using green alga Ulva lactuca and its activated carbon”, Journal of Hazardous Materials, 148 (2007) 216-228.

[114] Sankararamakrishnan N., Dixit A., Iyengar L., Sanghi R., “Removal of hexavalent chromium using a novel cross linked xanthated chitosan”, Bioresource Technology, 97 (2006) 2377-2382.

[115] Lazaridis N.K., Asouhidou D.D., “Kinetics of sorptive removal of chromium(VI) from aqueous solutions by calcined Mg–Al–CO_3 hydrotalcite”, Water Research, 37 (2003) 2875-2882.

[116] Lakatos J., Brown S. D., Snape C. E., “Coals as sorbents for the removal and reduction of hexavalent chromium from aqueous waste streams” Fuel, 81 (2002) 691-698.

[117] Sudha Bai R., Emilia Abraham T. “Studies on chromium(VI) adsorption–desorption using immobilized fungal biomass”, Bioresource Technology, 87 (2003) 17-26.

[118] Loukidou M.S., Zouboulis A.I., Karapantsios T.D., Matis K.A., “Equilibrium and kinetic modeling of chromium(VI) biosorption by Aeromonas caviae” Colloids and Surfaces A: Physicochemical and Engineering Aspects, 242 (2004) 93-104.

[119] Das S.K., Guha A.K., “Biosorption of chromium by Termitomyces clypeatus”, Colloids and Surfaces B: Biointerfaces”, 60 (2007) 46-54.

[120] Fraser B.G., “Use of Liquid Membrane Pertraction for the Removal and Concentration of Hexavalent Chromium from Electroplating Waste”, M.S Thesis, Chemical Eng. Dept., University of Waterloo, 1993.

[121] Zauhri A., Burgard M., Lakkis D., “ The use of dicyclohexane-18-crown-6 as an extractant-carrier for the recovery of chromic acid”, Hydrometalurgy, 38 (1995) 299-310.

[122] Zauhri A., Ernest B., Burgard M., “Bulk liquid membrane for the recovery of chromium(VI) from a hydrochloric acid medium using dicyclohexane-18-crown-6 as an extractant-carrier”, Sep.Sci.Techno., 38 (1999) 1891-1896.

[109] Mori Y., Uemae U., Hibino S., Eguchi S.E., “ Proper condition for the surfactant liquid membrane for the recovery and concentration of Cr(VI) from aqueous sulfuric acid solution”, Int.Chem.Eng. 30 (1990) 124-130.

[123] Kunar S.V., Ravindram M., Chandra M., Mudakavi J.R., “ Heavy metal removal using liquid membrane”, Ind.J.Chem.Technol., 1 (1994) 131-137.

[124] Salazar E., Ortiz M.I., Urtiaga A.M., Irabien J., “Kinetics of the separation-concentration of Cr(VI) with emulsion liquid membranes”, Ind.Eng.Chem., Res. 31 (1992) 1523-1529.

[125] Chakravarti A.K., Chowdhury S.B., Chakrabarty S., Chakrabarty T., Mukherjee D.C., “Liquid membrane multiple emulsion process of chromium(VI) separation from waste waters", Colloids Surf. A: Physicochem. Eng. Aspects 103 (1995) 59-65.

[126] Banerjea S., Datta S., Sanyal S.K., "Mass transfer analysis of the extraction of Cr(VI) by liquid surfactant membrane", Sep. Sci. Technol. 35 (2000) 483-490.

[127] Chiarizia R., "Application of supported liquid membranes for removal of nitrate, technetium(VII) and chromium(VI) from groundwater", J. Membr. Sci. 55 (1991) 39-47.

[128] Chaudry M.A., Ahmad S., Malik M.T., "Supported liquid membrane technique application for removal of chromium from tannery wastes", Waste Manage. 17 (1997) 211-219.

[129] Wang Y., Thio Y.S., Doyle F.M., "Formation of semi-permeable polyamide skin layers on the surface of supported liquid membranes", J. Membr. Sci. 147 (1998) 109.

[130] Kozlowski C.A., Wladslaw W., "Applicability of liquid membranes in chromium(VI) transport with amines as ion carriers", J.Membr.Sci., 266 (2005) 143-150.

[131] Castillo E., Granados M., Cortina J.L., "Chromium(VI) transport through the Raipore 1030 anion exchange membrane", Anal.Chim.Acta, 464 (2002) 15-23.

[132] Khan J., Triphathi B.P., Saxene A., Shahi V.K., " Electrochemical membrane reactor: In situ separation and recovery of chromic acid", Electrochim.Acta., 52 (2007) 6719-6727.

[133] Frenzel I., Stamatialis D.F., Wessling M., "Water recycling from mixed chromic acid waste effluens by membrane technology", Sep.Purif.Tech., 49 (2006) 76-83.

[134] Ghosh G.,. Bhattacharya P.Ki, "Hexavalent chromium ion removal through micellar enhanced ultrafiltration", Chemical Engineering Journal 119 (2006) 45–53.

[135] Baek K., Kim B.-K., Cho H.-J., Yang J.-W., "Removal characteristics of anionic metals by micellar-enhanced ultrafiltration" Journal of Hazardous Materials B99 (2003) 303–311.

[136] Gzara L., Dhahbi M., " Removal of chromate anions by micellar enhanced ultrafiltration using cationic surfactants", Desalination 137 (2001) 241-250.

[137] Tunçay M., Christian S.D., Tucker E.E., Taylor R.W., Scamehorn J.F., “Ligand-Modified Polyelectrolyte-Enhanced Ultrafiltration with Electrostatic Attachment of Ligands. 2. Use of Diethylenetriaminepentaacetic Acid/Cationic Polyelectrolyte Mixtures to Remove both Cations and Anions from Aqueous Streams”, Langmuir, 10 (1994) 4693-4697.

[139] Juang R.S., Xu Y.Y., Chen C.L., “Separation and removal of metal ions from dilute solutions using micellar-enhanced ultrafiltration”, J.Membr.Sci. 218 (2003) 257–267

[140] Tangvijitsri S., Saiwan C., Soponvuttikul C., Scamehorn, “Polyelectrolyte Enhanced Ultrafiltration Ultrafiltration of Chromate, Sulfate and Nitrate”, Separation Science and Technology, 37 (2002) 993-1007.

[141] Baek K., Yang J.-S., Kwon T.-S., Yang J.-W., “Cationic starch-enhanced ultrafiltration for Cr(VI) removal”, Desal., 206 (2007) 245-250.

[142] Aroua M.K., Zuki F.M., Sulaiman N.M., “Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration” J. Hazard. Mater., 147 (2007) 752-758.

[143] Palmer V., Zhou R.N., Geckeler K.E., “Cetylpridinium chloride-modified poly(ethylene imine) for the removal and separation of inorganic-ions in aqueous solution”, Angewandte Macromolekulare Chemie, 215 (1994) 175-188.

[144] Geffen N., Semiat R., Eisen M.S., Balazs Y., Katz I., Dosoretz C.G., “Boron removal from water by complexation to polyol compounds”, J. Mem.Sci., 286 (2006) 45-51.

[145] Lo S.L., Shiue S.F, “Recovery of Cr(VI) by Quaternary Ammonium Compounds”, Water Research, 32 (1998) 174-178.

[146] Modrzejewska Z., Kaminski W., “ Separation of Cr(VI) on Chitosan Membrane”, Ind. Eng. Chem. Res., 38 (1999) 4946-4950.

[147] Manning G.S. Molecular theory of polyelectrolyte solutions with applications to electrostatic properties of Polynucleotides. Quartely Rev. Biophys., 11(2),179-246, 1978.

[148] Gazi M., Bicak N., “Selective boron extraction by polymer supported 2-hydroxylethylamino propylene glycol functions”, Reac.Func.Polym., 67 (2007) 936-942.

[149] Bicak N., Şenkal B.F., "Polymer supported amino bis-(*cis*-propan 2,3 diol) functions for removal of trace boron from water", Reac. Func. Polym. 65 (2005) 143-148.

[150] Hutchinson R. A., Beuermann S., Paquet Jr. D. A., McMinn J. H., Jackson C., "Determination of Free-Radical Propagation Rate Coefficients for Cycloalkyl and Functional Methacrylates by Pulsed-Laser Polymerization", Macromolecules, 31 (1998) 1542-1547.

APPENDIX A

BORON DETERMINATION BY DRE-ICP-OES ANALYSIS METHOD AND SAMPLE CALCULATIONS

Before starting up the instrument and igniting the plasma, a protocol should be specified. Protocol is identified by opening a folder and selecting the element or elements that will be analyzed. Afterwards, operating conditions such as rinse time, uptake time, the peak line, and number of repetitive scannings should be input. Then, a standard solution should be introduced to the system for determining the background points on the wavelength for compensating any possible interferences in ICP. After determining the background points, the next step is source peaking for obtaining dependable analysis results. Before the calibration can be initiated, it is required to make certain if the plasma is at the position. Mn is selected as the peaking element. The instrument scans the plasma and finds out the best viewing height for analysis, using Mn line. After positioning the plasma, the system is ready for the analysis.

For the purpose of calibrating the instrument, standards for permeate and feed are prepared with ultrapure water. The permeate standards contain boron and ultrapure water, whereas the feed standards contain additional polymer in the concentration same as that of feed solution. Five standard solutions are introduced to the system for feed and permeate. These standards have boron concentrations of 0 mg/L, 2 mg/L, 4 mg/L, 8mg/L and 10 mg/L. These standard solutions are aspirated to plasma and the intensities of the standards are obtained. Intensity data obtained from permeate and feed calibrations are given in table A1 and A2, respectively. Sample calibration graph for permeate and feed are given in Figure A1 and A2, respectively. After the calibrations, samples are introduced and the intensities of the samples are obtained. By the help of the calibration curve and the obtained intensity calibration relation, the concentrations of the samples are found.

Table A.1 Sample Intensity Data of the Standard Solutions of Borate for Permeate

Permeate Calibration		
Concentration	**Intensity**	**Intensity**
0	300	0
2	1436	1136
4	2576	2276
8	5113	4813
10	6561	6261

Table A.2 Sample Intensity Data of the Standard Solutions of Borate for Feed

Feed Calibration for PNSL L:0.01 pH:9		
Concentration	**Intensity**	**Corrected Int.**
0	502	0
2	1902	1400
4	2905	2403
8	5472	4970
10	7183	6681

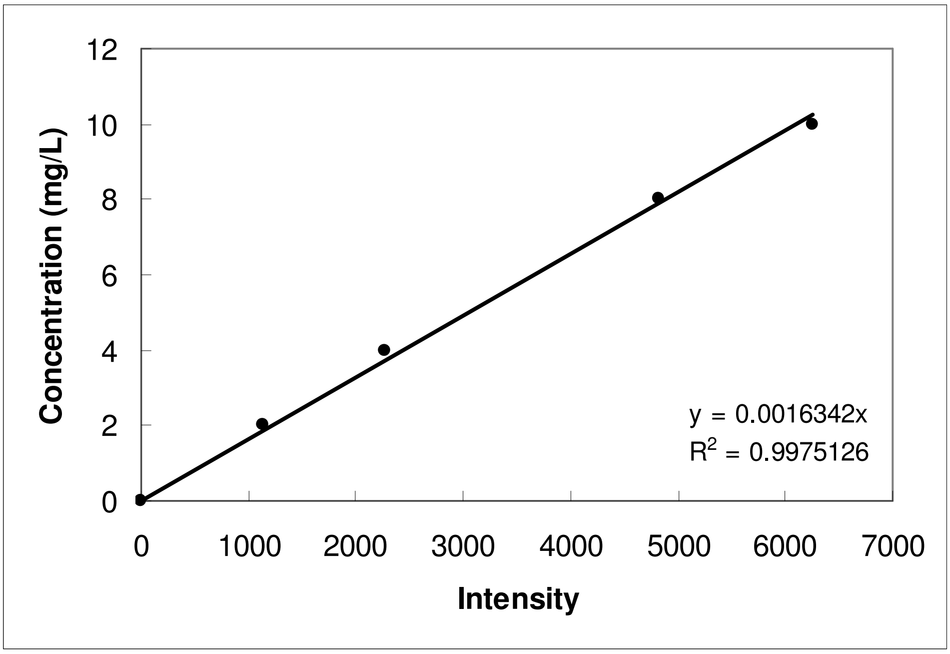


Figure A.1 Calibration Curve with the Intensity and Concentration Relation of the Related Permeate Analysis

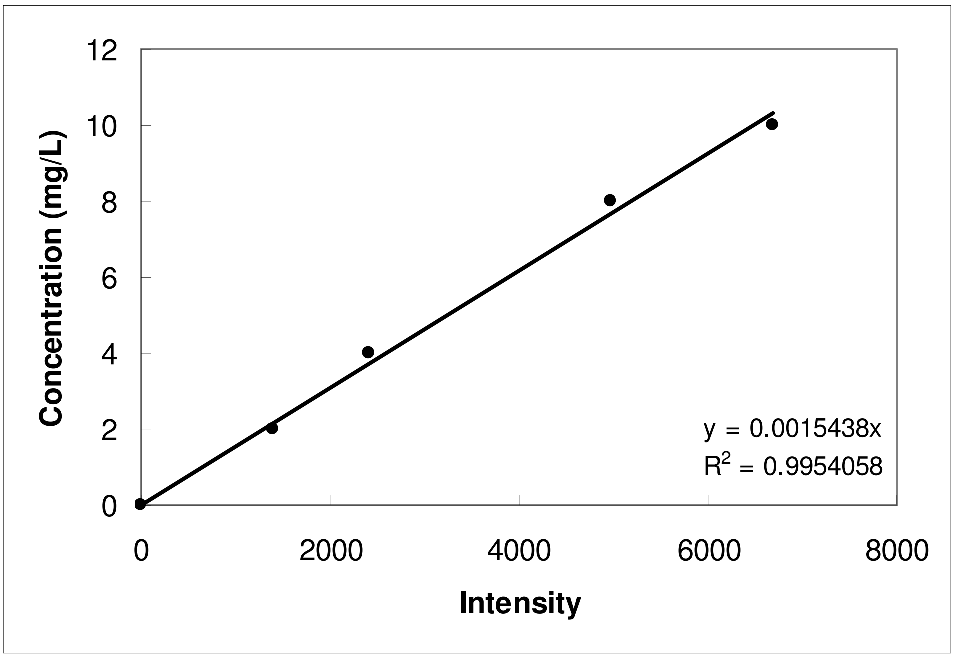


Figure A.2 Calibration Curve with the Intensity and Concentration Relation of the Related Feed Analysis

The concentrations of the permeate and feed samples were calculated by the equation given on the calibration curve plots, which relates the intensity to concentration. For a sample run having a loading of 0.05 and pH of 9 , the feed and permeate intensities and their corresponding concentrations are shown in table A3 and A4, respectively.

Table A.3 Sample Intensity Data and the Determined Concentration Values of Borate of the Feed Samples

Time (min)	Average Intensity	Corrected Intensity	Concentration (mg/L)
0	8955	8453	11.6
120	8950	8448	11.6
180	8960	8458	11.6
240	8955	8453	11.6

Table A.4 Sample Intensity Data and the Determined Concentration Values of Borate of the Permeate Samples

Time (min)	Average Intensity	Corrected Intensity	Concentration (mg/L)
60	9196	8896	8.8
90	9252	8952	8.9
120	9262	8962	8.9
180	9240	8940	8.8
240	9220	8920	8.8

APPENDIX B

CHROMIUM DETERMINATION BY FLAME AAS METHOD

Flame operation employs a 50mm burner which supports N_2O/acetylene flame used in the analysis of chromium. Gas flow control is via a binary flow control system accurately controlled by a digital output from the microprocessor. The input pressure of the fuel is internally regulated to ensure correct calibration. Data coded Hollow Cathode Lamp for each element was used so that the instrument is able to sense the element and maximum current. Standard samples for calibration were prepared from the atomic absorption standards for according to predetermined concentrations which give best signals. For the preparation of standard samples and as a blank solution ultrapure water having a specific conductance of $18.3 M\Omega cm^{-1}$ was used. Analysis of the polymer containing samples were made by calibrating the system with standard samples containing the same amount of polymer as the samples. At the beginning of each analysis system is calibrated by blank and standard solutions. Typical calibration curve for feed and permeate obtained during the analysis were shown in Figure B1 and Figure B2, respectively. Linear relationship was seen between concentration and absorbance in the calibration curve which means that Beer's Law is valid within the concentration range studied in the experiments. Five standard solutions are introduced to the system for feed and permeate. These standards have chromium concentrations of 0 mg/L, 2 mg/L, 4.5 mg/L, 8mg/L and 10 mg/L for permeate and 0 mg/L, 2 mg/L, 4 mg/L, 8 mg/L and 10 mg/L for feed calibration. These standard solutions are aspirated to flame and absorbances of the standards are obtained. Intensity data obtained from permeate and feed calibrations are given in table B1 and B2, respectively. Sample calibration graph for permeate and feed are given in Figure B1 and B2, respectively. After the calibrations, samples are introduced and the intensities of the samples are obtained. By the help of the calibration curve and the obtained intensity calibration relation, the concentrations of the samples are found.

Table B.1 Sample Intensity Data of the Standard Solutions of Cr(VI) for Permeate

Concentration	Absorbance	% RSD
0	0.000	0.00 (n:3)
2	0.163	0.07 (n:3)
4.5	0.355	0.12 (n:3)
8	0.583	0.16 (n:3)
10	0.721	0.10 (n:3)

Table B.2 Sample Intensity Data of the Standard Solutions of Cr(VI) for Feed

Concentration	Absorbance	% RSD
0	0.000	0.00 (n:3)
2	0.163	0.17 (n:3)
4	0.355	0.05 (n:3)
8	0.583	0.12 (n:3)
10	0.721	0.15 (n:3)

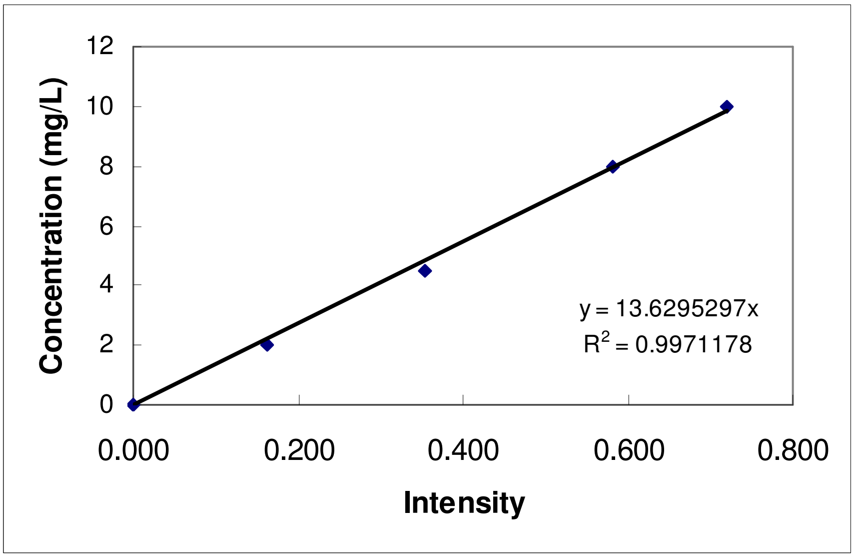


Figure B.1 Calibration Curve with the Intensity and Concentration Relation of the Related Permeate Analysis

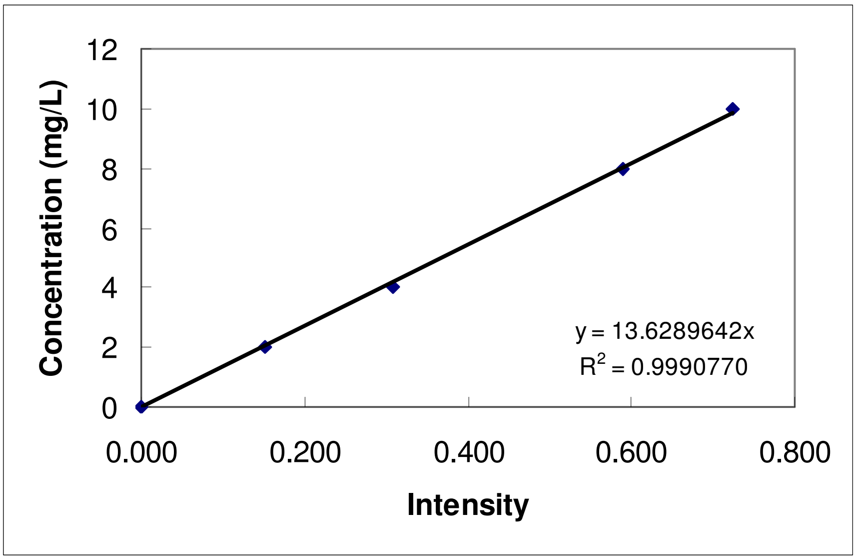


Figure B.2 Calibration Curve with the Intensity and Concentration Relation of the Related Feed Analysis

The concentrations of the permeate and feed samples were calculated by the equation given on the calibration curve plots, which relates the intensity to concentration. For a sample run having a loading of 0.01 and pH of 4 , the feed and permeate intensities and their corresponding concentrations are shown in table B3 and B4, respectively.

Table B.3 Sample Intensity Data and the Determined Concentration Values of the Permeate Samples

Time (min)	Absorbance	Concentration (mg/L)	% RSD
60	0.194	2.6	0.06 (n:3)
120	0.192	2.6	0.20 (n:3)
180	0.190	2.6	0.11 (n:3)
240	0.190	2.6	0.09 (n:3)

Table B.4 Sample Intensity Data and the Determined Concentration Values of the Feed Samples

Time (min)	Absorbance	Concentration (mg/L)	% RSD
0	0.760	10.2	0.12 (n:3)
60	0.758	10.1	0.19 (n:3)
120	0.755	10.1	0.08 (n:3)
240	0.752	10.1	0.15 (n:3)

APPENDIX C

ION CHROMATOGRAPHY CALIBRATION CURVES

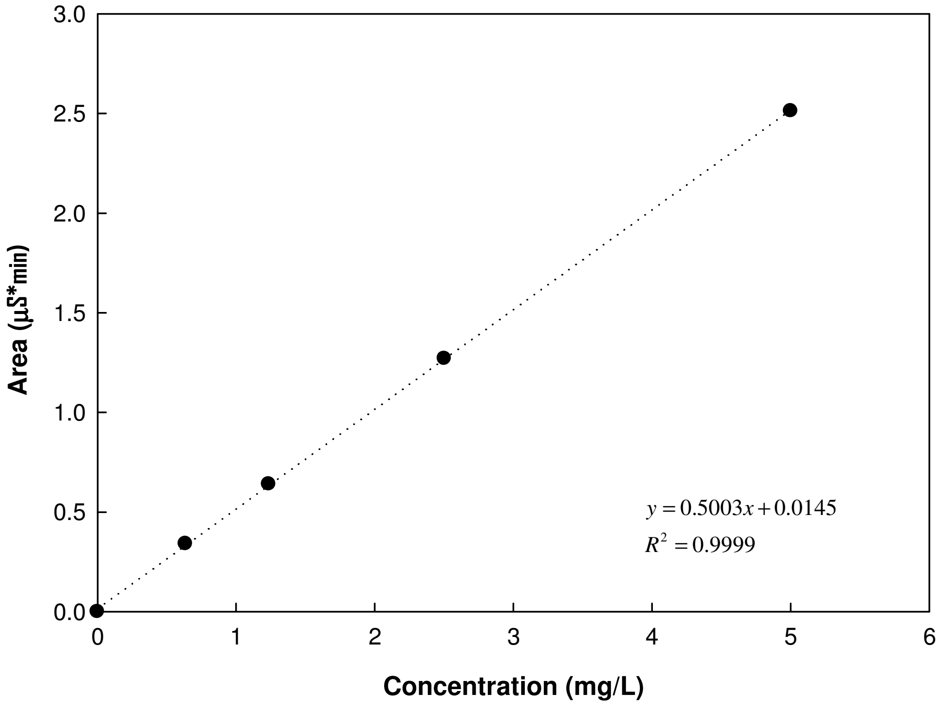


Figure C.1 Calibration Curve for Chloride

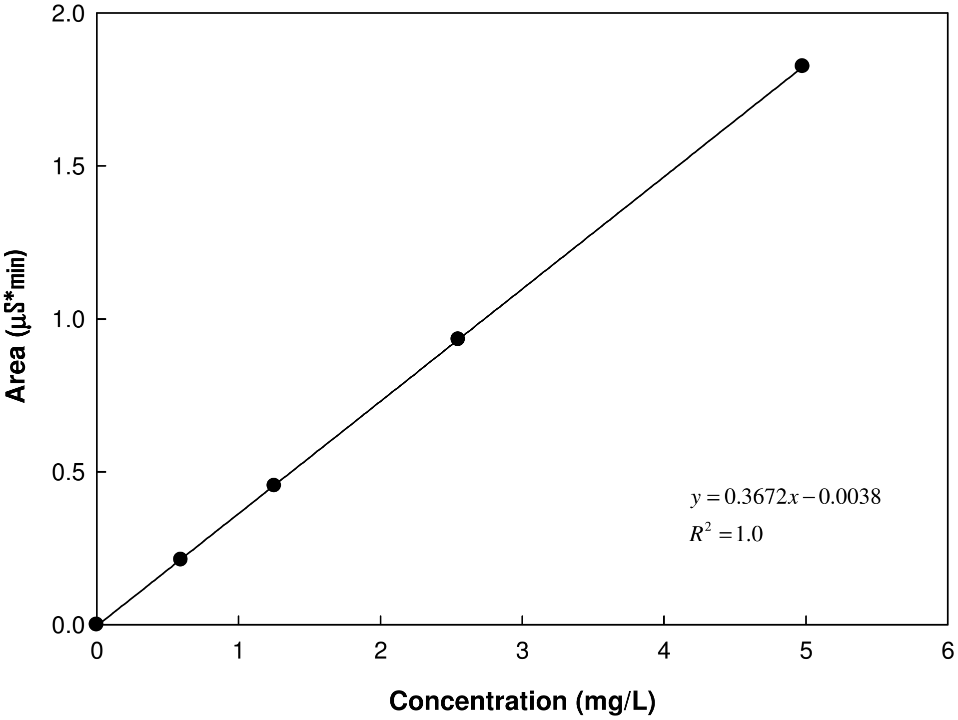


Figure C.2 Calibration Curve for Sulfate

APPENDIX D

DATA TABLES OF PEUF EXPERIMENTS

Table D.1 Data Tables for PEUF Experiments for Borate Retention

	Polymer: PNSH	L:0.05	pH: 9	Anion: Borate
t (min)	0	60	120	240
F_p (L/m^{2}h)		63.6	62.7	62.7
pH	9.00	8.99	9.03	9.05
T(°C)	22.8	22.8	23.1	23.3
C_f	10.20	10.20	10.20	10.20
C_p		9.3	9.4	9.4
R		0.088	0.078	0.078
	$F_{p,avg}$= 62.7	$C_{f,av}$=10.2	$C_{p,av}$=9.38	R_{av}=0.079

	Polymer: PNSH	L: 0.5	pH:9	Anion: Borate
t (min)	0	60	120	240
F_p (L/m^{2}h)		116.50	116.80	116.30
pH	9	9	9	9
T(°C)	22.8	23.00	23.30	23.50
C_f	9.9	9.9	9.9	10.0
C_p		6.8	7.0	7.1
R		0.31	0.29	0.29
	$F_{p,avg}$= 107.44	$C_{f,avg}$= 9.92	$C_{p,avg}$= 7.00	R_{avg}= 0.294

	Polymer: PNSH	L: 0.2	pH:9	Anion: Borate
t (min)	0	60	120	240
F_p (L/m^{2}h)		160.2	160.2	154.8
pH	9.01	9.04	9.00	9.00
T(°C)	25.4	24.0	24.0	23.9
C_f	11.0	11.0	11.0	10.9
C_p		7.6	7.5	7.5
R		0.31	0.32	0.32
	$F_{p,avg}$= 156.6	$C_{f,avg}$= 11.0	$C_{p,avg}$= 7.5	R_{avg}= 0.318

Table D.1 (continued)

	Polymer: PNSH	**L: 0.5**	**pH:7**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		129.3	127.7	127.7
pH	7.00	7.00	7.02	7.01
T(°C)	25.2	25.0	25.0	24.9
C_f	9.9	10.0	10.0	9.9
C_p		8.7	8.8	8.5
R		0.13	0.12	0.14
	$F_{p,avg}$= 128.2	**$C_{f,avg}$= 9.95**	**$C_{p,avg}$= 8.7**	**R_{avg}= 0.125**

	Polymer: PNSH	**L: 0.5**	**pH:10**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		122.2	122.2	122.2
pH	10.00	10.02	10.01	10.02
T(°C)	25.0	24.9	24.9	24.9
C_f	10.0	10.0	9.9	10.0
C_p		6.4	6.1	6.1
R		0.36	0.38	0.39
	$F_{p,avg}$= 122.2	**$C_{f,avg}$= 9.97**	**$C_{p,avg}$= 6.2**	**R_{avg}= 0.378**

	Polymer: PNSH	**L: 0.2**	**pH:7**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		154.8	149.8	149.8
pH	7.06	7.04	7.06	7.08
T(°C)	22.4	23.0	23.0	23.3
C_f	10.8	10.8	10.8	10.8
C_p		9.1	9.2	9.0
R		0.16	0.15	0.16
	$F_{p,avg}$= 151.5	**$C_{f,avg}$= 10.8**	**$C_{p,avg}$= 9.1**	**R_{avg}= 0.157**

	Polymer: PNSH	**L: 0.2**	**pH:10**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		165.9	160.2	160.2
pH	10.00	9.99	10.03	10.02
T(°C)	22.8	23.0	23.2	23.3
C_f	10.9	10.9	10.9	10.9
C_p		6.5	6.4	6.4
R		0.40	0.41	0.41
	$F_{p,avg}$= 162.1	**$C_{f,avg}$= 10.9**	**$C_{p,avg}$= 6.4**	**R_{avg}= 0.412**

Table D.1 (continued)

	Polymer: PNSM	**L: 0.0005**	**pH:9**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		47.0	47.0	47.0
pH	9.00	9.00	9.02	9.02
T (°C)	25.2	25.2	25.6	25.6
C_f	10.0	10.0	10.0	10.0
C_p		3.9	3.9	4.0
R		0.61	0.61	0.60
	$F_{p,avg}$= 47.0	**$C_{f,avg}$= 10.0**	**$C_{p,avg}$= 3.9**	**R_{avg}= 0.61**

	Polymer: PNSM	**L: 0.002**	**pH:9**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		47.0	47.0	47.0
pH	9.02	9.01	9.00	9.00
T (°C)	25.6	25.6	25.8	25.8
C_f	10.4	10.5	10.5	10.4
C_p		5.0	5.0	5.0
R		0.53	0.52	0.52
	$F_{p,avg}$= 47.0	**$C_{f,avg}$= 10.5**	**$C_{p,avg}$= 5.0**	**R_{avg}= 0.52**

	Polymer: PNSM	**L: 0.005**	**pH:9**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		48.4	48.4	48.4
pH	9.02	9.00	9.00	9.00
T (°C)	25.0	25.0	25.0	25.0
C_f	10.5	10.4	10.4	10.4
C_p		5.4	5.4	5.4
R		0.48	0.48	0.48
	$F_{p,avg}$= 48.4	**$C_{f,avg}$= 10.4**	**$C_{p,avg}$= 5.4**	**R_{avg}= 0.48**

	Polymer: PNSM	**L: 0.05**	**pH:9**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		51.0	51.0	51.0
pH	9.03	9.00	9.02	9.00
T (°C)	25.0	25.0	25.0	25.0
C_f	10.7	10.6	10.7	10.7
C_p		7.9	8.0	7.9
R		0.250	0.260	0.260
	$F_{p,avg}$= 51	**$C_{f,avg}$= 10.7**	**$C_{p,avg}$= 7.9**	**R_{avg}= 0.26**

Table D.1 (continued)

	Polymer: PNSM	**L: 0.002**	**pH: 10**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		48.0	48.0	48.0
pH	10.00	10.00	10.00	10.00
T (°C)	29.0	29.0	29.0	29.0
C_f	10.1	10.0	10.0	10.0
C_p		4.2	4.2	4.2
R		0.58	0.58	0.58
	$F_{p,avg}$= 48.0	**$C_{f,avg}$= 10.1**	**$C_{p,avg}$= 4.4**	**R_{avg}= 0.58**

	Polymer: PNSM	**L: 0.0005**	**pH: 10**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		47.0	47.0	47.0
pH	10.2	10.1	10.0	10.0
T (°C)	27.0	27.0	27.0	27.0
C_f	11.2	11.2	11.3	11.2
C_p		3.6	3.5	3.6
R		0.68	0.69	0.68
	$F_{p,avg}$= 47.0	**$C_{f,avg}$= 11.2**	**$C_{p,avg}$= 3.6**	**R_{avg}= 0.68**

	Polymer: PNSL	**L: 0.001**	**pH: 9**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		47.0	47.0	47.0
pH	9.00	9.00	9.01	9.00
T (°C)	25.0	25.0	25.0	25.0
C_f	10.4	10.4	10.4	10.4
C_p		4.5	4.5	4.6
R		0.57	0.57	0.56
	$F_{p,avg}$= 47.0	**$C_{f,avg}$= 10.4**	**$C_{p,avg}$= 4.5**	**R_{avg}= 0.57**

	Polymer: PNSL	**L: 0.002**	**pH: 9**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		47.0	47.0	47.0
pH	9.00	9.00	9.01	9.00
T (°C)	25.0	25.0	25.0	25.0
C_f	10.4	10.4	10.4	10.4
C_p		4.5	4.5	4.6
R		0.57	0.57	0.56
	$F_{p,avg}$= 47.0	**$C_{f,avg}$= 10.4**	**$C_{p,avg}$= 4.5**	**R_{avg}= 0.57**

Table D.1 (continued)

	Polymer: PNSL	L: 0.005	pH: 9	Anion: Borate
t (min)	0	60	120	240
F_p (L/m^{2}h)		47.0	47.0	47.0
pH	9.00	9.01	9.01	9.00
T (°C)	25.0	25.0	25.0	25.0
C_f	10.4	10.5	10.5	10.5
C_p		5.8	5.7	5.7
R		0.45	0.46	0.46
	$F_{p,avg}$= 47.0	$C_{f,avg}$= 10.5	$C_{p,avg}$= 5.7	R_{avg}= 0.46

	Polymer: PNSL	L: 0.01	pH: 9	Anion: Borate
t (min)	0	60	120	240
F_p (L/m^{2}h)		47.4	47.3	47.4
pH	9.00	9.02	9.03	9.02
T (°C)	24.0	24.0	24.4	24.8
C_f	10.8	10.9	10.9	10.8
C_p		6.6	6.6	6.6
R		0.394	0.394	0.389
	$F_{p,avg}$= 47.4	$C_{f,avg}$= 10.85	$C_{p,avg}$= 6.6	R_{avg}= 0.393

	Polymer: PNSL	L: 0.02	pH: 9	Anion: Borate
t (min)	0	60	120	240
F_p (L/m^{2}h)		46.5	46.5	46.5
pH	9.00	9.02	9.00	9.02
T (°C)	21.7	22.0	22.0	23.0
C_f	10.8	10.7	10.7	10.8
C_p		6.8	7.0	7.0
R		0.364	0.346	0.352
	$F_{p,avg}$= 46.5	$C_{f,avg}$= 10.75	$C_{p,avg}$= 7.0	R_{avg}= 0.354

	Polymer: PNSL	L: 0.05	pH: 9	Anion: Borate
t (min)	0	60	90	120
F_p (L/m^{2}h)		47.3	47.6	47.3
pH	9.01	9.03	9.00	9.00
T (°C)	26.0	26.0	26.0	26.0
C_f	11.6	11.6	11.6	11.6
C_p		8.8	8.8	8.8
R		0.24	0.24	0.24
	$F_{p,avg}$= 47.4	$C_{f,avg}$= 11.6	$C_{p,avg}$= 8.8	R_{avg}= 0.24

Table D.1 (continued)

	Polymer: PNSL	L: 0.005	pH: 7	Anion: Borate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		47.0	47.0	47.0
pH	7.00	7.02	7.00	7.00
T (°C)	25.0	25.0	25.0	25.0
C_f	11.7	11.7	11.7	11.7
C_p		8.9	8.9	9.0
R		0.24	0.24	0.23
	$F_{p,avg}$= 47.0	**$C_{f,avg}$= 11.7**	**$C_{p,avg}$= 8.9**	**R_{avg}= 0.236**

	Polymer: PNSL	L: 0.005	pH: 10	Anion: Borate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		47.0	47.0	47.0
pH	10.00	10.00	10.00	10.00
T (°C)	25.0	25.0	25.0	25.0
C_f	11.8	11.7	11.8	11.8
C_p		5.4	5.4	5.4
R		0.54	0.54	0.54
	$F_{p,avg}$= 47.0	**$C_{f,avg}$= 11.8**	**$C_{p,avg}$= 5.4**	**R_{avg}= 0.54**

	Polymer: PNSL	L: 0.001	pH: 7	Anion: Borate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		47.0	47.0	47.0
pH	9.00	9.00	9.01	9.00
T (°C)	25.0	25.0	25.0	25.0
C_f	10.2	10.2	10.2	10.3
C_p		7.3	7.3	7.5
R		0.28	0.28	0.27
	$F_{p,avg}$= 47.0	**$C_{f,avg}$= 10.2**	**$C_{p,avg}$= 7.3**	**R_{avg}= 0.28**

	Polymer: PNSL	L: 0.001	pH: 10	Anion: Borate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		47.0	47.0	47.0
pH	9.00	9.00	9.00	9.00
T (°C)	25.0	25.0	25.0	25.0
C_f	10.2	10.2	10.2	10.2
C_p		3.6	3.7	3.7
R		0.65	0.64	0.64
	$F_{p,avg}$= 47.0	**$C_{f,avg}$= 10.2**	**$C_{p,avg}$= 3.7**	**R_{avg}= 0.64**

Table D.1 (continued)

	Polymer: COP	L: 0.001	pH: 9	Anion: Borate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		41.0	41.0	41.0
pH	9.00	9.01	9.01	9.00
Cf	11.1	11.0	11.1	11.1
Cp		6.2	6.2	6.3
R		0.44	0.44	0.43
	$F_{p,avg}$= 41.0	**Cf,avg=11.1**	**Cp,avg=6.0**	**Ravg=0.44**

	Polymer: COP	L: 0.002	pH: 9	Anion: Borate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		40.3	40.3	40.3
pH	9.01	9.01	9.01	9.00
Cf	10.2	10.2	10.2	10.2
Cp		5.7	5.7	5.7
R		0.44	0.44	0.44
	$F_{p,avg}$= 40.3	**Cf,avg=10.2**	**Cp,avg=5.7**	**Ravg=0.44**

	Polymer: COP	L: 0.005	pH: 9	Anion: Borate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		41.2	41.2	41.2
pH	9.00	9.01	9.02	9.00
Cf	11.0	11.0	11.0	10.9
Cp		6.0	6.0	5.9
R		0.45	0.45	0.46
	$F_{p,avg}$= 41.2	**Cf,avg=11.0**	**Cp,avg=6.0**	**Ravg=0.45**

	Polymer: COP	L: 0.01	pH: 9	Anion: Borate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		42.3	42.3	42.3
pH	9.00	9.01	9.02	9.00
Cf	10.7	10.8	10.8	10.8
Cp		6.5	6.5	6.4
R		0.40	0.40	0.41
	$F_{p,avg}$= 42.3	**Cf,avg=10.8**	**Cp,avg=6.5**	**Ravg=0.40**

Table D.1 (continued)

	Polymer: COP	L: 0.02	pH: 9	Anion: Borate
t (min)	**0**	**60**	**120**	**180**
F_p (L/m^{2}h)		41.0	41.0	41.0
pH	9.02	9.00	9.00	9.00
C_f	10.9	10.9	10.9	10.9
C_p		7.4	7.3	7.4
R		0.32	0.33	0.32
	$F_{p,avg}$= 41	**$C_{f,avg}$= 10.9**	**$C_{p,avg}$= 7.36**	**R_{avg}= 0.323**

	Polymer: COP	L: 0.001	pH: 10	Anion: Borate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		40.0	40.0	40.0
pH	10.00	10.00	10.02	10.04
Cf	10.2	10.2	10.3	10.1
Cp		4.4	4.4	4.4
R		0.57	0.57	0.56
	$F_{p,avg}$= 40	**Cf,avg=10.2**	**Cp,avg=4.4**	**Ravg=0.567**

	Polymer: COP	L: 0.002	pH: 10	Anion: Borate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		40.0	40.0	40.0
pH	10.00	10.02	10.02	10.01
Cf	10.5	10.5	10.5	10.5
Cp		4.6	4.6	4.6
R		0.56	0.56	0.56
	$F_{p,avg}$= 40	**Cf,avg=10.5**	**Cp,avg=4.6**	**Ravg=0.56**

	Polymer: COP	L: 0.005	pH: 10	Anion: Borate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		41.0	41.0	41.0
pH	10.00	10.00	10.00	10.00
Cf	10.5	10.5	10.5	10.5
Cp		4.7	4.7	4.7
R		0.56	0.56	0.56
	$F_{p,avg}$= 41.0	**Cf,avg=10.5**	**Cp,avg=4.7**	**Ravg=0.56**

Table D.1 (continued)

	Polymer: COP	**Loading: 0.01**	**pH: 10**	**Anion: Borate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		40.0	40.0	40.0
pH	10.00	10.00	10.02	10.01
Cf	10.3	10.3	10.3	10.3
Cp		5.5	5.5	5.5
R		0.47	0.47	0.47
	$F_{p,avg}$= 40.0	**Cf,avg=10.3**	**Cp,avg=6.5**	**Ravg=0.47**

Table D2 Data Tables of PEUF Experiments for Chromate Retention

	Polymer: PDAM	**L: 0.005**	**pH: 4**	**Anion: Chromate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		81.02	81.02	81.02
pH	5.00	5.00	5.00	5.00
T (°C)	25.0	25.0	25.0	25.0
C_f	10.0	10.0	10.0	10.0
C_p		3.2	3.2	3.2
R		0.68	0.68	0.68
	$F_{p,avg}$= 81.02	**$C_{f,avg}$= 10.0**	**$C_{p,avg}$= 3.2**	**R_{avg}= 0.68**

	Polymer: PDAM	**L: 0.01**	**pH: 4**	**Anion: Chromate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		81.0	81.0	81.0
pH	4.00	4.00	4.01	4.00
T (°C)	25.6	25.6	25.8	26.0
C_f	10.2	10.1	10.1	10.1
C_p		2.6	2.6	2.6
R		0.74	0.74	0.74
	$F_{p,avg}$= 81	**$C_{f,avg}$= 10.1**	**$C_{p,avg}$= 2.6**	**R_{avg}= 0.74**

	Polymer: PDAM	**L: 0.02**	**pH: 4**	**Anion: Chromate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		80.6	80.6	80.6
pH	4.00	4.00	4.01	4.00
T (°C)	25.6	25.6	25.8	26.0
C_f	10.2	10.1	10.1	10.1
C_p		3.4	3.4	3.5
R		0.66	0.66	0.65
	$F_{p,avg}$= 80.6	**$C_{f,avg}$= 10.1**	**$C_{p,avg}$= 3.4**	**R_{avg}= 0.656**

Table.D2 (continued)

	Polymer: PDAM	L: 0.2	pH: 4	Anion: Chromate
t (min)	0	60	120	240
F_p (L/m^{2}h)		81.0	81.0	81.0
pH	4.00	4.00	4.02	4.01
T (°C)	21.7	21.7	21.7	22.0
C_f	10.1	10.0	10.1	10.1
C_p		4.9	4.9	4.8
R		0.51	0.51	0.52
	$F_{p,avg}$= 81	$C_{f,avg}$= 10.1	$C_{p,avg}$= 4.9	R_{avg}= 0.513

	Polymer: PDAM	L: 0.005	pH: 5	Anion: Chromate
t (min)	0	60	120	240
F_p (L/m^{2}h)		81.90	81.02	81.02
pH	5.00	5.00	5.00	5.00
T (°C)	25.0	25.0	25.0	25.0
C_f	10.2	10.2	10.1	10.1
C_p		3.7	3.8	3.7
R		0.64	0.62	0.63
	$F_{p,avg}$= 81.31	$C_{f,avg}$= 10.2	$C_{p,avg}$= 3.7	R_{avg}= 0.63

	Polymer: PDAM	L: 0.01	pH: 5	Anion: Chromate
t (min)	0	60	120	240
F_p (L/m^{2}h)	81.97	81.97	81.97	81.97
pH	5.00	5.03	5.00	5.02
T (°C)	25.0	25.0	25.0	25.0
C_f	10.1	10.0	10.1	10.1
C_p		3.2	3.2	3.1
R		0.68	0.68	0.69
	$F_{p,avg}$= 81.97	$C_{f,avg}$= 10.1	$C_{p,avg}$= 3.2	R_{avg}= 0.683

	Polymer: PDAM	L: 0.05	pH: 5	Anion: Chromate
t (min)	0	60	120	240
F_p (L/m^{2}h)		83.0	83.0	82.2
pH	5.00	5.00	5.00	5.00
T (°C)	25.0	25.0	25.0	25.0
C_f	10.3	10.2	10.3	10.3
C_p		3.7	3.8	3.7
R		0.64	0.63	0.64
	$F_{p,avg}$= 82.7	$C_{f,avg}$= 11.14	$C_{p,avg}$= 4.3	R_{avg}= 0.64

Table. D2 (continued)

	Polymer: PDAM	L: 0.005	pH: 8	Anion: Chromate
t (min)	0	60	120	240
F_p (L/m^{2}h)		114.9	114.9	114.9
pH	8.05	8.07	8.03	8.05
T (°C)	21.4	21.4	21.4	21.9
C_f	10.1	10.0	10.1	10.2
C_p		4.4	4.3	4.4
R		0.56	0.57	0.57
	$F_{p,avg}$= 114.9	$C_{f,avg}$= 10.1	$C_{p,avg}$= 4.4	R_{avg}= 0.566

	Polymer: PDAM	L: 0.01	pH: 8	Anion: Chromate
t (min)	0	60	150	240
F_p (L/m^{2}h)		119.1	119.1	119.1
pH	8.02	8.02	8.03	8.04
T (°C)	23.2	23.2	23.9	24.0
C_f	9.1	9.2	9.2	9.1
C_p		3.5	3.6	3.5
R		0.62	0.61	0.62
	$F_{p,avg}$=119.1	$C_{f,avg}$= 9.15	$C_{p,avg}$= 3.65	R_{avg}= 0.62

	Polymer: PDAM	L: 0.05	pH: 8	Anion: Chromate
t (min)	0	60	120	240
F_p (L/m^{2}h)		105.6	105.6	105.6
pH	8.07	8.07	8.10	8.00
T (°C)	25.8	25.8	26.0	26.1
C_f	10.4	10.3	10.3	10.3
C_p		4.2	4.3	4.2
R		0.59	0.58	0.59
	$F_{p,avg}$= 104	R_{avg}= 0.59	$C_{f,avg}$= 10.3	$C_{p,avg}$= 4.2

	Polymer: PDAM	L: 0.2	pH: 8	Anion: Chromate
t (min)	0	60	120	240
F_p (L/m^{2}h)		105.6	105.6	101.0
pH	8.0	8.1	8.0	8.1
T (°C)	21.7	21.7	21.7	22.0
C_f	10.1	10.0	10.1	10.3
C_p		5.5	5.6	5.6
R		0.45	0.45	0.46
	$F_{p,avg}$= 110.6	$C_{f,avg}$= 10.1	$C_{p,avg}$= 5.6	R_{avg}= 0.45

Table. D2 (continued)

	Polymer: PDAM	**L: 0.01**	**pH: 6**	**Anion: Chromate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		113.3	113.4	113.3
pH	6.05	6.05	6.05	6.04
T (°C)	22.0	22.3	22.9	22.7
C_f	10.5	10.4	10.5	10.6
C_p		3.2	3.2	3.1
R		0.69	0.70	0.71
	$F_{p,avg}$= 113.3	**$C_{f,avg}$= 10.5**	**$C_{p,avg}$= 3.16**	**R_{avg}= 0.70**

	Polymer: PDAM	**L: 0.01**	**pH: 7**	**Anion: Chromate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		120.1	120.7	120.7
pH	7.00	7.00	7.04	7.02
T (°C)	21.2	22.0	22.0	22.0
C_f	9.1	9.1	9.1	9.0
C_p		3.2	3.2	3.1
R		0.65	0.65	0.66
	$F_{p,avg}$= 120.4	**$C_{f,avg}$= 9.1**	**$C_{p,avg}$= 3.13**	**R_{avg}= 0.65**

Polymer: PDAM, 200 mg/L		**L: 0.01**	**pH: 4**	**Anion: Chromate, 2mg/l**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		80.00	80.00	80.00
pH	4.00	4.00	4.00	4.00
T (°C)	25.0	25.0	25.0	25.0
C_f	2.22	2.19	2.21	2.24
C_p		0.73	0.71	0.75
R		0.66	0.68	0.67
	$F_{p,avg}$= 80.0	**$C_{f,avg}$= 2.21**	**$C_{p,avg}$= 0.73**	**R_{avg}= 0.67**

Polymer: PDAM, 500 mg/L		**L: 0.01**	**pH: 4**	**Anion: Chromate, 5mg/l**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		75.00	75.00	75.00
pH	4.00	4.01	4.01	4.00
T (°C)	25.0	25.0	25.0	25.0
C_f	5.10	5.10	5.20	5.10
C_p		1.50	1.60	1.50
R		0.71	0.69	0.71
	$F_{p,avg}$= 75	**$C_{f,avg}$= 5.1**	**$C_{p,avg}$= 1.5**	**R_{avg}= 0.70**

Table. D2 (continued)

Polymer: PDAM, 2500 mg/L		**L: 0.01**	**pH: 4**	**Anion: Chromate, 25mg/l**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		78.2	78.2	78.2
pH	4.00	4.00	4.00	4.01
T (°C)	25.0	25.0	25.0	25.0
C_f	25.4	25.1	25.2	25.4
C_p		10.3	10.4	10.4
R		0.59	0.59	0.59
	$F_{p,avg}$= 78.2	**$C_{f,avg}$= 25.3**	**$C_{p,avg}$= 9.93**	**R_{avg}= 0.59**

Polymer: PDAM, 5000 mg/L		**L: 0.01**	**pH: 4**	**Anion: Chromate, 50mg/l**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		77.42	77.42	77.42
pH	4.00	4.00	4.02	4.01
T (°C)	25.0	25.0	25.0	25.0
C_f	50.0	49.6	49.2	49.3
C_p		23.6	23.3	23.3
R		0.52	0.53	0.53
	$F_{p,avg}$= 77.42	**$C_{f,avg}$= 49.5**	**$C_{p,avg}$= 23.4**	**R_{avg}= 0.53**

PDAM	**L: 0.01**	**pH:4**	**Sulfate: 10mg/l**	**Anion: Chromate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		81.0	81.0	81.0
pH	4.00	4.00	4.01	4.01
T (°C)	25.0	25.0	25.0	25.0
C_f	10.0	10.1	10.0	10.0
C_p		4.9	4.9	4.9
R		0.51	0.51	0.51
	$F_{p,avg}$= 81.0	**$C_{f,avg}$= 10.1**	**$C_{p,avg}$= 4.9**	**R_{avg}= 0.51**

PDAM	**L: 0.01**	**pH:4**	**Sulfate: 100mg/l**	**Anion: Chromate**
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		80.0	80.0	80.0
pH	4.00	4.00	4.00	4.00
T (°C)	25.0	25.0	25.0	25.0
C_f	10.6	10.5	10.5	10.5
C_p		7.3	7.4	7.4
R		0.30	0.30	0.30
	$F_{p,avg}$= 80	**$C_{f,avg}$= 10.5**	**$C_{p,avg}$= 7.4**	**R_{avg}= 0.30**

Table. D2 (continued)

PDAM	L: 0.01	pH:4	Sulfate: 500mg/l	Anion: Chromate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		79.0	79.0	79.0
pH	4.00	4.00	4.01	4.01
T (°C)	25.0	25.0	25.0	25.0
C_f	10.7	10.6	10.6	10.7
C_p		8.3	8.3	8.3
R		0.22	0.22	0.22
	$F_{p,avg}$= 79	**$C_{f,avg}$= 10.7**	**$C_{p,avg}$= 8.3**	**R_{avg}= 0.22**

PDAM	L: 0.01	pH:4	Chloride: 10mg/l	Anion: Chromate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		81.0	81.0	81.0
pH	4.00	4.00	4.01	4.01
T (°C)	25.0	25.0	25.0	25.0
C_f	10.1	10.2	10.1	10.1
C_p		4.1	4.1	4.2
R		0.59	0.59	0.58
	$F_{p,avg}$= 81.0	**$C_{f,avg}$= 10.1**	**$C_{p,avg}$= 4.1**	**R_{avg}= 0.59**

PDAM	L: 0.01	pH:4	Chloride:100mg/l	Anion: Chromate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		80.0	80.0	80.0
pH	4.00	4.02	4.01	4.01
T (°C)	25.0	25.0	25.0	25.0
C_f	9.9	10.0	10.0	9.9
C_p		5.2	5.2	5.2
R		0.48	0.48	0.47
	$F_{p,avg}$= 80.0	**$C_{f,avg}$= 10.0**	**$C_{p,avg}$= 5.2**	**R_{avg}= 0.48**

PDAM	L: 0.01	pH:4	Chloride:500mg/l	Anion: Chromate
t (min)	**0**	**60**	**120**	**240**
F_p (L/m^{2}h)		79.0	79.0	79.0
pH	4.00	4.02	4.01	4.01
T (°C)	25.0	25.0	25.0	25.0
C_f	9.6	9.6	9.6	9.6
C_p		5.8	5.9	5.9
R		0.40	0.39	0.39
	$F_{p,avg}$= 79.0	**$C_{f,avg}$= 9.6**	**$C_{p,avg}$= 5.9**	**R_{avg}= 0.39**

APPENDIX E

DATA TABLES OF THE GRAPHS GIVEN IN CHAPTER 4

Table E.1 Effect of Loading on Boron Retention and Flux using PNSH at pH 9

Loading	Retention (%)	Flux
0.05	7.9	62.4
0.2	32	109.4
0.5	30	116.5

Table E.2 Effect of pH on Boron Retention using PNSH

	Retention	
pH	**L:0.2**	**L:0.5**
7	15.6	13.0
9	32.0	30.0
10	40.7	37.6

Table E.3 Effect of Loading on Boron Retention and Flux using PNSL at pH 9

Loading	Retention (%)	Flux
0.001	56.3	47.0
0.002	50.0	47.0
0.005	45.6	47.0
0.01	39.3	47.3
0.02	35.4	46.5
0.05	24.0	47.4

Table E.4 Effect of pH on Boron Retention using PNSL

	Retention	
pH	**L:0.001**	**L:0.005**
7	27.5	23.6
9	56.3	45.6
10	64.3	54.0

Table E.5 Effect of Loading on Boron Retention and Flux using PNSM at pH 9

Loading	Retention (%)	Flux
0.0005	61.0	47.0
0.002	52.0	47.6
0.005	48.0	48.4
0.02	35.0	50.0
0.05	26.0	51.0

Table E.6 Effect of pH on Boron Retention using PNSM

	Retention	
pH	**L:0.002**	**L:0.0005**
9	52.0	61.0
10	58.0	68.0

Table E.7 Effect of Loading on Boron Retention and Flux using COP at pH 9

Loading	Retention (%)	Flux
0.001	44.0	40.9
0.002	44.0	40.3
0.005	44.3	41
0.01	40.3	42.3
0.02	32.3	38.6
0.05	26.0	41.6

Table E.8 Effect of pH on Boron Retention using COP

pH	L:0.001	L:0.002	L:0.005	L:0.01
9	44.0	44.0	44.3	40.3
10	56.6	56.0	56.0	47.0

Table E.9 Effect of Loading on Hexavalent Chromium Retention and Flux using PDAM at pH 4

Loading	Retention (%)	Flux
0.005	68.0	80.0
0.010	70.0	81.0
0.020	65.6	80.6
0.100	55.6	80.6
0.200	51.3	80.3

Table E.10 Effect of Loading on Hexavalent Chromium Retention and Flux using PDAM at pH 5

Loading	Retention (%)	Flux
0.005	63.0	81.3
0.01	68.3	81.9
0.05	64.0	82.7

Table E.11 Effect of Loading on Hexavalent Chromium Retention and Flux using PDAM at pH 8

Loading	Retention (%)	Flux
0.005	56.6	114.0
0.01	64.6	114.0
0.05	59.0	105.6
0.2	45.0	110.0

Table E.12 Effect of pH on Hexavalent Chromium Retention using PDAM at L:0.01

pH	Retention (%)
4	74.0
5	72.0
6	70.0
7	65.0
8	61.6

Table E.13 Effect of PDAM Concentration on Hexavalent Chromium Retention and Flux at pH 4 and L:0.01

PDAM (mg/L)	Retention (%)	Flux
200	67.0	80.0
500	70.3	75.0
1000	70.0	81.0
2500	59.0	78.2
5000	52.6	77.4

Table E.14 Effect of Sulfate Concentration on Hexavalent Chromium Retention and Flux at pH 4 and L:0.01

	Retention (%)		
Sulfate (mg/L)	**Cr(VI)**	**Sulfate**	**Flux**
0	70	0	81
10	51	14	81
100	30	29	79
500	22	35	80

Table E.15 Effect of Sulfate Concentration on Hexavalent Chromium Retention at pH 4 and L:0.01

	Retention (%)		
Chloride (mg/L)	**Cr(VI)**	**Chloride**	**Flux**
0	70	0	81
10	58.6	4	81
100	47.6	10	80
500	39.3	18	79

Table E.16 Comparison of Boron Retention Performances of PNSM and COP

	Boron Retention (%)	
Loading	**COP**	**PNS**
0.001	44	57
0.002	44	50
0.005	45	46
0.01	40	39

APPENDIX F

GUINIER PLOTS OBTAINED BY THE STATIC LIGHT SCATTERING MEASUREMENTS

Table F.1 Data Obtained from Guinier Plot of PNSM/Water Solution at pH 7

	Conc./(g/dm^3)	**Mw(app)/(g/mol)**	**<S^2>(app)/µm^2**	**Rg(app)/nm**
Conc.=0	0.0	8.99E+07	6.53E-02	255.587
PNSM (pH7)	1.0	8.98E+05	1.76E-02	132.625
PNSM (pH7)	0.8	1.65E+06	2.74E-02	165.618
PNSM (pH7)	0.455	5.96E+06	4.22E-02	205.325
PNSM (pH7)	0.2	2.49E+07	5.53E-02	235.099
A2: 3.883e-08 mol dm^3/g^2 (± 19.4 %) Rg: 2.556e+02 nm (± 7.88 %)				

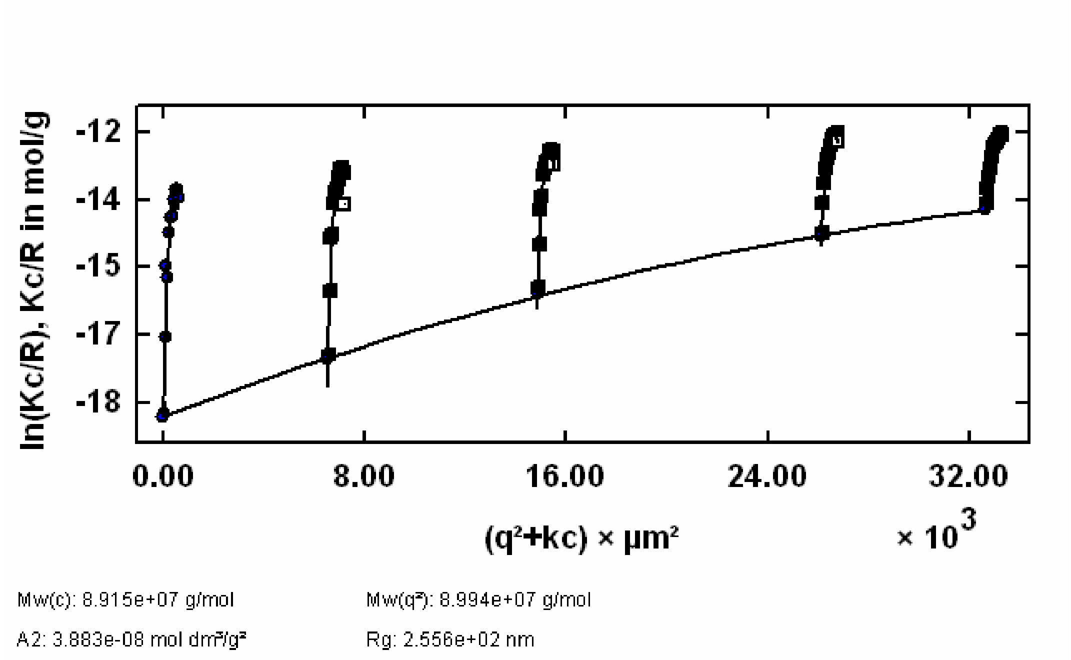
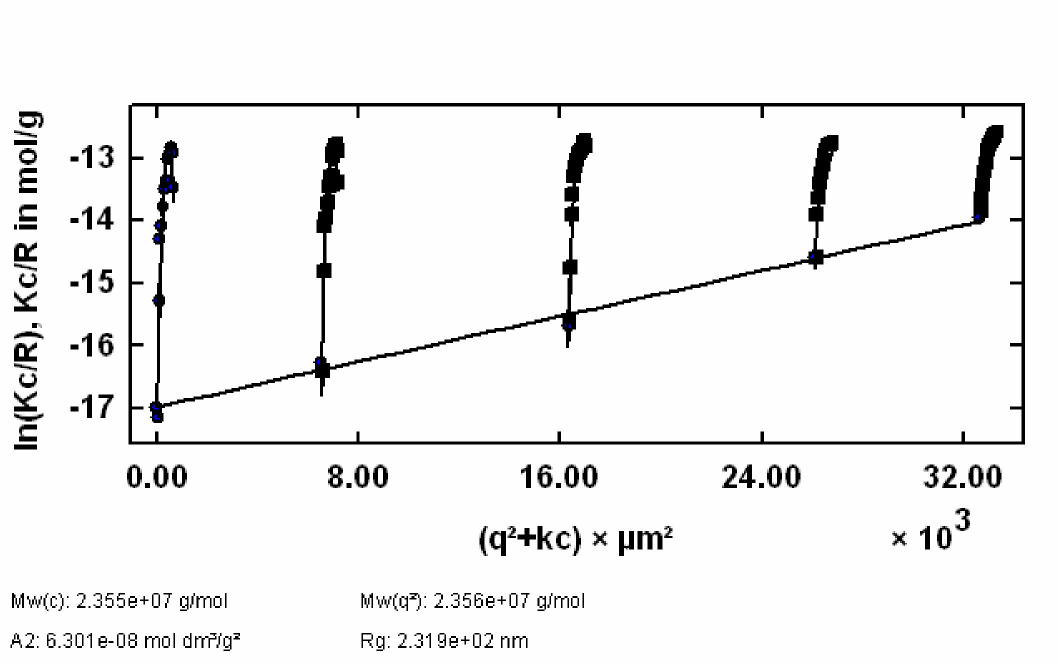


Figure F.1 Guinier Plot of PNSM / Water Solution at pH 7

Table F.2 Data Obtained from Guinier Plot of PNSM/Water Solution at pH 9

	Conc./(g/dm^3)	**Mw(app)/(g/mol)**	**<S^2>(app)/µm^2**	**Rg(app)/nm**
Conc.=0	0.0	2.36E+07	5.38E-02	231.915
PNSM (pH9)	1.0	1.15E+06	1.36E-02	116.61
PNSM (pH9)	0.8	2.14E+06	2.15E-02	146.568
PNSM (pH9)	0.5	6.39E+06	3.71E-02	192.672
PNSM (pH9)	0.2	1.17E+07	4.41E-02	209.979
A2: 6.301e-08 mol dm^3/g^2 (± 21 %) Rg: 2.319e+02 nm (± 7.78 %)				

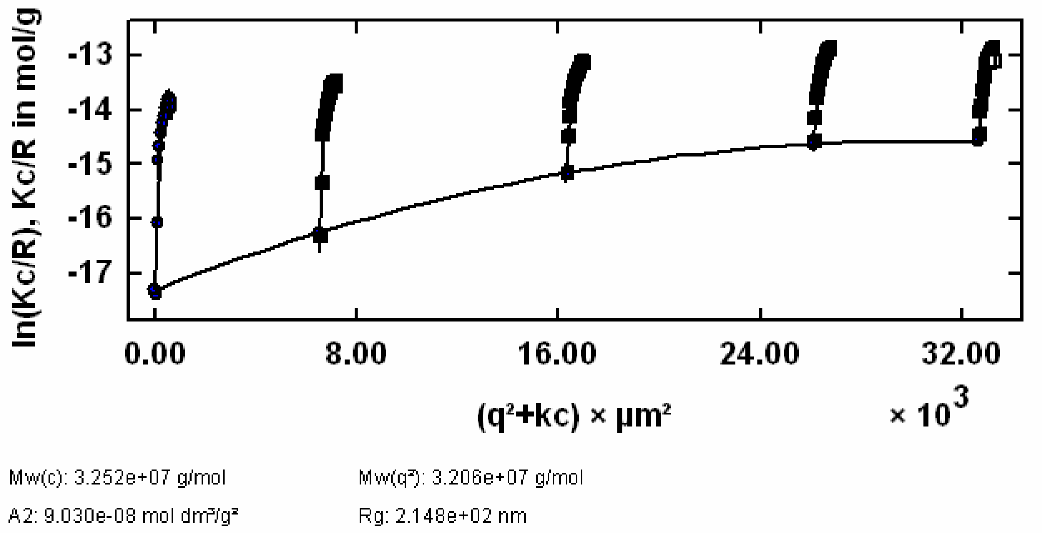


Mw(c): 2.355e+07 g/mol
Mw(q²): 2.356e+07 g/mol
A2: 6.301e-08 mol dm³/g²
Rg: 2.319e+02 nm

Figure F.2 Guinier Plot of PNSM / Water Solution at pH 9

Table F.3 Data Obtained from Guinier Plot of PNSM/Water Solution at pH 10

	Conc./(g/dm³)	**Mw(app)/(g/mol)**	**<S²>(app)/µm²**	**Rg(app)/nm**
Conc.=0	0.0	3.21E+07	4.61E-02	214.796
PNSM (pH10)	1.0	2.15E+06	1.84E-02	135.677
PNSM (pH10)	0.8	2.26E+06	1.84E-02	135.577
PNSM (pH10)	0.5	3.77E+06	2.25E-02	149.976
PNSM (pH10)	0.2	1.14E+07	3.49E-02	186.717
A2: 9.030e-08 mol dm³/g² (± 3.65 %) Rg: 2.148e+02 nm (± 7.91 %)				



Mw(c): 3.252e+07 g/mol Mw(q²): 3.206e+07 g/mol

A2: 9.030e-08 mol dm³/g² Rg: 2.148e+02 nm

Figure F.3 Guinier Plot of PNSM / Water Solution at pH 10

Table F.4 Data Obtained from Guinier Plot of PNSM/Boron/Water Solution (pH~8.5)

	Conc./(g/dm^3)	Mw(app)/(g/mol)	<S^2>(app)/µm^2	Rg(app)/nm
Conc.=0	0.0	1.05E+07	4.47E-02	211.5
PNSM-Boron	1.0	1.18E+06	1.85E-02	136.097
PNSM-Boron	0.8	1.55E+06	3.06E-02	174.826
PNSM-Boron	0.5	3.80E+06	2.89E-02	169.895
PNSM-Boron	0.2	6.42E+06	4.11E-02	202.751
A2: 1.071e-07 mol dm^3/g^2 (± 17.7 %) Rg: 2.115e+02 nm (± 7.6 %)				

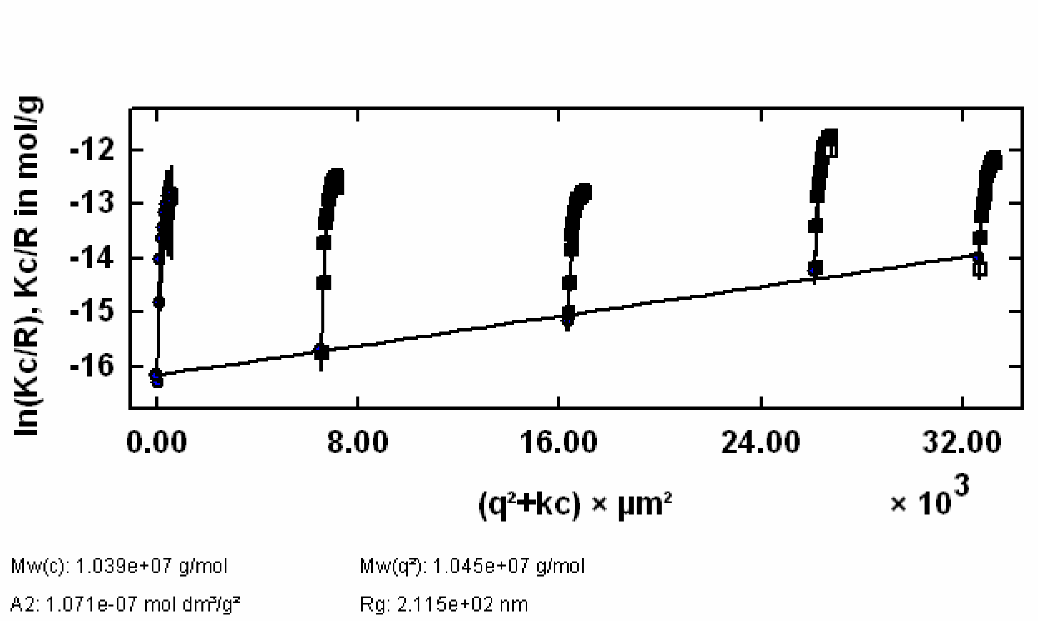
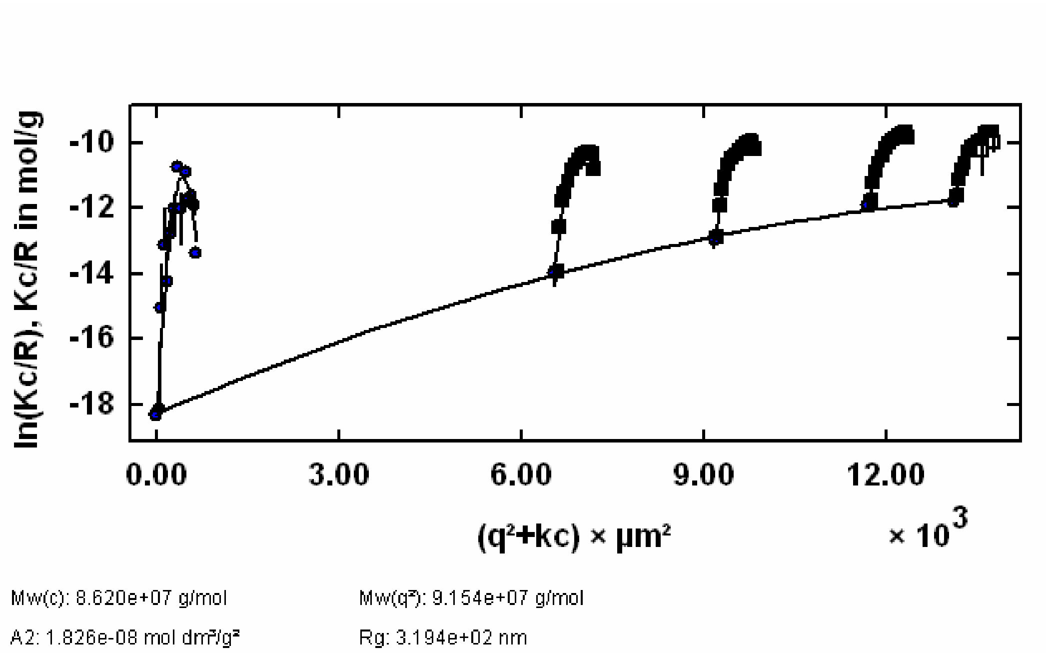


Figure F.4 Guinier Plot of PNSM / Boron / Water Solution

Table F.5 Data Obtained from Guinier Plot of COP/ Water Solution at pH 7

File	Conc./(g/dm^3)	Mw(app)/(g/mol)	<S^2>(app)/µm^2	Rg(app)/nm
Conc.=0	0.0	9.15E+07	1.02E-01	319.431
COP (pH 7)	3.3	1.34E+05	2.48E-02	157.513
COP (pH 7)	2.9	1.47E+05	2.50E-02	158.115
COP (pH 7)	2.3	4.30E+05	3.68E-02	191.923
COP (pH 7)	1.7	1.19E+06	4.83E-02	219.66
A2: 1.826e-08 mol dm^3/g^2 (± 709 %) Rg: 3.194e+02 nm (± 7.69 %)				



Mw(c): 8.620e+07 g/mol

Mw(q^2): 9.154e+07 g/mol

A2: 1.826e-08 mol dm^3/g^2

Rg: 3.194e+02 nm

Figure F.5 Guinier Plot of COP / Water Solution at pH 7

Table F.6 Data Obtained from Guinier Plot of COP/ Water Solution at pH 9

File	Conc./(g/dm³)	Mw(app)/(g/mol)	<S²>(app)/µm²	Rg(app)/nm
Conc.=0	0.0	1.38E+07	8.00E-02	282.85
COP (pH 9)	3.3	1.13E+05	2.45E-02	156.488
COP (pH 9)	2.9	2.08E+05	3.22E-02	179.495
COP (pH 9)	2.3	3.72E+05	3.57E-02	188.901
COP (pH 9)	1.7	1.33E+06	5.34E-02	231.043
A2: 5.500e-08 mol dm³/g² (± 49.7 %) Rg: 2.828e+02 nm (± 4.98 %)				

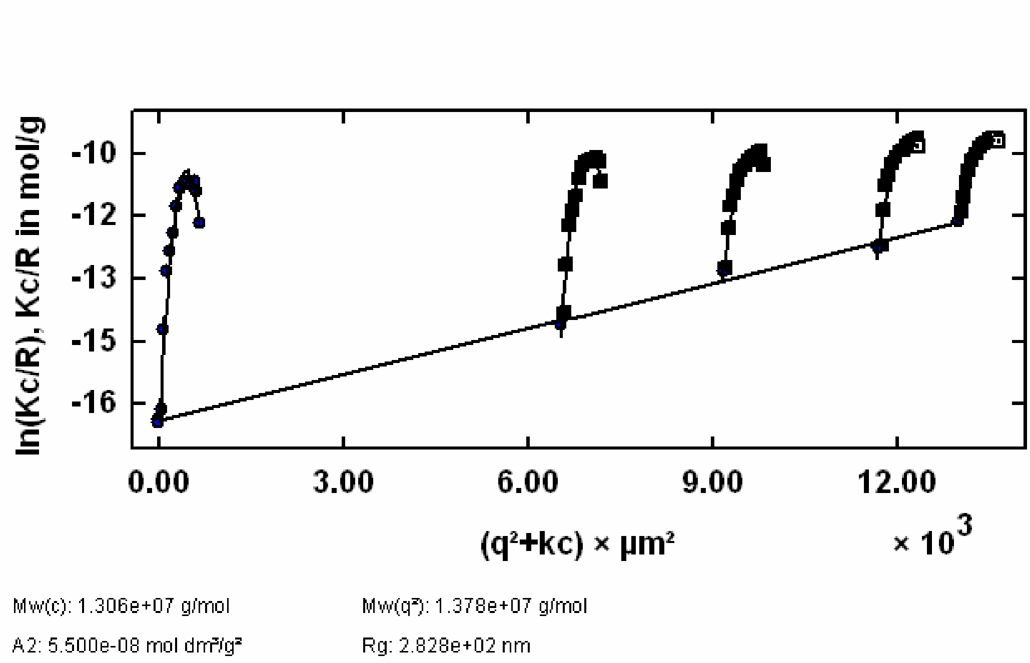


Figure F.6 Guinier Plot of COP / Water Solution at pH 9

Table F.7 Data Obtained from Guinier Plot of COP/ Water Solution at pH 10

File	Conc./(g/dm³)	Mw(app)/(g/mol)	<S²>(app)/µm²	Rg(app)/nm
Conc.=0	0.0	6.34E+06	5.29E-02	229.934
COP (pH 10)	3.3	2.13E+05	3.34E-02	182.649
COP (pH 10)	2.9	1.82E+05	3.10E-02	176.153
COP (pH 10)	2.3	7.82E+05	4.82E-02	219.469
COP (pH 10)	1.7	9.52E+05	4.00E-02	200.065
A2: 8.040e-08 mol dm³/g² (± 138 %) Rg: 2.299e+02 nm (± 6.76 %)				

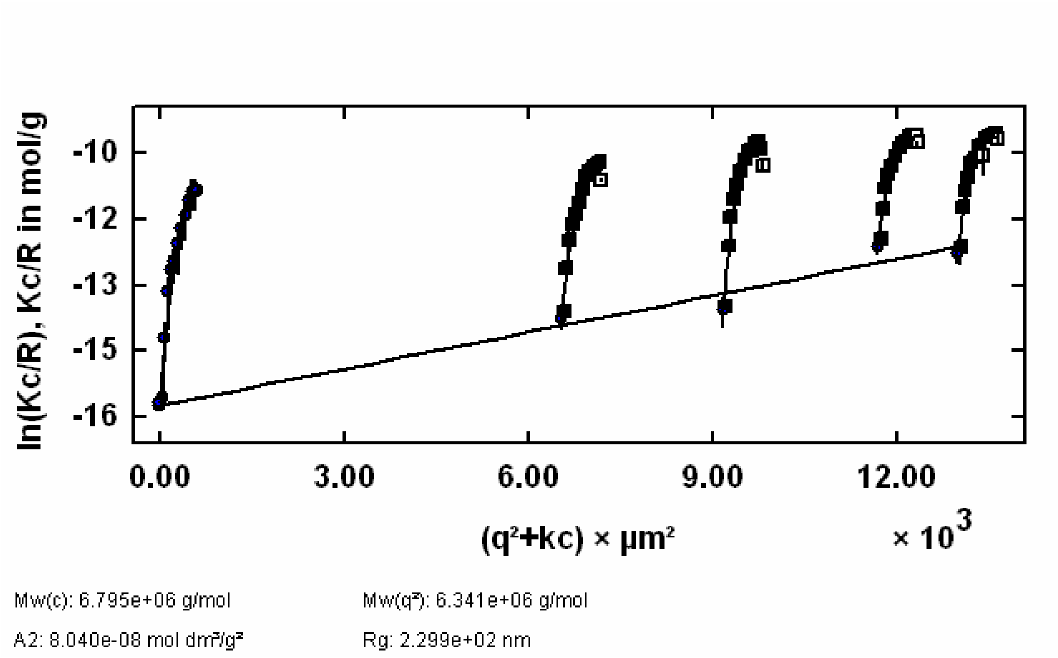


Figure F.7 Guinier Plot of COP / Water Solution at pH 10

Table F.8 Data Obtained from Guinier Plot of COP/Boron /Water Solution(pH ~9.5)

File	Conc./(g/dm^3)	Mw(app)/(g/mol)	<S^2>(app)/µm^2	Rg(app)/nm
Conc.=0	0.0	2.20E+06	6.31E-02	251.1
COP-Boron	3.3	2.53E+05	3.04E-02	174.2
COP-Boron	2.9	2.48E+05	3.45E-02	185.6
COP-Boron	2.3	2.88E+05	3.51E-02	187.5
COP-Boron	1.7	6.90E+05	4.67E-02	216.1
A2: 1.928e-07 mol dm^3/g^2 (± 84.6 %) Rg: 2.511e+02 nm (± 7.23 %)				

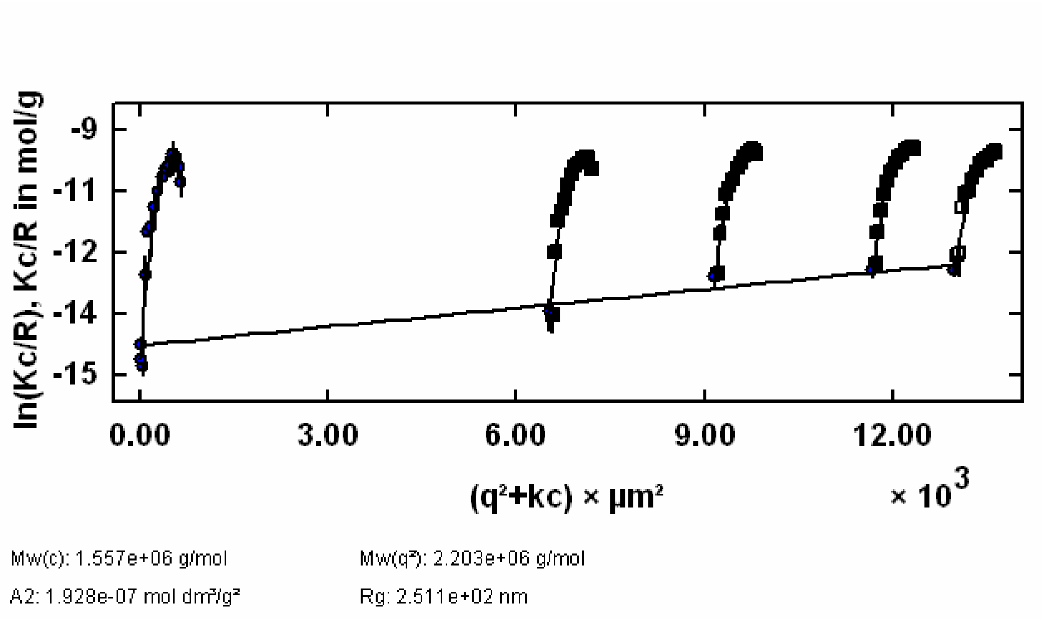


Figure F.8 Guinier Plot of COP / Boron / Water Solution

APPENDIX G

DETERMINATION OF VISCOSITY AVERAGE MOLECULAR WEIGHT OF PNS

In order to determine the viscosity average molecular weight, first, intrinsic viscosity of PNS solutions were determined using Ubbelohde capillary viscometer. In the second step Mark-Houwink relationship was used to calculate viscosity average molecular weight of the polymer solutions. Table G.1 demonstrates the concentration versus relative viscosity (η_{rel}) data obtained in the viscosity measurement experiments. All of the values given below are the average of three measurements.

Table G.1 Concentration versus Relative Viscosity Data

PNSH			
Concentration (g/dL)	**$t_{solvent}$ (sec)**	**$t_{(solution)}$ (sec)**	**η_{rel} (dL/g)**
0.4	72.7	162.7	2.24
0.3	72.7	120.0	1.65
0.24	72.7	102.0	1.40
0.2	72.7	91.0	1.25
0.16	72.7	84.3	1.16
PNSM			
Concentration (g/dL)	**$t_{solvent}$ (sec)**	**$t_{(solution)}$ (sec)**	**η_{rel} (dL/g)**
0.8	72.7	137.0	1.89
0.6	72.7	105.7	1.45
0.48	72.7	94.7	1.30
0.4	72.7	87.0	1.20
PNSL			
Concentration (g/dL)	**$t_{solvent}$ (sec)**	**$t_{(solution)}$ (sec)**	**η_{rel} (dL/g)**
0.8	72.7	117.7	1.62
0.6	72.7	96.0	1.32
0.48	72.7	88.0	1.21
0.4	72.7	83.7	1.15

After obtaining the relative viscosity (η_{rel}) values for different concentrations, ln(η_{rel})/Concentration versus concentration graph was constructed. The intercept of the graph gives the intrinsic viscosity of the given polymer solution. Figure G.1, G.2 and G.3 depict the ln(η_{rel})/Concentration versus concentration graphs of PNSH, PNSM and PNSL, respectively.

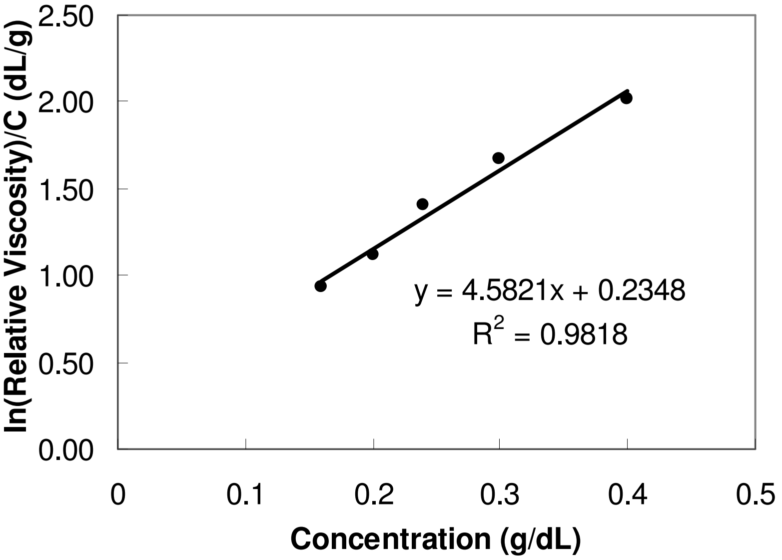


Figure G.1 Relative viscosity versus concentration graph for PNSH

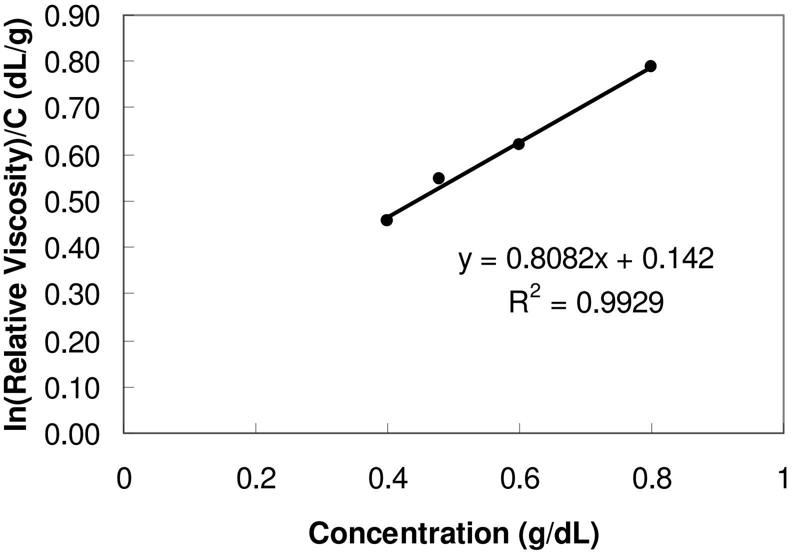


Figure G.2 Relative viscosity versus concentration graph for PNSM

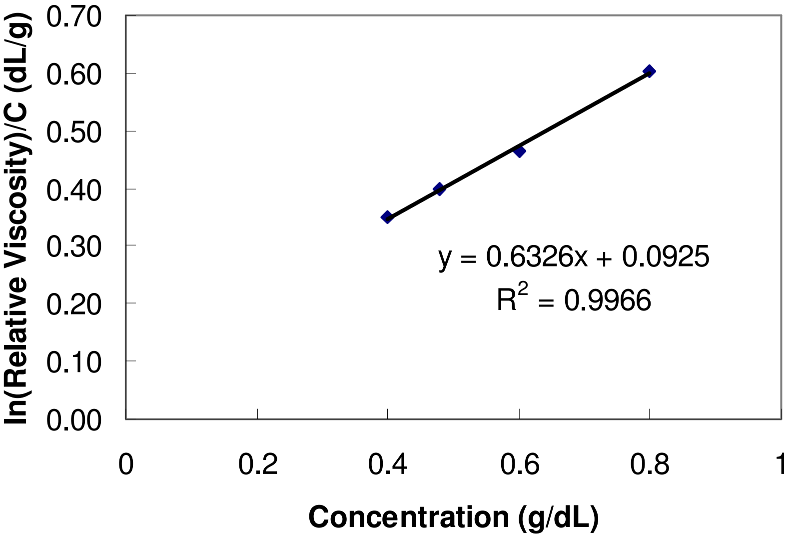


Figure G.3 Relative viscosity versus concentration graph for PNSL

Mark-Houwink constants of the polymers are found from literature as [150]:

$\eta = K.(M_v)^a$

$K = 27.8*10^{-5}$

$a = 0.537$

Using the given constants and Mark-Houwink relationship, M_v of PNSH, PNSM and PNSL are found as follows:

Table G.2 Viscosity average molecular weights of PNSH, PNSM and PNSL

	Mv
PNSH	281,842
PNSM	110,480
PNSL	49,733

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- Attendee to “Intensive Course on Protein Chromatography and New Polymer Systems”, Hacettepe University, Ankara, Turkey, 2005.

- Attendee to “Euromembrane 2006 Conference”, Giardini-Naxos-Italy, September 2006.

- Attendee to “7th National Chemical Engineering Conference”, Anadolu University, Faculty of Engineering and Architecture, Department of Chemical Engineering, Eskişehir, Turkey, September 5-8, 2006 (Poster Presentation).

- Attendee to “Somer Symposium Series 1”, Middle East Technical University, Ankara, Turkey, May 14-15, 2007 (Audience).

- Attendee to COST Action 637- Metals and Related Substances in Water, Antalya, Turkey, October 24-26 (Poster Presentation)

PUBLICATIONS

Journal Articles:

- Pınar Çalık, Eda Çelik, İlkin E. Telli, Ceren Oktar and Elif Özdemir, “Protein-based complex medium design for recombinant serine alkaline protease production”, Enzyme and Microbial Technology, 33 (2003) 975-986.
- Ceren Oktar Doğanay, H. Önder Özbelge, Levent Yılmaz, Niyazi Bicak “Removal and recovery of metal anions via functional polymer based PEUF”, Desalination, 200 (2006) 286-287.
- Ceren Oktar Doğanay, Levent Yılmaz, H. Önder Özbelge, Niyazi Bicak, “Selective Mercury Uptake by Polymer Supported Hydroxyethyl Sulfonamides”, Reactive and Functional Polymers (accepted).

Conference Proceedings:

- Yagız M., Oktar C., Çulfaz M., Ion Exchange of lead & cadmium in Western Anatolia clinoptilolite, EMCC-2, Book of abstracts, 2001.
- Oktar Doğanay C., Özbelge H.Ö., Yılmaz L., Bıçak N., "Metal Anyonların İşlevsel Polimerler Kullanılarak Polimer Komplekslemeli Ultrafiltrasyon ile Ayırımı ve Geri Kazanımı", UKMK 7, Book of Abstracts, 594-596.
- Oktar Doğanay C., Özbelge H.Ö., Yılmaz L., Bıçak N., "Use of Functional Polymers in the Removal and Recovery of Metal Anions from Waste Water", COST Action 637-Metals and Related Substances in Water, Book of Abstracts,