EFFECT OF IONIC STRENGTH ON THE PERFORMANCE OF POLYMER ENHANCED ULTRAFILTRATION IN HEAVY METAL REMOVAL FROM AQUEOUS SOLUTIONS

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Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Nurcan Baç
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Levent Yılmaz
Supervisor

Examining Committee Members

Prof. Dr. H. Önder Özbelge	(METU, CHE)	
Prof. Dr. Levent Yılmaz	(METU, CHE)	
Assoc. Prof. Nihal Aydoğan	(Hacettepe, CHE)	
Assoc. Prof. Serpil Şahin	(METU, FDE)	
Asst. Prof. Yusuf Uludağ	(METU, CHE)	

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Name, Last name : Sezin İslamoğlu

Signature :

ABSTRACT

EFFECT OF IONIC STRENGTH ON THE PERFORMANCE OF POLYMER ENHANCED ULTRAFILTRATION IN HEAVY METAL REMOVAL FROM AQUEOUS SOLUTIONS

İslamoğlu, Sezin
Ph.D., Department of Chemical Engineering
Supervisor: Prof. Dr. Levent Yılmaz

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Effect of ionic strength on the efficiency of heavy metal removal and recovery from aqueous solutions via continuous mode polymer enhanced ultrafiltration (PEUF) method was examined. Application of PEUF to divalent ions of cadmium, nickel and zinc after their prior linking with polyethylenimine (PEI) results in complete removal of metal ions from single component aqueous solutions at high pHs.

Binding ability and hence the extent of metal retention in high ionic strength medium exhibits differences between solutions containing single and multicomponent metal mixtures. In single component metal solutions, extent of retention decreases but binding order of metals remains unaffected both in low and high ionic strength medium. But, in binary component metal mixtures, with increase in ionic strength the binding order of metals changes.

Fractional separation of Cd, Ni and Zn ions from equimolar binary and ternary mixtures of these metals and effect of ionic strength on fractional separation efficiency were investigated. Depending on pH and salt concentration and metal pairs present in the solution fractional separation can be achieved.

Dynamic and static light scattering experiments were performed in order to gain 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.

A chemical equilibrium model was developed in order to estimate the apparent binding constants of metal-PEI complexes. Based on the data obtained from continuous and batch mode PEUF experiments apparent binding constants were estimated and compared to reveal the performance differences between these operational modes.

Keywords: Ultrafiltration, Membrane Separation Techniques, Ionic Strength, Heavy Metal Removal, Polyethylenimine

ÖZ

SULU ORTAMLARDAN POLİMER KOMPLEKSLEMELİ ULTRAFİLTRASYON YÖNTEMİYLE AĞIR METALLERİN AYRILMASINDA İYONİK GÜCÜN ETKİSİ

İslamoğlu, Sezin
Doktora, Kimya Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Levent Yılmaz

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Metal bileşikleri içeren sulu ortamlardan, ağır metallerin ayrılması amacıyla kullanılan polimer kompleksleme li ultrafiltrasyon (PKUF) yönteminde, ortamın iyonik gücünün ve pH seviyesinin proses performansına etkisi incelenmiştir. Yüksek pH seviyesinde, PKUF yöntemiyle, metallerin tekli metal bileşikleri içeren sulu ortamlardan tamamen uzaklaştırılabileceği saptanmıştır.

İyonik gücün ve pH etkisinin, tekli ve çoklu metal bileşikleri içeren çözeltilerde farklılıklar gösterdiği belirlenmiştir. Tekli metal bileşikleri içeren çözeltilerde, iyonik gücün artmasıyla metal iyonlarının alıkonma oranı azalırken, PEI-metal bağlanma sırasının değişmediği saptanmıştır. İkili metal bileşikleri içeren çözeltilerde ise iyonik gücün artmasıyla alıkonma oranındaki azalmanın yanısıra metallerin bağlanma sırasının da değiştiği gözlenmiştir.

İkili veya üçlü kadmiyum, nikel ve çinko metal bileşikleri içeren sulu ortamlarda, iyonik güç, pH ve ortamda bulunan metal çeşidine bağlı olarak metallerin kademeli olarak ayrıştırılabileceği belirlenmiştir.

Polietilenimin moleküllerinin sıvı ortam içerisinde, ortamın tuz dengesine ve asit seviyesine göre gösterebileceği biçimsel değişiklikleri inceleyebilmek amacıyla dinamik ve statik ışık saçılımı yöntemiyle çeşitli analizler yapılmıştır. Analizler sonucunda iyon dayancındaki artışın polietilen makromolekül boyutlarında küçülmeye neden olduğu belirlenmiştir.

Polietilenimin metal kompleksleme sabitlerinin hesaplanmasına olanak sağlayan teorik bir model geliştirilmiştir. Kesiksiz ve kesikli PKUF yöntemleriyle elde edilen veriler doğrultusunda hesaplanan sabitler karşılaştırılarak yöntemler arasındaki olası performans farklılıkları incelenmiştir.

Anahtar Kelimeler: Ultrafiltrasyon, Membranlı Ayırma Yöntemleri, İyon Dayancı Ağır Metallerin Ayrılması, Polietilenimin

To Sevim, Erdal and Erol İslamoğlu

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AAS	Atomic Absorption Spectrometry
A_2	Second Virial Coefficient
Cd	Cadmium
CEUF	Complexation Enhanced Ultrafiltration
CoUF	Colloid Enhanced Ultrafiltration
Da	Dalton
DLS	Dynamic Light Scattering
EPA	Environmental Protection Agency
HPVP	Poly(vinyl pyrrolidone hydrolyzate)
I	Iodine
K_{app}	Apparent Binding Constant
L	Loading (Metal/Polymer ratio)
MEUF	Micellar Enhanced Ultrafiltration
MF	Microfiltration
MWCO	Molecular Weight Cut-Off
MS	Poly(hexamethylene guanidinehydrochloride)
mS	Millisiemens
NF	Nanofiltration
Ni	Nickel
OPVP	Oxyquinoline derivate of poly(vinyl pyrrolidone)
PEI	Polyethylenimine
PEUF	Polymer Enhanced Ultrafiltration
PPEI	Phosphorylated poly(ethylenimine)
Pr	Praseodymium
Q_F	Feed stream flow rate (l/h)
Q_P	Permeate stream flow rate (l/h)
R	Retention
R_g	Radius of gyration, (nm)
R_H	Hydrodynamic Radius, (nm)
R_L	Polymer retention

R_M	Total metal retention
R_{MF}	Free metal retention
RO	Reverse Osmosis
SLS	Static Light Scattering
Th	Thorium
UF	Ultrafiltration
X	Ligand
V	Reactor volume (l)
Zn	Zinc
Zr	Zirconium

	Subscripts
R	Retentate
P	Permeate
X	Ligand

CHAPTER 1

INTRODUCTION

1.1 Environmental Impacts of Heavy Metals

Metal species released into the environment by technological activities tend to persist indefinitely, circulating and eventually accumulating throughout the food chain, becoming a serious threat to the environment [1]. Environmental pollution by toxic metals occurs globally through military, industrial, and agricultural processes, coal, natural gas, paper, mining, and chlor-alkali and electroplating industries [2, 3]. Fuel and power industries generate 2.4 million tons of As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn annually. The metal industry adds 0.39 million tons per year of the same metals to the environment, while agriculture contributes 1.4 [4].

Among heavy metals, cadmium (Cd) is considered in many regards as a significant pollutant because it is one of the most toxic metals at elevated concentrations. According to the regulations of U.S. Environmental Protection Agency, the highest level of cadmium that is allowed in drinking water is 5 ppb. It is also reported that, ingestion of water which contains 5ppb or more cadmium, may cause a kidney damage [5].

The most remarkable properties of cadmium are great resistance to corrosion, excellent electric conductivity, and low melting point. For these reasons, cadmium is employed in many important industrial applications, even though its release in the environment can cause ecological and health hazards [6]. Cadmium is used primarily for metal plating and coating operations, including transportation equipment, machinery and baking enamels, photography, television phosphors. In spite of its toxic nature and high cost, cadmium plating is preffered because of its ability to provide a corrosion protective coating with an attractive appearance on various basis metals, especially on iron and steel. Due to the relatively high price of cadmium, it is largely applied in the form of thin coatings. Aircraft, marine, and military outdoor uses are common. The electrical industry makes use of Cd-plate on steel and other metals because it is easily soldered and has low contact resistance. Cadmium plating is often used on parts of assemblies consisting of dissimilar metals, such as steel and brass to minimise the galvanic corrosion [7]. It is also used in nickel-cadmium and solar batteries, in pigments, as a stabilizer in plastics and synthetic products, alloys and other uses [6].

In aqueous environment Cd^{2+} shows a relative mobility: it depends on pH, presence of organic molecules and water hardness. High acidity increases the release of Cd^{2+} and consequently, its uptake by plants and bioaccumulation. In aquatic environment, invertebrates accumulate Cd rapidly, followed by fish and aquatic plants and in some cases the presence of Cd in soil inhibits the growth of some plants [8].

Nickel (Ni) and zinc (Zn) are also elements of environmental concern. Ni is known as hazardous pollutant with general toxicity causing skin allergies and asthma. Cancer of the lung and nasal sinus is the most serious consequence from long term exposure [9]. For nickel and zinc, there are no primary drinking water regulations which are legally enforceable standards apply to public water systems. However according to secondary drinking water regulations which are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water, maximum allowable zinc level is reported to be 5ppm [5].

Zinc (Zn) and its compounds found in wastewaters in elevated levels can be harmful although low levels of zinc are essential for maintaining good health. Zn generally plays either catalytic or a structural role; in some metalloproteins that interact with DNA. It is an essential constituent of many enzyme systems. There is more than 2g of zinc in the average adult. There are believed to be 200 zinc requiring enzymes in the human body. Zinc is essential for healty skin and proper wound healing, for a strong immune system, for bone metabolism and for normal taste and smell whereas exposure to large amounts of zinc can cause stomach cramps, anemia, and changes in cholesterol levels [10].

Nickel is used in many industrial and consumer products, including stainless steel, magnets, coinage, and special alloys. It is also used for plating and as a green tint in glass. Nickel is pre-eminently an alloy metal, and its chief use is in the nickel steels and nickel cast irons, of which there are innumberable varietes. It is also widely used for many other alloys, such as nickel brasses and bronzes, and alloys with copper, chromium, aluminum, lead, cobalt, silver and gold. Nickel consumption can be summarized as: nickel steels (60%), nickel-copper alloys and nickel silver (14%), malleable nickel, nickel clad (9%), plating (6%), nickel cast irons (3%), heat and electric resistance alloys (3%), nickel brasses and bronzes (2%), others (3%) [9].

Wastewater from electroplating processes usually contains a high concentration of heavy metal ions such as $Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Cr(VI)$, etc. If it was discharged into a natural water body without any treatment, there would have been an environmental disaster, because these inorganic micropollutants are nonbiodegradable, highly toxic, and of carcinogenic effect [11]. In recognition of this growing problem, there has been an increase in the number of environmental regulations introduced by various bodies to protect the quality of surface, ground water and drinking water from pollutants such as cadmium [12]. In Table 1.1, recommended water quality criteria published by EPA (Environmental Protection Agency), for priority toxic pollutants were given [13] and, in Table 1.2, EPA standards for plants discharging 38,000 liters (10,000 gal) or more per calendar day of electroplating process wastewater were tabulated [14].

Increasingly stringent legislation on the decontamination of wastewater is forcing the manufacturing industries to take responsibility for the treatment of their own waste. In the water industry, such legislation is causing an increase in wastewater disposal cost. This increase has made the development of efficient on-site processes for the disposal of the waste effluent [15]. Besides the negative environmental and health effects, heavy metals are non-renewable resources and production of these metals

Table 1.1: EPA Recommended Water Quality Criteria for Priority Toxic Pollutants

	Freshwater		Saltwater		Human Health For Consumption of	
					Water+Organism	Organism only
	MC (ppb)	CC (ppb)	MC (ppb)	CC (ppb)	MC (ppb)	MC (ppb)
As	340	150	69	36	0.018	0.14
Cd	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	0.050	0.051
Ni	470	52	74	8.2	610	4600
Pb	65	2.5	210	8.1	-	-
Zn	120	120	90	81	9100	69000

Table 1.2: Common Metals Facilities Discharging 38000 Liters or More Per Day Discharge Limitations

Pollutant or pollutant property	Maximum for any 1 day (ppm)
Cu	4.5
Ni	4.1
Cr	7.0
Zn	4.2
Pb	0.6
Cd	1.2
Total metals	10.5

for commercial uses is difficult. Therefore recovery of heavy metals as reusable compounds for industrial applications is as crucial as removal of them from waste effluents. Recent developments in separation processes are in the way of establishing cost-effective methods for fractional separation and recovery of heavy metals.

1.2 Wastewater Treatment Alternatives

Various alternative processes have been developed for the removal and recovery of heavy metals from industrial effluents. Adsorption, precipitation, liquid-liquid extraction and ion-exchange are some of the techniques used in the removal and recovery of heavy metals from waste streams [16]. While choosing the suitable operation for the removal and the recovery of metals, characteristics of the wastewater, desired concentration range for the end product and the feasibility of the recovery process should be considered [17].

The conventional method for treatment of metal waste is precipitation [18]. Chelating ligands and/or precipitating agents are used to bind the heavy metals or precipitate them as metal chelates. Many of these ligands are easily obtained and relatively inexpensive but are not specifically designed to bind the targeted heavy metals and may often results in unstable metal ligand precipitates which can decompose and release the metals back into the environment over varying periods of time [19–21] and the sludge obtained is difficult to treat to recover the metals (i.e; sludge dewatering), particularly if it is a multi-metal sludge [22, 23]. The sludge is often disposed of at landfill sites, resulting in loss of useful resources and possible environmental problems at the sites. In order to minimize the sludge treatment, process scheme consisting of an absorbent media coated on the sand surface in a packed column [24] and in fluidized bed [25, 26] to collect heavy metals from synthetic waste water was developed. In this processes the packed column and fluidized sand bed provided a great amount of specific area for heavy metals to be precipitated. Since the heavy metals were coated on the sand surface, there was no need for sludge dewatering.

When lime is used for hydroxide precipitation then, depending on the level of acidity and amount of heavy metals present in the effluent, variable quantities of Ca^{2+} will be introduced into the system and forms a number of secondary precipitates by either direct reaction with the spectator anions to produce an insoluble salt, or by the possible formation of a multicomponent solid phase [27]. Secondary precipitates significantly destabilise the primary heavy metal precipitates by inducing colloid formation, thus making solid-liquid separation a difficult proposition [28]. In another precipitation study with lime it was stated that, hydroxide precipitation with lime may be unsatisfactory for removal of cadmium, due to the high pH requirement for effective treatment. The use of sodium sulphide for cadmium precipitation is said to be feasible [29].

Ligands with multiple bonding sites such as pyridine-thiol was also used for precipitation of heavy metals. By this method , metal ion concentrations of feeds containing 50ppm copper solution , pH of 4.5 and 50ppm cadmium solution , pH of 6, can be reduced to 0.00093 ppm ($>$ 99.99% removal) and 0.06 ppm ($>$ 99.88% removal), respectively [21].

A more sustainable and effective precipitation method was rectified for heavy metal removal and recovery by a process scheme which can achieve selective separation of metals and produce reusable pure metal sludges could be developed. This process scheme was developed by pH sequencing with the optimisation of parameters like ; added doses and kind of precipitating agents, waiting period before removing the precipitate from solution [17]. Cost-effective precipitation schemes may be developed depending on the composition of the waste water and the desired end product, by optimizing operating parameters. For instance from Cd dominated waste water containing Fe, Cu, Ni, Zn and impurities (Co, Mn), Cd was recovered as pure $Cd(OH)_2$ and CdS which are valuable compounds for electroplating and paint industries [17]. Although it is generally used as a stand alone method [30, 31] chemical precipitation may not satisfy the produce end products obeying the environmental regulations but when it is systematized properly, can be very appropriate as a first step of a hybrid separation processes. Precipitation of sparingly soluble metal compounds followed by micro- or ultrafiltration [32], bioaccumulation and microfiltration [33], precipitation followed by polymer enhanced ultrafiltration [34] are among the possibilities as the second step of the hybrid processes.

Solvent extraction is widely utilized in metal recovery operations including; copper recovery using oil soluble extractants [35], Ni, Cu, Mn, Co extraction by extractant di(2-ethylhexyl)phosphoric acid (DEHPA) [36]. In metal recovery operations, the target metal ion is extracted from an aqueous solution (e.g., heap leach solution or effluent from a plating operation) into an organic solvent such as kerosene which contains the active reagent [37–39]. Solvent extraction is reported to be most suitable for removal of solutes that are present in high concentrations; for very dilute solutions the cost of the solvent becomes high as compared to the cost of the recovered material [40].

Another widely reported techniques for removing heavy metals from a solution is adsorption. Much research has been addressed to identify inexpensive and satisfactory adsorption materials [41–45]. Among these, clays show good adsorbent properties both for organic species and for metals because of their large surface areas and negative charges [46–51]. Montmorillonite [52], hematite [53], clinoptilolite [30] and paper mill sludges, those deriving from papermaking processes that use kaolinite [54] as the reagent have also been considered as a possible sorbing matrix. Adsorption studies showed that the sorption process is influenced by the nature of the ionic charge: cations are sorbed much more readily than anions; the affinity series for the cations tested is $Cu(II) > Pb(II) > Cd(II) \approx Ag(I)$ [55]. A similar sequence was found by Reynolds [56] for zeolites and by Weiss and Amstutz [57] for clay minerals. Modified barks [58], apple residues [59], a blast furnace waste material [60], cross-linked carboxymethyl corn starch [61], were the materials also used as an absorbing agents used for heavy metal removal. The adsorption on sorbents is reported to be effective method for the removal of metal ions in low (ppm) concentrations, but for the multicomponent mixtures with high metal concentrations this method may became ineffective [16].

The process of ion-exchange refers to the replacement of toxic heavy metal ions in the solution by the more benign counter ions that balance the surface charge of the solid exchanger, and is an alternative heavy metal removal processes. Synthetic aluminosilicate zeolites [62, 63], Na-Y zeolite [64] and cation-exchanger textiles (CET) carrying carboxylate, sulfonate or phosphate functional groups [65], act as an efficient porous solid exchange media. Lacour [65], studied the removal of cadmium and copper by three different cation exchanger textiles (CET) being a weak acid CET, a strong acid CET and a chelating cation exchanger and observed that, exchangers exhibit higher affinity for divalent cations than for monocovalent cations in infinitely dilute solutions and CET showed better affinity for the H^+ counter-ion than for divalent cations. Na-Y zeolite is reported as effective for removal of trace amounts of metals and zeolite affinity was proved to be decreased by increasing metal concentration. Disadvantages of the ion-exchange method were reported to be, high resin cost, solvent wash-out for impregnated resins and slow rate of operation [66].

Flocculation with hydroxyapatite [67], ammoniacal leaching [68], foam separation [69], biosorption [70] are some of the examples of other alternative heavy metal removal techniques. Among these techniques biosorption is considerably a new technology investigated for toxic metal removal, but contacting large volumes of metal-bearing aqueous solutions with microbial biomass in conventional unit processing operations is not practical, largely because of solid/liquid separation problems [71]. In foam separation technique the separation efficiency mainly depends on ionic strength. Generally efficieny decreases with an increase in ionic strength. Because industrial wastewater is a complex mixture, this drawback is the main reason holding back their wider applications [69].

Although classical treatment techniques have now reached an advanced stage of optimization, the growing development over the last 40 years of membrane separation techniques has made them attractive for the heavy metal removal and recovery from waste streams [72]. The main element of any membrane separation process is the semipermeable membrane. Certain solution components will pass through the membrane forming the permeate, whereas others will be retained by the membrane forming the retentate or concentrate [73]. There are various methods to enable substances to penetrate a membrane. Examples of these methods are the applications of high pressure, the maintenance of a concentration gradient (i.e.,pervaporation, gas separation, dialysis and liquid membranes) or temperature gradient (i.e.,thermoosmosis, membrane distillation) on both sides of the membrane and the introduction of an electric potential. Membrane processes involving an electrical potential difference are electrodialysis and electroosmosis. The nature of these processes differs from that of other processes involving a pressure, temperature or concentration difference as the driving force, since only charged molecules or ions are affected by the electrical field [74].

1.3 Use of Membrane Technology in Wastewater Treatment

Today, membrane technologies have been one of the emerging technologies used in a large number of separation processes. Low energy consumption, ease of upscaling and combination with other separation processes, mild separation conditions and variable membrane properties are the benefits of the membrane processes, however concentration polarisation, fouling and low membrane lifetime can be listed as the disadvantages of these processes [74].

In the development period of membrane technology, firstly liquid membrane processes were used and previously most of the studies for removal of heavy metals has been carried out with liquid membranes [75, 76]. Liquid membrane systems contains a hydrophobic membrane phase which acts as an ion barrier between two aqueous phases. An ion carrier may be dissolved in the membrane. The carrier is a liposoluble molecule that is capable of increasing ion solubility in the membrane, and of providing ion fluxes and transport selectivities because of specific ion-carrier interactions. The aqueous phase, containing ions to be transported is commonly designated as the source phase or feed solution, while the aqueous phase into which ions are transported is called as the receiving phase or stripping solution [77].

Mainly, three types of liquid membranes have been used for the separation and transport of metals from aqueous solutions:

- Bulk liquid membranes: This membrane type consists of a bulk organic phase separating two aqueous phases. In order to establish the movement of the cation from the source phase into organic phase, stable metal-carrier complex should be formed. However, the stability of this complex must be less than that of the metal-anion species in the receiving phase for cation transportation [78].
- Emulsion liquid membranes: This type of membranes are prepared in two steps. Firstly, two immiscible phases, water and oil for example, are mixed and emulsion droplets are formed, which are stabilized by the addition of surfactant. Secondly, the obtained water-oil emulsion is added to a vessel containing an

aqueous phase where a water/oil/water emulsion is now formed, the oil phase being the liquid membrane in this concept [74].

- Supported liquid membranes: Such membranes can easily be prepared by impregnating a hydrophobic porous membrane with a suitable organic solvent. The liquid film is immobilized within the pores of a porous membrane. The porous membrane serves only as a framework or supporting layer for the liquid film [74].

Bulk liquid membranes are quite inefficient as ion transport systems because of low fluxes caused by small interfacial areas and thick membranes. Supported liquid membrane processes (SLM), combine the process of extraction and stripping in a single unit operation. Several different membrane supports have been used to make SLMs. These include PP, PVDF, PTFE, silicones etc. [79–81]. Various studies focused on the separation of lanthanides, actinides and many other metals by the SLM process [82–84]. The emulsion liquid membranes (ELM) have also been studied for the preconcentration and separation of metal ions [85, 86], and it was reported that the stability of the membranes may be a problem for emulsion liquid membranes, since breakdown of the organic films causes loss in extraction efficiency and loss of stripping solutions [66]. The most serious problem of supported liquid membrane operation is due to instability caused by the dissolution of the liquid membrane solution, which is held in the micropores of support membranes by the capillary force, in aqueous source and receiving phases [87].

Special attention was also given to commercially available pressure driven membrane processes for their applications in wastewater treatment. With respect to the membrane pore size and applied pressure parameters used in the process pressure driven membrane filtration can be divided up between micro and ultrafiltration on the one hand and nanofiltration and Reverse Osmosis (RO or hyper filtration) on the other hand.

1.4 Pressure-Driven Membrane Processes

Improvement of membrane pressure-driven technologies makes them a suitable alternative to be used in a large number of industrial activities such as, water treatment, production of paint and coating, biotechnology and many others [88].

Various pressure-driven membrane processes can be used to concentrate or purify a dilute aqueous or non-aqueous solution. The particle or molecular size and chemical properties of the solute determine the structure, especially the pore size, necessary for the membrane employed. There are various processes which can be distinguished related to the particle size of the solute and consequently to membrane structure. These processes are microfiltration, ultrafiltration, nanofiltration and reverse osmosis [74].

As we go from microfiltration through ultrafiltration and nanofiltration to reverse osmosis, the size (or molecular weight) of the particles or molecules separated diminishes and consequently the pore sizes in the membrane must 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. Comparison of the various pressure driven processes is given in Table 1.3 [74].

Among the pressure driven membrane processes, reverse osmosis (RO) was originally developed for the purpose of seawater and brackish water desalination. Today, RO processes can be used for a wide range of applications, most of which are in the purification of water, mainly desalination of brackish and seawater to produce potable water. In these applications, the salt content of brackish water and seawater can be as high as 1000-5000 ppm and 35000 ppm, respectively. Production of ultrapure water for semiconductor industry, the concentration of fruit juice, sugar and coffee in food industry and reclamation of process waters and wastewaters are examples of the other RO applications [74]. Separation principle in RO can be explained by solution-diffusion model, where solvent and solute dissolve and diffuse. During diffusion, in order to overcome molecular friction between the particles in the permeate stream and membrane polymer, large operating pressures should be applied [89].

Table 1.3: Comparison of Various Pressure Driven Membrane Processes

Microfiltration	**Ultrafiltration**	**Nanofiltration Reverse Osmosis**
Separation of particles	Separation of macromolecules	Separation of low MW solutes
Osmotic pressure negligible	Osmotic pressure negligible	Osmotic pressure high($1-25$ bar)
Applied pressure low ($<$ 2 bar)	Applied pressure low ($\approx$1-10 bar)	Applied pressure high ($\approx$10-60 bar)
Symmetric structure Asymmetric structure	Asymmetric structure	Asymmetric structure
Thickness of separating layer Symmetric $10-150\mu m$ Asymmetric $1\mu m$	Thickness of separating layer $0.1-1.0\mu m$	Thickness of separating layer $0.1-1.0\mu m$
Separation based on particle size	Separation based on particle size	Separation based on differences in solubility and diffusivity

Nanofiltration (NF) falls between UF and RO; its separation characteristics are based on sieve effect, but most of commercial NF membranes are charged. So, the rejection of ions by NF membranes is the consequence of the combination of electrostatic and steric interactions associated with charge shielding, Donnan exclusion and ion hytration [90–92]. These interactions depend on the characteristics of the solution to be treated and the membrane itself. NF is mainly used in water softening, removal of trihalomethanes and natural organic matter, retention of dyes and metals [93].

Microfiltration (MF) mainly used in food and pharmaceutical industries for sterilisation and clarification, for the removal of particles for ultrapure water production in semiconductor industry and for cell harvesting in biotechnology [74]. In MF the separation is achieved by sieving mechanism [94]. As the size of the particles retained by MF are larger than the sizes of solutes retained by NF or RO, the osmotic pressure for MF process is negligible, and required transmembrane pressure is relatively small as compared to other pressure driven membrane processes.

Ultrafiltration (UF) was initially developed for the treatment of wastewaters and sewage, however today it is also being used extensively in the food, pharmaceutical, biotechnology(enzyme recovery, membrane bioreactors) and electrocoating (automobile electrocoat paint) industries. A recent survey cited over 100 000 m^2 of installed membrane capacity in the dairy industry (sugar refining, vegetable oils, corn, fruit juices, wine and beer, fluid milk, cheese and whey) alone [95]. It is also used for kaolin dewatering, for fermentation broth clarification, antibiotic recovery [96]. UF needs lower transmembrane pressure for operation as compared to that of RO and typical permeate fluxes in UF are lower than those of MF.

The performance of the ultrafiltration process is evaluated with two main criteria, which are the retention of the target component and permeate flux.

Retention can be expressed as;

$$R = 1 - \frac{C_P}{C_F} \tag{1.1}$$

where C_P is the solute concentration in the permeate and C_F is the solute concentration in the feed stream.

Permeate flux can be defined as:

$$PermeateFlux = \frac{PermeateFlowRate}{EffectiveMembraneArea} \tag{1.2}$$

For the filtration of multicomponent mixtures, the selectivity of a membrane towards a mixture is generally expressed by one of the two parameters; the retention or the separation factor.

Membrane selectivity towards gas mixtures and mixtures is usually expressed in terms of a separation factor α. For a mixture consisting of components A and B the selectivity factor $\alpha_{A/B}$ is given by:

$$\alpha_{A/B} = \frac{y_A/y_B}{x_A/x_B} \tag{1.3}$$

where y_A and y_B are the concentrations of components A and B in the permeate and x_A and x_B are the concentrations of components A and B in the feed stream.

Membrane selectivity towards liquid mixtures (S) containing binary solute species is expressed as:

$$S_{A/B} = \frac{C_{pB}/C_{fB}}{C_{pA}/C_{fA}} = \frac{1-R_B}{1-R_A} \tag{1.4}$$

where C_{pA} and C_{pB} are permeate and C_{fA} and C_{fB} are feed concentrations. R_A is the retention of component A, R_B is the retention of component B in the mixture.

In pressure driven membrane processes, the difference between the pressures of the feed side and the permeate side of the membrane is the driving force of the separation process. Higher pressure gradients result in higher permeate fluxes, but it should be taken into account that when polymer containing solutions are ultrafiltered, deformation of polymeric molecules may occur due to high fluxes which results in a passage of macromolecules through the pore.

The retention of a component by the membrane depends on many parameters including solute type, solution composition, pH, temperature, ionic strength, membrane material, pore size, hydrodynamics, etc. In many cases, however, the size of a dissolved component is the crucial factor for retention [73].

If the dimensions of target component and non-target component differ significantly, then a good separation of target component from the solution containing non-target component should be expected. 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 retained by the membrane (reverse osmosis) or will pass through it (diafiltration, ultrafiltration, microfiltration).

Because of the size of the ions, as hydrated ions or as low molecular weight complexes, reverse osmosis is the only technology which could allow a direct separation of heavy metal ions, but from an economical point of view, this method suffers from the fact that high fluxes of permeate need high transmembrane pressure ($> 690 kPa$), which results in high energy costs [97]. Reverse osmosis also is not suited for achieving selective separation of metal ions since the size difference between the metal ions were 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 [98].

In order improve the separation, with high permeate fluxes, low pressure and low energy costs with high rejection coefficients, complexation and ultrafiltration based processes have been developed. In complexation enhanced ultrafiltration, in order to improve separation, the target component can be bound to macromolecules, thus enlarging the molecular dimensions of one of the components to be separated.

1.5 Complexation-Enhanced Ultrafiltration Processes

Ultrafiltration allows relatively high fluxes combined with low operating pressures, but the typical molecular weight cut-off of usual membranes is too high, as compared to the size of metallic ions; the lowest molecular weight substance which can be separated from a liquid medium by ultrafiltration is approximately 500 Da [99], as a consequence, a poor retention of ions is achieved. In order to improve separation, the metallic ions can be bound to macroligands, thus enlarging the molecular dimensions of the components to be separated. This constitutes the basis of complexation enhanced ultrafiltration (CEUF) in which, metal complex and the complexing agent can be retained by the membrane while water and non-complexed ions pass through the membrane. 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 [100], groundwater and seawaters [101] and separation of radionuclides [102]. CEUF can be classified according to the complexation agent used [103];

- Micellar Enhanced Ultrafiltration (MEUF)

  In MEUF, the advantage of a surfactant's ability to associate with itself and form ”micelles” above a certain concentration known as critical micelle concentration (CMC) is used. Surfactants are emphiphiles;i.e, they contain a hydrophobic tail, which is generally a hydrocarbon chain, while the hydrophilic head consists of anionic, cationic or nonionic groups [104–109]. The separation of the micellar pseudophase from the purified continuous aqueous phase can be achieved by ultrafiltration using membranes with pore diameters smaller than the size of the micelles. The surfactant forms micelles which are spherical aggregates containing 50-150 surfactant molecules [110]. The advantage of using micelles may be found in the large variety of commercially available surfactants used in the process. The hydrophobic core of micelles, owing to its hydrocarbon-like structure, may solubilize lipophilic substances such as hydrophobic extractants [111–113]. This offers a way of removing metal ions which shows strong similarity with solvent extraction [114]. In MEUF, ions with the same charge are removed with approximately equal rejection [108] since binding of the cations to oppositely charged micelle surface is primarily electrostatic in nature. To enhance selectivity in MEUF, together with the surfactant an amphiphilic ligand was added to the contaminated solution under conditions where most of the surfactant is present as micelles. The ligand has a high degree of solubilization in the micelles and a tendency to selectively complex the target metal ion [115, 116].

- Colloid Enhanced Ultrafiltration (CoEUF)

  In CEUF, colloids of metal hydroxides, especially iron and aluminium hydroxides were used as a complexing agent to enlarge the target metal molecular size [117]. Because of low selectivity and pH limitations this technique is not used widely.

- Polymer Enhanced Ultrafiltration (PEUF)

  In PEUF, water-soluble polymers are used as a complexing agent to bind metals to form macromolecular complexes. In the polymer binding membrane assisted separation processes, the membrane is just a barrier that has to retain everything bound to polymer and allow permeation of all unbound components [73]. Thus, selective and efficient separation of ions can be achieved. In addition to the removal of heavy metals from aqueous solutions, it is possible to recover metals and polymer by PEUF in such a way that: linking of metal ions with polymer ligands is a reversible process so it is possible to regenerate the retentate in order to recover the metal and complexing agent by changing the equilibrium and introducing a successive ultrafiltration stage [118]. Possibility of the recovery of the metals and regeneration of the polymeric agents is the important features making PEUF a preferable process.

1.6 Polymer Enhanced Ultrafiltration (PEUF) Processes

The majority of the applications of polymer enhanced ultrafiltration are related to the removal and recovery of heavy metals from liquid waste effluents. It was reported that metals, such as copper, nickel, lead, chromium, mercury and arsenic, can be selectively removed from multicomponent solutions of different origins [119–121]. It is also used to remove components from natural waters, groundwater [122] and seawater [123].

The separation process will be succesfull if the polymer used has high affinity toward target component, inactivity towards nontarget component, high molecular mass, 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 chemical groups present as a moiety. Many of these polymers were designed for different industrial applications, but only some functional soluble polymers were found to be suitable for PEUF processes [124].

Most of the PEUF studies employ batch [125, 126] or semi-continuous processes [127], but the feasibility of a continuous PEUF process applied to water softening [128] and heavy metal separation [129–131] has also been studied. In the previous studies of our research group continuous mode polymer enhanced ultrafiltration processes were applied for boron [132, 133], mercury and cadmium [98, 103] removal from aqueous solutions.

1.7 Aim and Scope of the Study

The performance of the ultrafiltration process is evaluated with two main criteria, which are the amount of retention of the target component by the membrane and permeate flux. Operational parameters such as pH, temperature, feed concentration, membrane type and configuration affect the degree of retention and permeate flux and hence the performance of the process.

In polymer enhanced ultrafiltration processes in addition to these conventional operational parameters, factors directly affecting polymer-metal binding characteristics can be very important for the process performance [134].

Aim of this study is to investigate the effect of ionic strength and presence of counter anions on polymer-metal complexation together with other operational parameters in order to improve heavy metal removal and recovery from single, binary and ternary metal mixtures by polymer enhanced ultrafiltration.

As a first step of the study, performance of two different membrane materials and configurations: polysulfonic flat sheet and cellulosic spiral wound membranes were compared in order to select the suitable membrane material and configuration for effective heavy metal removal.

Cadmium, zinc and nickel were selected as target metals for this study because these three metals are widely used in industrial applications, even though their release into the environment can cause serious ecological and health problems. Polyethylenimine (PEI) was used as a complexation agent.

In polymer enhanced ultrafiltration, the separation process is supposed to be successful if the polymer used has high molecular mass, possibility of regeneration, chemical and mechanical stability and has high affinity towards target metals and inactivity towards non-target components present in the solution. Proven ability of polyethylenimine (PEI) to strongly bind heavy metals and to stay inactive towards alkali earth metals make it prefferred polymer to be used in this study.

This research can be divided into two experimental parts: In the first part, ultrafiltration experiments were performed in order to observe the retention behaviours of Cd^{2+}, Zn^{2+} and Ni^{2+} in single, binary and ternary mixtures of these metals at different pH and loading (amount of metal/amount of PEI) values and impact of high ionic strength conditions on the retention profiles of Cd^{2+}, Zn^{2+} and Ni^{2+} were investigated.

In the second part of the experimental study, the characteristics of association between highly branced PEI and metal ions and effect of salt concentration on this association were investigated by performing dynamic and static light scattering measurements. Radius of gyration, hydrodynamic radius and second order virial coefficient of PEI macromolecule and metal-PEI complexes were estimated for different experimental conditions.

The binding (complexation) constants of various metal-polymer complexes and the corresponding average coordination number for such polymeric solutions have been extensively evaluated. They were usually determined either from potentiometric or pH titration curves by Bjerrum's method [135–137], or by a spectroscopic method through the molar absorption coefficient of the bound metals and the peak position in the spectra [138–140], or by the equilibrium dialysis method using an ion-exchange membrane [140]. Recently ultrafiltration is used as a preferrable alternative method to estimate the binding constants of metals with various polyelectrolytes and polychelatogens. Besides the experimental parts, this study also covers the development of a theoretical model that best fits the experimental data for the estimation of binding constants of Cd^{2+}, Zn^{2+} and Ni^{2+} with PEI at different pH values and with varying amounts of salt.

CHAPTER 2

LITERATURE SURVEY

2.1 Polymeric Ligands Used in PEUF Studies

There are many studies related with the removal of heavy metals from aqueous solutions by means of PEUF and, most of them deal with selection and synthesis of a special ligand for target metals [118, 141–143]. The choice of polymers and macroligands remains important for developing this technology and it was stated that the separation process will be successful if the polymer used has high affinity toward target component and inactivity toward non-target components, high molecular mass, possibility of regeneration, chemical and mechanical stability and low cost [144].

The molecular mass of the polymeric ligands should be high enough to ensure efficient separation of the non-target components and complete retention according to the molecular exclusion limit of the membrane. However, if the molecular mass is too high, this results in a high viscosity of the solution when such a polymer is added to it, as macromolecules reduce their size in concentrated polymer solutions [145]. This size reduction along with concentration polarization result in an increased polymer permeation through the membrane. This will reduce the permeate flux and increase the process cost. Frequently, polymers with a molecular mass in the range between 30 000 and 100 000 g/mol are employed when the ultrafiltration membranes having a molecular weight cut-off 10 000 g/mol are used [73].

Mechanical and chemical stability of the polymers are other important parameters that should be considered while selecting a suitable polymer for operation because, feed solutions containing polymer are pumped through the ultrafiltration unit by different pumps (i.e., centrifugal, diaphragm pumps), if polymer has low mechanical stability degradation may occur due to the mechanical shearing caused by the pump [123].

Chemical instability may also be a problem in such a way that, degradation of soluble polymer may occur by hydrolysis effects [73].

The great majority of polymers or polymer-based materials are water insoluble and in many cases they are required to be water resistant (i.e: rubber, silk, cotton, paper, wood). On the other hand, there is a relatively small but important group of polymers that are water-soluble, where their solubility is an important feature of their applications in polymer enhanced ultrafilration [146].

Water-soluble polymers can be mainly divided into three groups:

- Natural water soluble polymers include many important examples of the so-called biopolymers. Well known example of biopolymers mostly used in PEUF applications is chitosan [131, 141, 147–149].
- Semisynthetic water soluble polymers: these are natural polymers which have been modified to make them water soluble, in particular cellulose ethers (i.e: methyl-,hydroxyethyl-, hydroxypropyl-, carboxymethyl-). Amoung these polymers carboxyl methyl cellulose was used in some of the PEUF studies for metal removal [129, 150, 151].
- Synthetic water soluble polymers

Water soluble synthetic polymers may be non-ionic, or they may be polyelectrolytes, possessing many ionizable groups that give rise to anionic or cationic character in aqueous solution or they may be polychelatogens, bearing functional groups with the ability to form coordination bonds. Polychelatogens are preferable polymeric ligands in heavy metal removal from aqueous solutions, because of their affinity towards transition metals and inactivity towards alkali and alkali earth metals [73].

Examples of common synthetic non-ionic water-soluble polymers are poly (acrylamide), poly (oxyethylene), poly(vinylalcohol) and poly(vinyl pyrrolidone). Polyvinyl alcohol can be used for removal of anions such as Br [152] and boron [132] and also cations [153, 154] from aqueous solutions. Poly(vinyl pyrrolidone) was previously used for Pb^{2+} [155], Zr^{4+}, Pr^{3+}, Th^{3+} [156] removal from aqueous solutions and also iodine (I) removal from highly mineralized groundwater [157].

Common synthetic anionic polyelectrolytes are poly (phosphoric acid), poly (styrene sulphonic acid) and poly (acrylic acid) which was reported to be effectively used for Pb^{2+} removal [158] and selective separation of metal ions from groundwater [159] by membrane filtration techniques.

Poly (vinylamine), poly (dimethyldiallylammonium chloride) [160], poly (4-vinyl pyridine), poly (allylamine) [161] and poly (ethylenimine) are the examples of common synthetic cationic polymers [162]. In the previous studies, poly (allylamine) was used for uranium recovery from sea water [163], poly (vinylamine) was used for Cu^{2+} [164] and Cd^{2+}, Ni^{2+} [165] removal from single component synthetic solutions.

Among the synthetic water-soluble polymers, poly(ethylenimine) has high binding ability, because of having unshared electron pair on the N atom which can form donor bonds with coordination unsaturated transition metals [160]. Poly(ethylenimine) (PEI) is a basic polymer synthesized by acid-catalyzed polymerization of ethyleneimine (aziridine) and is known to exist as a linear structure (LPEI) [166] or a branched structure (BPEI). Under normal conditions for synthesis, the polymer has a high degree of branching at the amine nitrogens [167]. LPEI has only secondary amino groups in the main chain [168] and therefore it has chelating sites only in the main chain. Branchy poly(ethylenimine) (PEI) contains ethylamine as the repeating unit. The tertiary amino nitrogens are the branching points (Fig. 2.1) [169]. A typical PEI of MW 60000 contains ca. 350 primary amines, ca. 700 secondary amines, and ca. 350 tertiary amines [170] and it has chelating sites both in the main chain and side chains.

Having a branchy structure, high solubility in water, and ready modification of its amines by acylation, alkylation, or imine formation polyethleneimine (PEI) has found a number of interesting applications in biotechnology, e.g., in facilitating protein recovery [171] and biocatalyst immobilization [172]. It has also been shown to

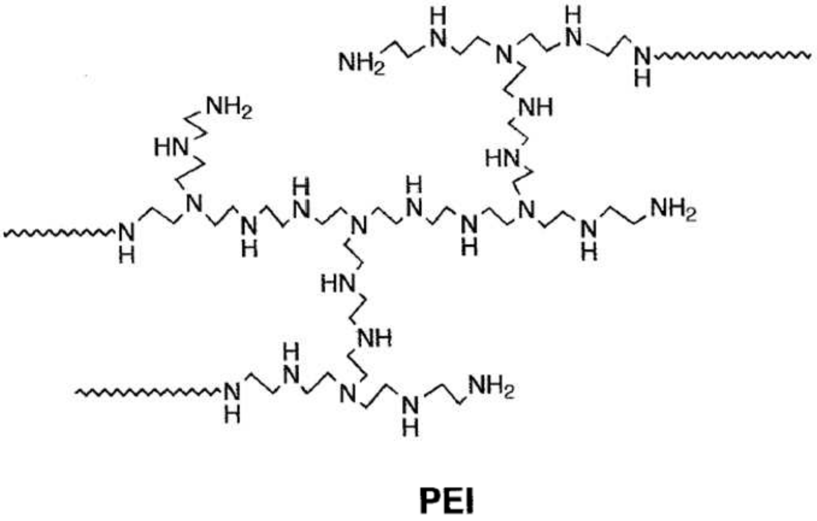


Figure 2.1: Structure of Branched PEI

have a stabilizing effect on several enzymes in solution [173–177] as well as in biosensors [178]. Because of high binding ability towards the ions of transition metals, PEI was widely used in previous studies for the removal of transition metal ions from synthetic wastewaters via PEUF. In Table 2.1, examples of heavy metal removal studies by PEUF and target metals in these studies were summarized.

Table 2.1: Examples of PEUF Studies with PEI

Polymer	Target Metal(s)	Reference
PEI	Cu(II), Pb(II), Cd(II), Hg(II), Ag(I)	[155]
PEI	Hg(II)	[179]
PEI	Cu(II), Co(II), Ni(II), Zn(II)	[180]
PEI	Cu(II), Ni(II), Co(II), Pb(II), Cd(II), Zn(II)	[181]
PEI	Ni(II)	[182]
PEI	Cu(II)	[183]
PEI	Cr(III)	[184]
PEI	Cu(II), Ni(II), Zn(II), and Cd(II)	[185]
PEI	Cu(II), Ni(II), Zn(II), and Cd(II)	[186]
PEI	Cu(II), Ni(II)	[187]
PEI	Hg(II), Cd(II)	[134]
PEI	Hg(II)	[188]

Some of the sample studies presented in Table 2.1, can be summarized as follows; In the study of Osipova [155], the stability of the metal complexes with PEI was found to be in the order $Hg(II) > Cu(II) > Ag(I) > Cd(II) > Pb(II)$ for $pH < 5$. Effect of pH and ionic strength on the removal efficiency of Hg(II) was examined in the studies of Uludag [188] and Zambrano [179] respectively. It was found that, PEI-Hg(II) complexation was favourable for $pH > 4$, and extent of binding decreases for $pH < 4$ because of the protonation of PEI molecules [188]. Chloride ion has a strong effect on mercury retention rate for pH lower than 5. The retention of mercury decreases as the chloride ion concentration increases. However for pH higher than 6 the chloride ions do not affect the complexation of mercury by the PEI. The retention rate reaches a plateau ($R \geq 95\%$) and the retention values are the same that observed without chloride ions [179]. Juang and Chen [180], proposed a chemical equilibrium model to estimate the equilibrium constants for the binding of poly(ethylenimine) (PEI) with the ions of Cu, Co, Ni, Zn in the aqueous sulfate solutions by batch ultrafiltration (UF) in the pH range of 3.0-3.8. According to the estimated binding constants, binding order of the metals was found to be; $Cu(II) > Ni(II) > Zn(II) > Co(II)$. In the study of Rivas [181], it was reported that PEI showed the highest metal-retention values, particularly at higher pHs, towards Cu(II), Ni(II), Co(II), Cd(II), Zn(II) whereas Pb(II) was only poorly retained. The affinity for all the metal ions, except Pb(II), increased significantly at pH 5. Molinari [183] compared the affinity of several chelating agents towards Cu ions and in this study it was reported that, amoung the chelating agents like polyetilenimine(PEI), polyacrylic acid (PAA), polyacrilic acid sodium salt (PAASS), and poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) (PDEHED), PEI showed the highest Cu retention values.

2.2 Batch and Continuous Mode PEUF Studies

In most of the PEUF studies, batch systems are employed [125,126]. In these studies, the binding properties were documented in retention profiles, which are plots of the retention (R) versus the filtration factor (Z) [189]. Z is defined as the ratio of the volume of the filtrate and the volume of the cell solution. Since the concentration of feed solution can not be kept constant throughout the batch processes, as Z increases the retention value of the metals are reported to decrease or increase due to the changes in feed concentration therefore it is difficult to observe the effects of concentration and loading on rejection and flux.

One step forward in the processing mode of operation is the operation and modelization of semi-continuous processes in which a permeate stream goes out from a system comprising a reactor and membrane module, and a feed stream of equal flow rate was added from a reservoir to this system in order to maintain constant volume [127].

Continuous mode of ultrafiltration was reported to be preferrable for large scale processes [190]. In one of the previous studies 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) [128] and it was shown that that the proposed system can continuously removes Ca^2 from water in a satisfactory way.

In the study of Schlichter et.al. [129], continuous hybrid ultrafiltration process consisting of consequitive separation and regeneration units were used for the separation of Cu^{2+}, Co^{2+} and Pb^{2+} and at the same time for the regeneration of the bonding agent (i.e., carboxymethyl cellulose).

Continuous mode ultrafiltration was also applied for Cu^{2+} and Zn^{2+} removal by zeolite [130] and to measure the extent of heavy-metal complexation by dissolved organic-matter [191].

Sabate [131], analyzed extensively the running of a continuous PEUF applied to the separation of heavy metals that join a chitosan by complexation binding. It was reported that, by the simulations based on the process, the way that the process works may be understood and the conditions required to achieve a given treated water composition, saving reagents and energy can be determined. In another study, design and construction of a modular pilot plant operating in continuous mode, was made for the treatment of oil-containing wastewaters [192].

In the previous studies of our research group continuous mode polymer enhanced ultrafiltration processes were applied for boron [132,133], mercury and cadmium [98, 103] removal from aqueous solutions and effects of operational parameters like metal/polymer ratio and pH on the performance of the process can be observed by courtesy of continuous mode operation.

Uludag [188], studied polymer enhanced ultrafiltration in continuous mode in order to separate Hg^{2+} by complexing with polyethyleneimine, and was able to observe the effect of loading on retention which is not possible to do with batch ultrafiltration. In this study it has been observed that, the retention rate reaches a plateau ($R \geq 98\%$) up to the critical loading. When loading exceeds 1, sharp decrease in retention profiles was observed. It was also reported that, retention is dependent on the ratio of the mercury and polymer rather than on their amounts. This means that concentration level of Hg^{2+} does not pose a limit to the application of the process.

2.3 Effects of Operational Parameters on Performance of PEUF Process

Rejection of polyelectrolytes, polychetalogens and metal complexes of these macroligands are pH dependent, therefore effect of pH, on the binding ability of polymers and as a consequence on the performance of the PEUF operation was the subject of various studies in literature [141, 179, 183, 185, 193, 194]. It was reported that, polyethyleneimine (PEI) has a high cationic charge density owing to the protonation of amine groups as a function of pH. When PEI takes part in the complexation with metal ions the relationship between pH and charge density of PEI plays an important role. Complexation efficieny rises, as amine groups are deprotonated. Stable complexes of heavy metals with PEI are formed at a pH interval from 5 up to 7.5 [144]. In the study of Rivas and Villoslada, the retention capacities of the $Poly[acrylamide-co-1-(2-hydroxyethyl)aziridine]$ and $Poly[1-(2-hydroxyethyl)aziridine]$ with Cu(II), Cd(II), Co(II), Cr(III), Ni(II), Pb(II), Zn(II), and Fe(II) were studied at different pH by PEUF technique and the results are compared with those of branched polyethylenimine. It is concluded that, PEI has high complexing capacity for Cu, Cd, Co, Ni and Zn as compared to other two chelating agents [195]. In another study, complexation of Cd(II), Co(II), Hg(II), Pb(II) and Ni(II) with polyethyleneimine were studied, and metal ion bonding mechanisms is elucidated by using two-phase potentiometry. It is concluded that Ni(II) is somewhat better complexed by PEI than Co(II) and Cd(II), Pb(II) would be best removed at high pH by ultrafiltration and pH dependence of Hg(II) removal would not be so critical as compared to that of Cd(II) [196]. This observations are in complete agreement with the polymer enhanced ultrafiltration work performed by Muslehiddinoglu [134].

Ionic strength is another important parameter in polymer enhanced ultrafiltration, which can be expressed by the following formula [197]:

$$\text{Ionicstrength} = \mu = \frac{1}{2}\left([A]\,Z_A^2 + [B]\,Z_B^2 + [C]\,Z_C^2 + \ldots\right)$$

where [A], [B], [C],... represent the species molar concentrations of ions A, B, C,... and Z_A, Z_B, Z_C... are their charges.

It was reported that the amount of metal ions free in solution and that of bound to polymer and the retention of the metal ions are strongly dependent on the ionic strength [198]. Degree of dependency of the forces that direct the metal-polymer interactions on ionic strength was related with the characteristics of the bonds. Bonds may be electrostatic or coordinating bonds. In this sense, chelating polymers may be differentiated from polyelectrolytes. Polyelectrolytes-metal interactions are generally dominated by electrostatics whereas polychetalogens formed coordinative bonds with metal ions [196, 199] which are significantly more selective than ionic interactions [200].

It is known that the interactions which are dominated by electrostatics are more sensitive to the ionic strength as compared to the coordinative bonds [201] but it was also reported that neutral salts like sodium chloride or sodium nitrate influence the complexation of metal-polychetalogen complexation [202].

Some of the examples of studies cited in literature dealing with the effects of ionic strength on the complexation mechanism of the components present in aqueous solutions are; biosorption of metals by marine algae [203], retention of Ni on illite [204], adsorption of metal ions on activated carbons [205], metal-ligand interactions in the Co^{2+}-citrate and Ni^{2+}-citrate systems [206]. 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. For instance in case of metal adsorption on activated carbons, when the interaction between the metal ions and the carbon surface were repulsive, a progresive increase of the ionic strength also brought about a progresive increase in the adsorption of metal ions. Thus, the electrostatic interactions, either attractive or repulsive, can be reduced by increasing the ionic strength of the solution [205]. In the case of copper, cobalt and nickel ion absorption on solid polyamine-polyurea resins, experimental trials show a general increase in the absorption of the metal ions by adding NaCl to the analyte solutions, this enhancement was predicted to be caused by an ionic strength effect which would cause an increase in the metal-amine formation constant on the resin or may be due to the promotion of the absorption of metal-chloride ion pairs which are more readily formed under excess chloride ion conditions [207].

Effect of ionic strength on the retention of ions in nanofiltration was studied using positively charged membranes by nanofiltration. Mechanism of retention of coions with positively-charged NF membranes was studied by varying salt concentration and it was found that, retention of cations(Na^+, tylosin and tetracycline) except H_3O^+ decreased with the increase in ionic strength [208]. Smidova et.al [209] studied the influence of ionic strength of dispersed systems on microfiltration and showed that the added salt (Na_3PO_4) resulted in the instability of the dispersion and reduction of permeate flux.

It is reported that the ionic strength of aqueous effluents can greatly influence the effectiveness of the PEUF process [101]. In studies with polyethylene imine or polyacrylic acid as the complexing polymer, loss of metal retention was observed when the salt concentration and thus the ionic strength was increased. In the case of polyethyleneimine, polymer precipitation can also occur in the presence of sulfate [210]. Rether et.al. [211], investigated the effect of sodium nitrate on the complexation of copper and nickel ions by the benzoylthiourea modified PAMAM dendrimer. The nitrate salt was used in a 70-fold molar excess in relation to the metal concentration in the aqueous solutions. It was observed that, the complexation of copper and nickel ions by BTUPAMAM is not significantly influenced by the added sodium nitrate salt in the studied pH range ($3 < pH < 8$). Same effect was also observed for complexation of Cu^{2+}, Zn^{2+}, Pb^{2+} and Ni^{2+} with carboxyl methyl cellulose (CMC); the ionic strength practically does not influence metal retention [150].

In the study of Rivas and Villoslada [212], semiemprical relations between the ionic strength and the experimental retention profiles were developed in order to predict the retention values of metallic cations that should be obtained in experiments where the initial ionic stregth is changing. Predicted retention values were compared with the mathematical results with those of a set of experiments performed with poly(sodium 4-styrenesulfonate)(PSS) in the presence of Cd^{2+} and variable amounts of Na^{+} in excess, and poly(vinyl alcohol)(PVA) in the presence of Pb^{2+} and variable amounts of Na^{+} in excess. PSS was chosen as a representative of a polyelectrolyte where the sulfonate groups produce typical electrostatic interactions with Cd^{2+}, and PVA was selected as a representative of a coordination-predominant polymer. It was reported that, for both PVA and PSS, the increase in ionic strength causes an increase in the dissociation constants of polymers and hence decrease in the retention ability of the polymer.

2.4 PEUF Studies with Multicomponent Metal Mixtures

In a limited number of studies effective removal and fractional separation of heavy metals from binary or multicomponent mixtures and/or real industrial effluents using PEUF have been reported.

It was shown that, Pb can be fractionated from solutions containing Cu-Pb binary mixture by the hybrid process comprising of bisorption onto Sphaerotilus natans cells confined by a ultrafiltration [213] and, Cu^{2+} can be fractionated from the multicomponent solution containing Cu, Mn, Fe and Pb by PEUF, when carboxyl methyl cellulose (CMC) was used as a water-soluble metal-binding polymer [150]. Other selected examples of the fractional separation studies by PEUF was summarized in Table 2.2.

Table 2.2: Fractional Separation of Metals from Multicomponent Metal Mixtures

Metal	Solution	Polymer	pH	Ref.
Au^{3+}	aq. soln. of Co^{2+}, Cu^{2+}, Ni^{2+}, Au^{3+} and Pt^{4+}	HPVP		[144]
Cu^{2+}	aq. soln. of Cu^{2+}, Cd^{2+}	MS	7.5	[121]
Cu^{2+}	aq. soln. of Cu^{2+}, Ni^{2+}, Co^{2+} and UO^{2+}	PEI	5.7	[214]
Zn^{2+}	aq. soln. of Zn^{2+}, UO_2^{2+}, Mg^{2+} Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}	PPEI	4	[214]
Pu^{4+}	aq. soln. of Pu^{4+}, Am^{3+}, Np^{5+}	OPVP	3.7	[156]

Muslehiddinoglu and Uludag et.al, studied the effects of pH and loading (metal/polymer ratio) for selective removal of Cd^{2+} and Hg^{2+} from aqueous streams by using PEI as complexation agent and in this study it was proven that the retention of cadmium is more sensitive to the pH than mercury. This enables selective separation of two metals at selected pH and loading (metal/polymer ratio) values [134]. In another study fractional separation of Ni(II) and Zn(II) was achieved by using sodium polyacrylate as a complexing agent [118]. But same success in fractional separation of metals from multicomponent aqueous solutions can not be achieved by poly(acrylic acid), because of the poor selectivity of the macroligand towards the target components [215, 216].

Application of the complexation enhanced ultrafiltration process was studied for the removal of Cu, Ni, Zn ions from galvanic wastewater by using InstarAS(which contains polyacrylic acid) as a complexing agent. It is stated that, application of the optimum amount of metal and suitable pH enabled the process to achieve retention values between 85-97% [100]. This technique has also been applied to the recuperation of metals, and data exists on the recuperation of Cu from residual streams using carboxymethyl cellulose [99], Cr(VI) from underground water using hexadecylpyridine [217], Cd from industrial waste streams by Na-dimethyl dithiocarbamate [72] and for selective concentration of scandium from brackish waters [218].

Hybrid precipitation and polymer enhanced ultrafiltration process was applied for fractional separation of heavy metals from real electroplating waste effluent. Samples contain large amount of Cd, Ni, Fe, Zn, Cu and trace amounts of Co and Mn. Metal complexes were decomposed by nitricacid, and after acid treatment large amount of Cd was recovered as $Cd(OH)_2$ by the addition of NaOH. At the end of the precipitation steps, concentrations of metals in the samples were reduced down to suitable limits for PEUF. By using PEI as a complexing agent metals were removed effectively [219].

2.5 Polymer-Metal Binding

Polymers may be roughly classified as polyelectrolytes and polychelatogens. Polyelectolytes have the ability to exchange metal ions whereas polychelatogens have the ability to form chelation complexes with metals [220, 221].

A chelating agent, or chelant, contains two or more electron donor atoms that can form coordinate bonds to a single metal atom. After the first such coordinate bond, each successive donor atom that binds creates a ring containing the metal atom. This cyclic structure is called a chelation complex or chelate, the name deriving from the Greek word chela for the great claw of the lobster [222].

The most investigated functional groups present in polychelatogens are amines, carboxylic acids, amides, alcohols, aminoacids, pyridines, thioureas, iminos, etc. Among them, polymers containing amino groups have been extensively studied in ultrafiltration, particularly functional polyethyleneimine. The most used polyelectrolytes include those with carboxylic acid, phosphoric acid, sulfonic acid in their structure [223].

The polyelectrolyte/metal-ion interaction can be only electrostatic in nature or can include the formation of coordinative bonds whereas polychelatogens/metal-ion interactions mainly include coordinative bonds. Coordinative bonds are significantly more selective than ionic interactions. Apart from the potential ability of some polyelectrolytes to form coordinating bonds with metal ions, all polyelectrolytes undergo electrostatic interactions with other ions. In polyelectrolyte theory, when long-range electrostatic interactions are dominant, polyelectrolytes are assumed to bind counterions nonspecifically and they are considered to move freely around the axis of the polymer chain [200, 224, 225]. Thus, the electrostatic water-soluble polymer metal ion interaction may be regarded as an adsorption phenomenon of counterions on the surface of the polymer domain.

Polymers containing sulfonic acid moieties, such as PVSA (poly(vinyl sulfonic acid)), do not act as ligands, but the functional-group/metal-ion interaction is predominantly of the electrostatic type [181] whereas the resins containing amino and imino groups form stable chelates with copper,nickel and other transition metals [226]. Binding of heavy metal ions onto PEI is an example [227]. In general, solid resins and water soluble polymers that have similar functional groups should demonstrate similar chemical properties, i.e., similar ability to bind certain ions. This analogy in the properties can be used in order to predict the behaviour of an unknown hydrophilic polymer if the properties of a similar resin are known [73].

Weakly basic exchange resins possess primary, secondary and/or tertiary amino groups as functional groups. At neutral pH the nitrogen atoms of these groups are not protonated. Therefore, they have a free electron pair and can act as LEWIS bases. Many heavy metals have only six electrons in their outer electron shell and, therefore, are LEWIS acids. Due to the interactions between LEWIS bases and acids the heavy metals are adsorbed. However, because this is not an exchange of ions but a mere adsorption of cations, a parallel co-adsorption of equivalent amounts of anions has to occur to maintain electroneutrality in the liquid and resin phases. As a total, the process develops as the adsorption of heavy metal salts. Using cadmium and sulfate as an example, the service cycle can be written as:

$$\overline{R-NH_2}+Cd^{2+}+SO_4^{2-} \rightleftharpoons \overline{R-NH_2(Cd^{2+}.SO_4^{2-})}$$

(Overbarred symbols refer to the resin phase). Corresponding to the coordination properties of both the resin and the metal, one ion can be linked to one, two or even more nitrogen atoms [228]. Alkaline earth ions do not have comparable LEWIS acid properties. As a consequence, they are excluded from the adsorption and an extreme selectivity for heavy metal salts is observed. Among different heavy metals there is a series of selectivity corresponding to $Hg^{2+} > Cu^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+}$ as reported by Kawamura and Holl [229, 230]. The nitrogen atoms of the functional groups strongly prefer the uptake of strong acids over that of heavy metal salts. With decreasing pH, therefore, the uptake of acids increases and the metal salts are desorbed [231].

Contrary to the adsorption of metal salts the uptake of acids develops stoichiometrically. In the acidic form, the exchanger cannot be reused for adsorption of heavy metal salts. In a second step of the entire regeneration it has, therefore, to be neutralized and reconverted to the free base form, e.g. by means of sodium hydroxide [228].

$$\overline{R-NH_3^+HSO_4^-}+2NaOH \rightleftharpoons \overline{R-NH_2}+Na_2SO_4+2H_2O$$

Considering the sorption equilibrium, this kind of process exclusively exhibits favorable equilibrium: There is a strong preference for heavy metal salts at neutral conditions and for strong acids at low pH values [228]. The reason of this preference can be explained as follows; when dissolved in water and depending on the solution pH, poly(ethylene imine) (PEI), can protonate via the donation of the lone pair of electrons on the N atoms within the polymer structure into empty H^+ orbital [181].

While molecules of PEI form chelates with transition metal ions in aqueous solutions. Alkali and alkali earth metals do not interact with this polymer [73]. This phenomenon may be explained as follows; it is a well known fact that alkali and alkali earth metals do not form stable ammonia complexes in water solution. In aqueous solution the hydrate is far more stable than the ammine. For these cations, the metal ion-ammonia bond in solution is weaker than the metal ion-water bond. On the other hand, cations such as copper(II), silver(I), cadmium(II) and zinc(II) which are found in Periodic Groups IB and IIB, form amine complexes which are much more stable in aqueous solution than are the hydrated ions. For these metals, the metal-ammonia bond is significantly stronger than the metal-water bond. It is also interesting that the coordinating ability of many metal cations with amines varies in the order $NH_3 \geq$ primary amine$>$secondary$>$tertiary amine [232].

In addition to solution pH, it is known that ionic strength has also an important role in the complex formation of PEI molecules. When the ionic strength of the solution is high polymer precipitation may occur due to the reduction in solubility of the polymer [146]. Protonation of PEI and charge effects are diminished by increasing the ionic strength of the solvent and it is also reasonable that increased ionic strength would open up the polymer chain and increase the ease of chelation [233].

2.5.1 Coordination Chemistry

The ability of the molecules to form complexes with metal ions depends on several variables, such as the charge/radius ratio, charge distribution, polarization of both ligands and the central atom and possibility of chelate formation. In Table 2.3, atomic and ionic radius of the selected metals and their electronic configurations are given [181].

Table 2.3: Ionic and Atomic Radius and Valence Electronic Configurations of the Metal Ions

Metal Ion	Ionic Radii (A)	Atomic Radii (A)	Electronic Configuration
Cd^{2+}	0.92	1.55	d^{10}
Zn^{2+}	0.74	1.35	d^{10}
Ni^{2+}	0.69	1.35	d^{8}

In ionic models, while determining the coordination ability of the ions, generally rigid, spherically symmetrical ions or molecules was assumed and it was suggested that, ionic potential, which is defined as the charge of the ion divided by its crystal radius in Angstrom units determines the strength of the bond formed by the ion. In general coordinating ability assumed to be increased with an increase in the ionic potential of the central ion [234]. However, Irving and Williams [235] have demonstrated that the ionic potential alone is not an adequate parameter for the estimation of complex stability constants of metal ions. In order to obtain reasonable agreement between fact and theory, concepts of ion deformation and interpenetration must be used along with any ionic model. Actually, the electronic clouds of each atom or ion are deformed by the fields which are set up by neighboring ions or dipolar molecules. This deformation of ions is related to their polarization.

The role of polarization and interpenetration in complex formation was illustrated in Figure 2.2 [232]. In Fig. 2.2X no deformation of either the cation or dipolar molecule has occured and the charges are separated by the distance r_X; in Fig. 2.2Y the coordinated groups have been deformed and the negative pole of the groups is pulled in toward the positive cation and the distance between the positive and negative charges become smaller $r_X < r_Y$ and the resulting potential energy of the system is reduced, giving a greater stability. In Fig. 2.2Z both the central ion and the coordinated groups have been deformed, producing a still smaller distance of separation r_Z; case Z represents the most stable bond.

The amount of distortion is determined by the strength of the distorting field and by the magnitude of the force binding the electron cloud to the atomic nucleus. If the cation has low polarizability (if it is tightly bound), little distortion occurs, on the contrary if an ion has large polarizability (if it is loosely bound), it may be seriously deformed from its spherical symmetry. As the positive charge on the central cation increases, its polarizability decreases. Cation polarizability and deformation have great importance in ions of low charge. The ions that belong to the B group in periodic table (i.e., Zn, Fe, Co, etc.) are easily deformed and penetrated as compared to A group ions (i.e., Na, Ca, Mg, etc.) [232].

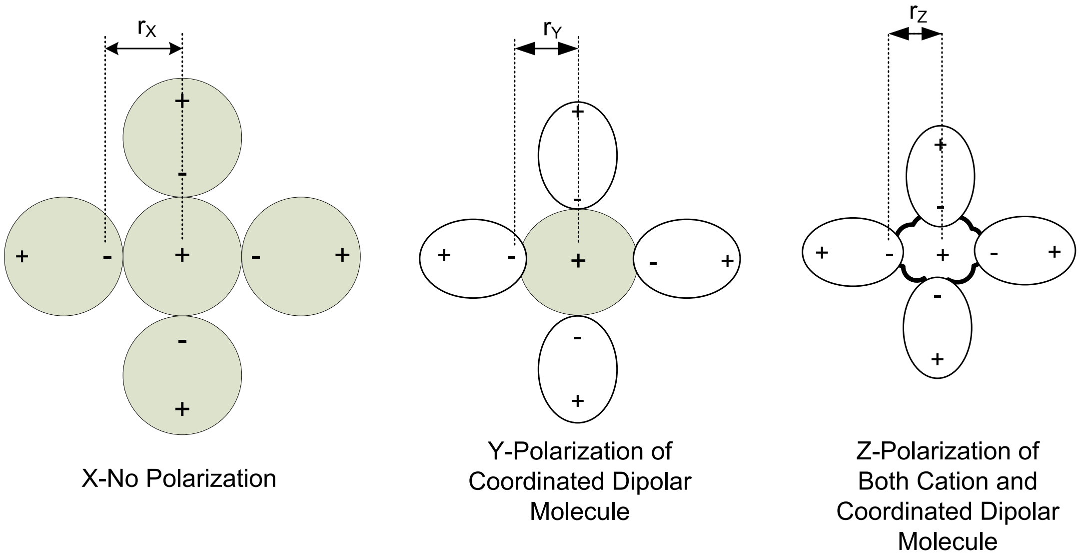


Figure 2.2: The Role of Deformation in Coordination

2.6 Characterization of Polymers and Polymer Complexes

Proceeding from observing macroscopic behavior of macromolecules (i.e., viscosity, solubility), one can make a decision about macromolecular structure of macromolecule-metal complex [236]. In order to observe the macroscopic behavior of macromolecules, characterization tests should be made. One important method for the characterization of particles in the solution phase involves scattering visible light in the solution.

Scattering light by the colloidal particles in solution is an important property which gives rise to characterization of particles. The incident light scatters in all directions. The intensity of light scattered of a solution is depend on ratio of size/molecular weight of the particle, scattering angle, concentration and shape of the partical. The difference between the coming light and scattered light is expressed in terms of scattering vector (q):

$$q = \frac{4\pi n \sin\left(\frac{\theta}{2}\right)}{\lambda} \tag{2.1}$$

where,

- θ is scattering angle
- n is refractive index
- λ is wavelength of the laser

The theory behind light scattering in gases was first proposed by Rayleigh in the late 1800s, and Smoluchowski and Einstein extended light scattering theory to liquids in 1908 and 1910 respectively [237]. These two scientists proposed that the patterns of light scattered from a pure liquid are caused by irregularities in the medium due to random thermal motion. In a solvent/solute system, light scattering is also caused by small variations in the solute concentration [237].

Different patterns of light scattered from a solvent/solute system can be measured by dynamic and static light scattering methods. In dynamic light scattering method by utilizing the real time intensities of scattered light, diffusion coefficient, hydrodynamic radius (R_H) of the particle can be estimated. Second virial coefficient (A_2), radius of gyration (R_g) and molecular weight are the characterization parameters that can be estimated by utilizing the time averaged intensities of the light scattered in static light scattering method [238]. Photon correlation spectroscopy is the most common way to analyze dynamic light scattering data [237].

2.6.1 Static Light Scattering Theory

Static light scattering measures the intensity of light scattered off of a solution at a single time (Fig. 2.3) and by using the time averaged light intensity data molecular weight of the sample can be estimated.

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). Kc/R value can be obtained by following equations:

$$K = 4\pi^2 n^2 \left(\frac{dn}{dc}\right)^2 N_A^{-1} \lambda_o^{-4} \tag{2.2}$$

where,

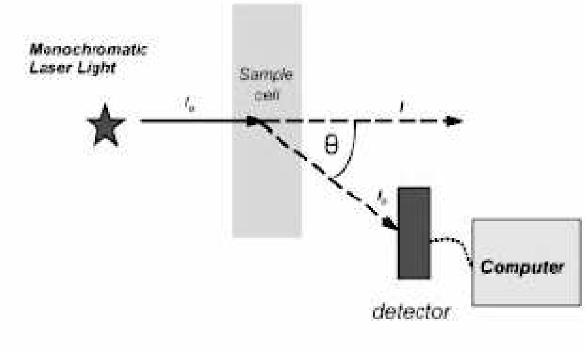


Figure 2.3: Schematic of Static Light Scattering

- n is the index of refraction
- dn/dc is the refractive index increment
- λ_o is the wavelength of the incident light
- N_A is the Avagadro′s number

$$R_\theta = R_c(90^o).\sin(\theta).(I_\theta/I_c) \tag{2.3}$$

where,

- $R_c(90\,\mathrm{deg})$: the absolute scattering intensity of toluene
- I_θ: the experimental intensity corrected by the software
- I_c: the corrected experimental intensity of toluene at $90\,\mathrm{deg}$

After obtaining Kc/R value, by using different methods such as Zimm, Guinier and Berry, average molecular weight, radius of gyration and second virial coefficient of the sample can be estimated.

1. Zimm Method

   In Zimm method, following equations are used:

$$\frac{Kc}{R} = \frac{1}{M_W\left(1-\frac{1}{3}R_g^2q^2\right)} + 2A_2c \tag{2.4}$$

(q^2+Kc) versus Kc/R plot is constructed according to equation 2.4. Then by using the polinomial equations 2.5 and 2.6, average molecular weight (eqn. 2.7, eqn. 2.8), radius of gyration (eqn. 2.9) and 2^{nd} virial coefficient (eqn. 2.10) of the sample can be estimated.

$$\left.\frac{Kc}{R}\right|_{c=\text{constant}} = a_1 + a_2q^2 + a_3q^4 + .. \tag{2.5}$$

$$\left.\frac{Kc}{R}\right|_{q^2=\text{constant}} = b_1 + b_2c + a_3c^2 + .. \tag{2.6}$$

$$\text{c = 0 , q}^2 \rightarrow 0 \qquad M_W\left(q^2\right) = \frac{1}{a_1} \tag{2.7}$$

$$\text{q}^2 \text{ = 0 , c} \rightarrow 0 \qquad M_W\left(c\right) = \frac{1}{b_1} \tag{2.8}$$

$$R_g = \sqrt{3a_2M_W\left(q^2\right)} \tag{2.9}$$

$$A_2 = \frac{b_2}{2} \tag{2.10}$$

2. Guinier Method

In Guinier method, following equation sets are used:

$$\ln\left(\frac{Kc}{R}\right) = \ln\left[\frac{1}{M_W\exp\left(-\frac{1}{3}R_g^2q^2\right)^2} + 2A_2c\right] \tag{2.11}$$

(q^2+Kc) versus $ln(Kc/R)$ plot is constructed according to equation 2.11. Then by using the polinomial equations 2.12 and 2.13, average molecular weight (eqn. 2.14, eqn. 2.15), radius of gyration (eqn. 2.16) and 2^{nd} virial coefficient (eqn. 2.17) of the sample can be estimated.

$$\ln\left(\frac{Kc}{R}\right)\Big|_{\text{c = constant}} = a_1 + a_2q^2 + a_3q^4 + \ldots \qquad (2.12)$$

$$\ln\left(\frac{Kc}{R}\right)\Big|_{q^2=\text{constant}} = b_1 + b_2c + b_3c^2 + \ldots \qquad (2.13)$$

$$\text{c = 0 , q}^2 \rightarrow 0 \qquad M_W\left(q^2\right) = \exp\left(-a_1\right) \qquad (2.14)$$

$$\text{q}^2 \text{ = 0 , c} \rightarrow 0 \qquad M_W\left(c\right) = \exp\left(-b_1\right) \qquad (2.15)$$

$$R_g = \sqrt{3a_2} \qquad (2.16)$$

$$A_2 = \frac{1}{2}\frac{b_2}{M_W\left(c\right)} \qquad (2.17)$$

3. Berry Method

   In this method following equation sets are used:

$$\left(\frac{Kc}{R}\right)^{\frac{1}{2}} = \left[\frac{1}{M_W\left(1-\frac{1}{6}R_gq^2\right)^2} + 2A_2c\right]^{\frac{1}{2}} \qquad (2.18)$$

$q^2 + Kc$ versus $(Kc/R)^{1/2}$ plot is constructed according to equation 2.18. Then by using the polinomial equations 2.19 and 2.20, average molecular weight (eqn. 2.21, eqn. 2.22), radius of gyration (eqn. 2.23) and 2nd virial coefficient (eqn. 2.24) of the sample can be estimated.

$$\left(\frac{Kc}{R}\right)^{\frac{1}{2}}\Big|_{\text{c = constant}} = a_1 + a_2q^2 + a_3q^4 + \ldots \qquad (2.19)$$

$$\left(\frac{Kc}{R}\right)^{\frac{1}{2}}\Big|_{q^2=\text{constant}} = b_1 + b_2c + b_3c^2 + \ldots \qquad (2.20)$$

$$\text{c = 0 , q}^2 \rightarrow 0 \qquad M_W\left(q^2\right) = \frac{1}{a_1^2} \tag{2.21}$$

$$\text{q}^2\text{ = 0 , c} \rightarrow 0 \qquad M_W(c) = \frac{1}{b_1^2} \tag{2.22}$$

$$R_g = \sqrt{6a_2\sqrt{M_W(q^2)}} \tag{2.23}$$

$$A_2 = \frac{b_2}{\sqrt{M_W(c)}} \tag{2.24}$$

2.6.2 Dynamic Light Scattering Theory

Dynamic light scattering (DLS) theory is a well established technique for measuring particle size over the size range from a few nanometers to a few microns. The concept uses the idea that small particles in a suspension move in a random pattern (Brownian Motion). According to Brownian Motion theory larger particles move more slowly than smaller ones if the temperature is the same. When a coherent source of light (such as a laser) having a known frequency is directed at the moving particles, the light is scattered, but at a different frequency (Fig. 2.4). This shift in frequency is termed a Doppler shift or broadening. For the purposes of particle measurement, the shift in light frequency is related to the size of the particles causing the shift. Due to their higher average velocity, smaller particles cause a greater shift in the light frequency than larger particles. It is this difference in the frequency of the scattered light among particles of different sizes that is used to determine the sizes of the particles present [237].

Dynamic light scattering is based on measuring fluctuations in the intensity of the scattered light arising from phase and/or amplitude fluctuations induced by particle dynamics [239]. In dynamic light scattering method fluctuation of scattered light intensity with time is measured and light scattering intensities recorded at various time are compared and by the help of the autocorrelator. Hydrodynamic radius of the particles can be estimated by using these data.

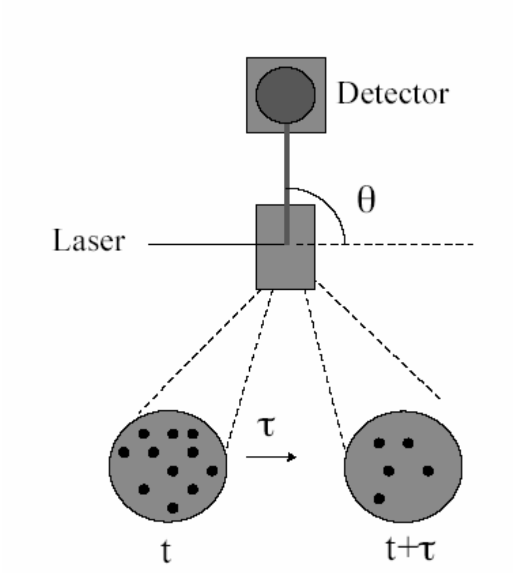


Figure 2.4: Schematics of Dynamic Light Scattering

By deriving the cumulant expansion hydrodynamic radius of the particle can be estimated :

$$D_{app} = \frac{\Gamma}{q^2} = D_z\left(1 + k_D c + ...\right)\left(1 + C\left\langle S^2\right\rangle q^2 + ..\right) \tag{2.25}$$

where,

- D_{app} is apparent diffusion coefficient
- Γ is cummulant
- q is scattering vector
- k_D is diffusional virial coefficient
- $C\left\langle S^2\right\rangle$ is constant related with polydispersity
- D_z is diffusion coefficient
- C is concentration

By using the polynomial expansion (eqn. 2.26 and 2.27)

$$D_{app}\big|_{c=\text{constant}} = a_1 + a_2q^2 + a_3q^4 + \ldots \tag{2.26}$$

$$D_{app}\big|_{q^2=\text{constant}} = b_1 + b_2c + b_3c^2 + \ldots \tag{2.27}$$

By using eqn. 2.28 and eqn 2.29, diffusion coefficient D_z can be estimated:

$$c = 0,\ q^2 \to 0 \qquad\qquad D_z\left(q^2\right) = a_1 \tag{2.28}$$

$$q^2 = 0,\ \text{c} \to 0 \qquad\qquad D_z\left(c\right) = b_1 \tag{2.29}$$

Other unknowns in eqn. 2.25: $C\left\langle S^2\right\rangle$ and k_D are obtained from the following equations:

$$C\left\langle S^2\right\rangle = \frac{a_2}{D_z\left(q^2\right)} \tag{2.30}$$

$$k_D = \frac{b_2}{D_z\left(c\right)} \tag{2.31}$$

finally, apparent hydrodynamic radius is calculated from Stokes-Einstein equation (eqn. 2.32)

$$R_H = \frac{kT}{6\pi\eta D_z} \tag{2.32}$$

where,

- R_H: Hydrodynamic radius
- k_b: Boltzmans constant
- T: temperature (Kelvin)
- η: viscosity of solvent

Static and dynamic light scattering give complementary pieces of information, and for this reason they are commonly used for characterization of polymer solutions [240–242].

In literature there are many studies related with the characterization of different polymers [238, 243], structure of polymer-metal complexes (i.e: Poly(methacrylic acid)-copper ion [244]), polymer-surfactant complexes [245, 246] and determining macromolecular size of polyelectrolytes containing ammonium and sulfonic acid groups [247] by dynamic and static light scattering methods.

Since considerable interest has focused on the use of PEI in the field of biotechnology, special attention was given to the characterization of PEI having molecular weight in the range between 2000-60000Das and PEI complexes by light scattering methods. Light scattering experiments performed with PEI (50 wt.%aqueous soln.,M.W. 50000-60000,Acros Organics) show very weak light scattering signals over the wavelength range of 200-700nm even if its concentration reaches 1x10^{-3} mol/l. Light scattering intensity of PEI is almost unchanged in the pH range of 1-10 and increase in the ionic strength did not change the intensity [248]. In the study of Andersson et.al. [249], R_g was estimated as 45nm at pH 7.2 for high molecular weight PEI (MW$\approx (0.6-1)$x10^6). In another study, at pH 7.4, R_H of PEI (MW 25000 g/mol, Aldrich) was found to be 4.7 ± 0.2 nm [250]. In addition to polymer characterization, details of interaction of PEI with nucleic acids [248], sodium dodecyl sulfate [251–253], short DNA fragments [250] and lactate dehydrogenase [249] were also studied by light scattering methods.

CHAPTER 3

MODELLING OF CONTINUOUS PEUF PROCESS

Interactions between polymers and different metal ions are an interesting field of study due to potential analytical and technological applications. The behavior of metals in the complexation reactions is intimately related to their physicochemical form. Many speciation methods were developed for determining the nature and concentrations of different chemical forms of metal ions [254, 255].

The binding constants of various metals with water soluble polymers and polyacids have been extensively evaluated by potentiometric techniques [255–257], particularly ion selective electrodes, fluorimetry [255, 258], and spectrometry [257, 259] or by voltammetric [260, 261] and chromatographic [262, 263] methods.

Recently several authors have tried to determine the equilibrium constants of complexes of metal ions and polymeric ligands by ultrafiltration technique [264–266].

3.1 Estimation of Binding Constants of Metal-Polymer Complexes by PEUF

The ultrafiltration technique has been previously used mainly to determine size distribution [267, 268]. It is also well known that ultrafiltration has frequently been used to investigate protein-drug binding equilibria (binding constants lying between 10^3 and 10^7) due to its simplicity of operation and installation [269]. Previously, biochemists used ultrafiltration technique to determine the binding constants for complexes between proteins and low molecular weight biological species, but the idea of adding a synthetic soluble macrocomplexing agent for industrial separation was first proposed by Michaels in 1968 [270] and several authors have tried to determine the equilibrium constants of complexes of metal ions and macromolecular ligands by this method [180, 271].

There are several approaches for modelling the batch mode polymeric binding/membrane separation process. First attempt for theoretical modelling for the determination of the equilibrium constant for the formation of a complex between a metal ion and water soluble macroligand by batch ultrafiltration technique was made by Nguyen et. al. [264]. The case of one metal reacting with a polyacidic chelating agent was considered with the following assumptions:

The ligand groups XH on the polymer chain behave as independent complexing groups;

- Only 1:1 complexes form
- The metal-polymeric complex is completely retained by the membrane
- There is no interaction between the membrane and free metal ions.

The reaction between the ligand group (XH) and the metal cation M^{n+} is represented by the following equilibrium equations:

$$XH \rightleftharpoons X^- + H^+ \quad ,K_A \tag{3.1}$$

$$X^- + M^{n+} \rightleftharpoons XM^{(n-1)+} \quad ,K_i \tag{3.2}$$

It is assumed that, protonated form of the ligand (XH) is not capable of forming complexes with the metal ions, complexaton occurs only between the metal ions and non-protonated form of the ligand (X).

The concentrations of the different species can be determined from the thermodynamic and mass balance equations:

$$K_A = \frac{[X^-]\,[H^+]}{[XH]} \qquad \text{K}_\text{A} \text{ is acidity constant}$$

$$K_i = \frac{[X^-]\,[M^{n+}]}{XM^{(n-1)+}}$$ $\mathrm{K_i}$ is stability constant

The total concentration of the chelating agent $[X]_t$ is the sum of the free [X] and protonated [XH] forms and of the form of the metal complex [MX]:

$$[X]_t = \left[X^-\right] + [XH] + \left[XM^{(n-1)+}\right]$$

The total concentration of the metal $[M]_t$ is the sum of the free metal [M] and the complex [MX]:

$$[M]_t = [M^{n+}] + [XM^{(n-1)+}]$$

The metal retention R_i can be expressed as :

$$R_i = 1 - \frac{[M]}{[M]_t}$$

and R_i can be found from the following equation, which links the total concentration of the metal and the polymer, the pH of the solution and the thermodynamic constants:

$$K = \frac{K_A\,[M]_t\,(1-R_i)}{K_A + 10^{-pH}}\,\frac{[X]_t}{[M]_t\,R_i} - 1$$

When the acidity constant (K_A) (K_A=1/protonation constant(K_p)) is known, all the other quantities are experimentally accessible for this model. This model can be applied for the estimation of binding constants of metals with polyacids or polymeric agents that have acidity constants easily determined by potentiometric titration methods. However as far as polyethyleneimine is concerned the presence of three different amine functional groups (primary, secondary and tertiary) complicates the calculation of protonation constants of this polymer [182] and inaccurate results may be obtained because of the errors coming from the determination of protonation constants of PEI.

A similar approach was made by Aulas et.al. [265]. Once again, the formation of 1:1 complexes and complete polymer rejection by a membrane were assumed. Buffle and Staub [272] developed a theoretical relationships which permit the computation of concentrations and equilibrium constants and test them with known ligands. Important features of that study are; other than 1:1 complexes between Zn-calgamite and Zn-tiron, 1:n complexes of Zn in natural medium were also studied. In another study, using poly acrylic acid (PAA) used as a complexing agent and the equilibrium binding constants of $Cu^{2+}, Ag^{+}, Ni^{2+}, Cd^{2+}$ were investigated taking into account the 1:n binding of metal ions to macroligand [273].

Effect of metal hydrolysis on the investigation of the the equilibrium constants was first analyzed by the authors Juang [274] and Volchek [275]. Simplifying assumptions of their model are as follows:

- There is no interaction between the free metal ions and the membrane
- Retention of a macromolecular complex is the same as that of the polymer
- The chemical equilibrium constants do not depend on pH or the concentration of species involved in the reaction

The reactions occurring in the solution include the dissociation of the ligand, metal-ligand complexation, and the formation of soluble metal hydroxy complexes:

$$HX \rightleftharpoons H^{+} + X^{-},\ \mathrm{K_a} \tag{3.3}$$

$$M^{2+} + nX^{-} \rightleftharpoons MX_n^{(2-n)+},\ 1/\mathrm{K_d} \tag{3.4}$$

$$M^{2+} + mOH^{-} \rightleftharpoons M(OH)_m^{(2-m)+},\ 1/\mathrm{K_s} \tag{3.5}$$

Where n is the average coordination number of ligands bound to one metal ion. K_a

and K_d are apparent dissociation constants.

Solute rejection by the membrane is expressed as:

$$R_j = 1 - \frac{[j]_p}{[j]_o} \tag{3.6}$$

Where $[j]_p$ and $[j]_o$ are the concentrations of species j in permeate and feed streams respectively.

The overall concentrations of the metal ion in the initial feed solution and in the permeate can be expressed by the following mass balance relations:

$$[M]_o = \left[M^{2+}\right] + \left[MX_n^{(2-n)+}\right] + \sum \left[M(OH)_m^{(2-m)+}\right] \tag{3.7}$$

$$[M]_p = \left[M^{2+}\right] + \left[MX_n^{(2-n)+}\right](1 - R_X) \tag{3.8}$$

Combining equations 3.6, 3.7 and 3.8, the following expression for metal retention R_M was obtained:

$$R_M = \left\{\left[MX_n^{(2-n)+}\right] R_X + \sum \left[M(OH)_m^{(2-m)+}\right]\right\} \Big/ [M]_o \tag{3.9}$$

or, R_M may be expressed in terms of retention coefficient of ligand and dissociation constants by combining eqns 3.4, 3.5 and 3.7.

$$R_M = \frac{[OH^-]^2 \Big/ K_s + \left\{[X^-]^n / K_d\right\} R_X}{1 + [X^-]^n / K_d + [OH^-]^2 \Big/ K_s} \tag{3.10}$$

In eqn. 3.10, the concentration of the free ligand $[X^-]$, is determined from the following mass balance equations:

$$[HX]_o = \left[X^-\right] + [HX] + n\left[MX_n^{(2-n)+}\right]$$
$$= \left[X^-\right] + \left[X^-\right]\left[H^+\right]/K_a + \mathrm{n}\left\{[\mathrm{M}]_o \left[X^-\right]^n / K_d\right\}\left\{1 + \left[X^-\right]^n \Big/ K_d + [\mathrm{OH}^-]^2 \Big/ K_s\right\}^{-1} \tag{3.11}$$

Provided that the values of n, K_a and K_d are known, the value of $[X^-]$ can first be calculated iteratively by eqn. 3.11 under the given experimental conditions, and then the rejection coefficient of the metal ion may be determined by eqn. 3.10.

Following similar equations listed above, Volchek [275] derived a model for polymer binding/ultrafiltration process for a multicomponent solution containing the ions of several metals, each of which is capable of forming coordination complexes with a polymeric complexing agent introduced into solution. Free ligand concentration in feed solution can be calculated by iterative procedure and based on this value rejection coefficient of each metal can be predicted if the protonation constant of the ligand is known. It was reported that, the computations given in that study are accurate should the volume of the feed solution remain more or less constant. Under practiced conditions, a significant decrease, possibly several orders of magnitude, is observed in the volume of feed solution for batch mode ultrafiltration process.

All the aforementioned models are derived by the equilibrium data obtained from batch ultrafiltration systems. In the systems that are operating in batch mode, permeate and retentate streams are not recycled back to the feed tank, this produces a substantial change in the composition of the feed solution, leading to a shift in the chemical equilibrium, which causes a change in the degree of metal binding and retention values. If the retention value of the metals can be kept constant through out the process, theoretical models based on the experimental parameters (i.e. retention, metal/polymer ratio) can be improved in terms of their accuracy. This may be achieved by the application of semi-continious and/or continius mode of ultrafiltration processes.

Equilibrium studies in semi-continuous mode ultrafiltration systems were made by Canizares et.al. [127]. Mathematical model used in this study was based on the model previously derived by Volchek [275]. The model was derived from conservation equations and analyses of equilibrium reactions in an aqueous solution. The following reactions were assumed to be taking place in solution;

$$\mathrm{HX} \leftrightarrow \mathrm{H}+\mathrm{X} \qquad \mathrm{K_A} = \frac{[H]\,[X]}{[HX]} \tag{3.12}$$

$$\mathrm{M}+\mathrm{X} \leftrightarrow MX \qquad \mathrm{K_1} = \frac{[MX]}{[M]\,[X]} \tag{3.13}$$

$$\mathrm{M}+\mathrm{nX} \leftrightarrow MX_n \qquad \mathrm{K_n} = \frac{[MX_n]}{[M]\,[X]^n} \tag{3.14}$$

Overall mass balance, polymer balance and metal ion balance were expressed by the following equations;

$$\mathrm{Q_P(t) = Q_F(t)} \tag{3.15}$$

$$\mathrm{V_R\frac{d[X]_R}{dt} = -Q_P[X]_P} \tag{3.16}$$

$$\mathrm{V_R\frac{d[M]_R}{dt} = Q_F[M]_F - Q_P[M]_P} \tag{3.17}$$

Metal ions and ligand retentions were found from the following formulas;

$$\mathrm{R_M = 1-\frac{[M]_P}{[M]_T}} \tag{3.18}$$

$$\mathrm{R_X = 1-\frac{[X]_P}{[X]_T}} \tag{3.19}$$

By substituting equations 3.18 and 3.19 into eqns. 3.16 and 3.17, following equations were obtained;

$$\mathrm{V_R\frac{d[X]_R}{dt} = -Q_P[X]_R(1-R_X)} \tag{3.20}$$

$$V_R \frac{d[M]_R}{dt} = Q_F[M]_F - Q_P[M]_R(1-R_M) \tag{3.21}$$

Total metal concentration is:

$$[M]_T = [M] + \sum_n [MX_n] \tag{3.22}$$

Assuming complex retention is the same as polymer retention, metal ion concentration in permeate stream can be expressed as;

$$[M]_P = [M](1-R_{MF}) + (1-R_X)\sum_n [MX_n] \tag{3.23}$$

where R_{MF} is the free metal retention. From Eqns. 3.22 and 3.23, metal retention can be estimated as;

$$R_M = 1 - \frac{(1-R_{MF})[M] + (1-R_X)\sum_n [MX_n]}{[M] + \sum_n [MX_n]} \tag{3.24}$$

By substituting Eqn. 3.14 into Eqn. 3.24, R_M can be expressed as;

$$R_M = \frac{R_{MF} + R_X \sum_n K_n [X]^n}{1 + \sum_n K_n [X]^n} \tag{3.25}$$

Total ligand concentration is:

$$[X]_T = [X] + [XH] + \sum_n n[MX_n] \tag{3.26}$$

Combining Eqns. 3.12, 3.13 and 3.26;

$$[X]_T = [X] + \frac{[X][H]}{K_A} + \sum_n nK_n[M][X]^n \tag{3.27}$$

From Eqn. 3.22, free metal concentration can be determined as;

$$[M] = \frac{[M]_T}{1+\sum_{n} K_n [X]^n} \tag{3.28}$$

Introducing Eqn. 3.28 into Eqn. 3.27;

$$[X]_T = [X] + \frac{[X][H]}{K_A} + \frac{[M]_T \sum_{n} nK_n [X]^n}{1+\sum_{n} K_n [L]^n} \tag{3.29}$$

The only unknown term in Eqn. 3.29 is free, so active, ligand concentration. As it is an equation of complex analytical resolution, numerical Newtons method was applied. After the estimation of free ligand concentration, metal retention can be calculated. By this model, rather than estimation of binding constant between metal ion and polymer, prediction of metal concentrations in retentate and permeate streams could be made, if polymer dissociation and polymer-metal complex formation constants are available.

In this study, we have tried to obtain a better understanding of the retention mechanism using a simple equilibrium model. Rather than trying to develop a universal model suitable for any metal and polymer system, an attempt has been made to adopt previous models used to estimate polymer-metal binding constants by batch PEUF method to continuous mode PEUF system. If the proposed model can be applicable for both batch and continuous mode PEUF systems and can give comparable results (i.e., similar apparent binding constants), then the results of batch mode experiments can be used to predict the performance of a continuous mode PEUF system. This gives rise to the scaling-up for industrial processes, since these systems can handle larger effluent volumes and various types of commercial membranes with different configurations.

Bearing in mind the benefits of continuous mode PEUF operation, developing an equilibrium model which allows:

- To determine the relation between the retention value of the metal ions to the complexation constants involved in the polymer-metal complexation reaction in continuous mode PEUF operation

- To compare the equilibrium data obtained from batch mode and continuous mode ultrafiltration systems

will be important outcomes of this study.

Binding constants of Cd^{2+}, Ni^{2+}, Zn^{2+} with polyethyleneimine (PEI) were calculated according to the model which is based on the following assumptions:

1. There is no interaction between free metal ions with the membrane, that is free metal ions are not retained by the membrane
2. Retention of unbound PEI, is the same as that of the metal-PEI complex
3. Formation of insoluble metal hydroxy complexes were assumed to be negligible since the formation of insoluble metal hydroxy complexes is not favorable in the pH range studied (pH 4-6.5)
4. Concentration polarization and/or membrane fouling does not occur in the concentration range studied
5. Only the non-protonated form of the PEI has the ability to form complexes with metal ions whereas the protonated form of the ligand (PEI) is inactive towards the metal ions.

For a single or multicomponent solution containing the ions of several metals, each of which is capable of forming coordination complexes with the polymeric complexation agent, following reactions were assumed to be occurring in the solution:

The formation of metal-PEI complexes:

$$M + nPEI \rightleftharpoons M \cdot PEI_n$$

Protonation of PEI molecules depending on the acidity level of the solution :

$$H + PEI \rightleftharpoons PEI \cdot H$$

The ionic charges have been omitted because they are not significant for modelling the process.

For a solution containing a total metallic species concentration $[M]_t$ and a total water soluble polymeric agent $[PEI]_t$, loading is defined as:

$$L = \frac{[M]_t}{[PEI]_t} \tag{3.30}$$

In contrast to the metal-ligand complex, free metal ions can pass through the membrane. The free metal concentration in the permeate may be expressed as $[M]_p$ and retention coefficient is defined as:

$$R = 1 - \frac{[M]_p}{[M]_t} \tag{3.31}$$

And the apparent binding constant K_{app} of complexes by:

$$K_{app} = \frac{[M \cdot PEI_n]}{[M]\,[PEI]^n} \tag{3.32}$$

Where

$[M \cdot PEI_n]$:total concentration of complexed metallic species

$[M]$:total concentration of non complexed metallic species

$[PEI]$:total concentration of free water soluble polymer

n:the number of ligand molecules per metal ligand complex

Total concentrations of metallic and ligand species are given by relations:

$$[M]_t = [M]_p + [M \cdot PEI_n] = [M] + [M \cdot PEI_n] \tag{3.33}$$

$$[PEI]_t = [PEI] + n\,[M \cdot PEI_n] \tag{3.34}$$

By substituting the equations 3.30- 3.34 into the relation 3.31 we obtain:

$$K_{app} = \frac{R}{(1-R)\,[PEI]_t^n\,[1-nLR]^n} \tag{3.35}$$

Apparent binding constants of Cd^{2+},Ni^{2+} and Zn^{2+} with PEI were determined from measurements of R, L and $[PEI]_t$. Loading (L) and $[PEI]_t$ are predetermined quantities and retention values were obtained experimentally. The only quantity that can not be determined experimentally is the number of ligand molecules per metal ligand complex. The number of PEI ligands participating in the complex formation with divalent metal ions was found to be either one, two or more than two amino groups, depending on the conditions [196, 264].

The presence of three different amine functional groups (primary, secondary and tertiary) in diverse proportions complicates the estimation of the number of PEI ligands (n) participating in the complex formation with divalent metal ions. Different speculations have been made based on the results of UV-visible spectroscopic titration analysis of the complexes. In one of the previous studies, stoichiometry of complex 1:1 (ML) was assumed and n is taken as 1 for Ni-PEI complex and polymer repeat unit comprising seven monomer units (C_2H_5N) was considered to be the ligand at pH 5 [182]. In cases where single monomer unit is considered as ligand, n (the number of PEI ligands participating in the complex formation with divalent metal ions was taken as 2.1 and 2.3 at pH 6 and pH 5 respectively.

In this work, each monomer unit is considered as ligand and complex formation is simply considered to proceed in a single step as it was assumed in several previous papers [269, 271]. For the number of ligand molecules per metal ligand complex only $n = 2$ is taken into account for the target metals. Although pH does not appear in the equations of the proposed model, for the three target metals (Cd^{2+}, Ni^{2+}, Zn^{2+}), effects of pH and ionic strength on the degree of binding were considered. For this reason, the complexation constant was named apparent binding constant. Impacts of low pH values and high salt concentrations were observed by estimating the apparent binding constants at different pH and ionic strength values. Calculations based on the proposed model were given in Section 5.7 of Chapter 5.

CHAPTER 4

MATERIALS AND METHODS

4.1 Materials

In the ultrafiltration experiments and in atomic absorption spectrometry analysis, polyethyleneimine (PEI) (Sigma) with average molecular weight of 60,000 Da, cadmium nitrate tetrahydrate $Cd(NO_3)_2.4H_2O$ (Merck), zinc nitrate hexahydrate $N_2O_6Zn.6H_2O$ (Acros), nickelous nitrate hexa-hydrate $Ni(NO_3)_2.6H_2O$ (J.T.Baker), sodium nitrate $NaNO_3$ (Merck), sodium sulfate anhydrous Na_2SO_4(J.T.Baker), sodium hydroxide $NaOH$ (Merck), nitric acid HNO_3 (Merck) and ultrapure water having a specific conductance of $18.3M\Omega cm^{-1}$ obtained from water purification system (Human Reverse Osmosis(RO)-UltraPure (UP) water purification systems) were used. All the chemicals used in this study were analytical grade reagents.

4.2 Apparatus

Throughout the experiments in this study, continuous mode pilot scale system was used. But for the selection of suitable membrane material and configuration, preliminary experiments were performed in laboratory scale continuous mode ultrafiltration system. In the final stage of experimental studies, limited number of experiments were carried out in dead end stirred cell ultrafiltration system. Therefore details of each equipment employed in the experimental studies were given in this section.

4.2.1 Pilot Scale Ultrafiltration System

In pilot scale experiments, SP20 ultrafiltration system has employed. The system can accomodate spiral wound regenerated cellulose cartridges having an effective area of $0.93m^2$, or polysulfone hollow fibre cartridges and contains integral reservoir which allows processing of feed volumes from 20 liters down to 1 liter. The flow is provided by a sanitary positive displacement lobe pump.

Helicon cartridges used in SP20 ultrafiltration system have an efficient spiral structure that maximizes available filtration area per unit volume. Comprised of alternating layers of Millipore Ultracel membrane and plastic separator screens wrapped concentrically around a hollow core.

Process solution enters the spiral cartridge via the inlet header and is directed into a series of flow channels between the membrane layers (Figure 4.1).

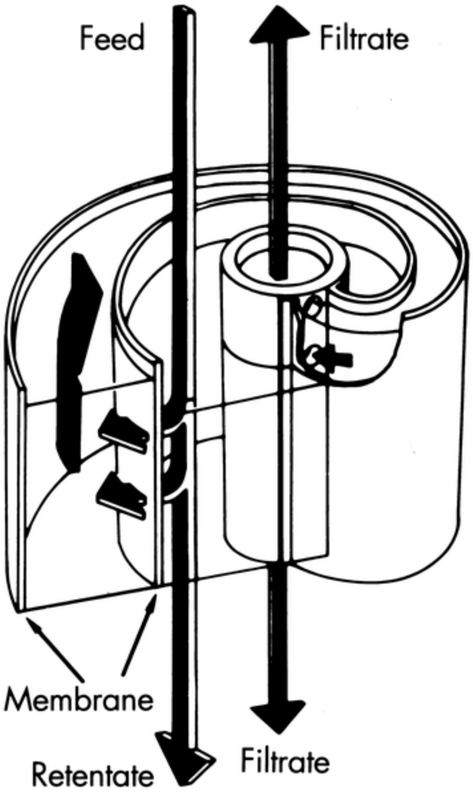


Figure 4.1: Millipore Spiral Cartridge

Transmembrane pressure drives solvent and low molecular weight solutes through the membrane, with permeate spiralling inward until it reaches perforated permeate collection tube at the cartridge center. Upon reaching the collection tube, the permeate (i.e., water, salts and low molecular weight materials) drains off through a port on the inlet header. After passing through the flow channels, process solution (containing retained solutes) exits the cartridge via the outlet header and is routed back to the sample reservoir.

The system is controlled by a dedicated microprocessor, which adjusts the pump speed and back pressure valve to enable optimal running conditions to be maintained throughout the process. The microcompressor exhibits 3 levels of control; manual, automatic and semiautomatic, in addition to holding the shut down set points for over pressurisation, over temperature and low feed volume. The operating temperature and pressure is displayed digitially on the control cabinet. In manual mode the inlet and outlet pressures are achieved by the operator. In semi-automatic mode the operator specifies the desired inlet and outlet pressures which are then maintained by the microprocessor controller. In full automatic mode the operator merely enters the cartridge configuration and the controller then selects and maintains optimal operating parameters.

Pressure of the feed side was 13kPa and that of permeate side was 5kPa, which produces a pressure gradient of 6kPa. Each experimental run for PEUF process perpetuates for 3.5 hours to reach steady state.

For particular application requirements several processing modes can be used. In this study semi-automatic continuous processing mode is used (Figure 4.2). In continuous processing mode both permeate and retentate streams are circulated back to the reservoir in order to keep the feed concentration constant. A circulating water bath is employed in order to keep temperature constant while pH of the feed solution is monitored by a pH meter (WTW, Germany) throughout the experiment.

4.2.2 Laboratory Scale Continuous Mode Ultrafiltration System

The experimental set-up for laboratory scale continuous mode ultrafiltration cell (Osmonics Sepa CF Membrane Cell) which is shown in Figure 4.3, mainly consists of membrane cell, rotameter, microprocessor controlled gear pump, a water bath, valves and teflon tubings. Cell body and cell holder were the two major components of the UF cell. Membranes having an effective area of $155cm^2$ were mounted on the cell

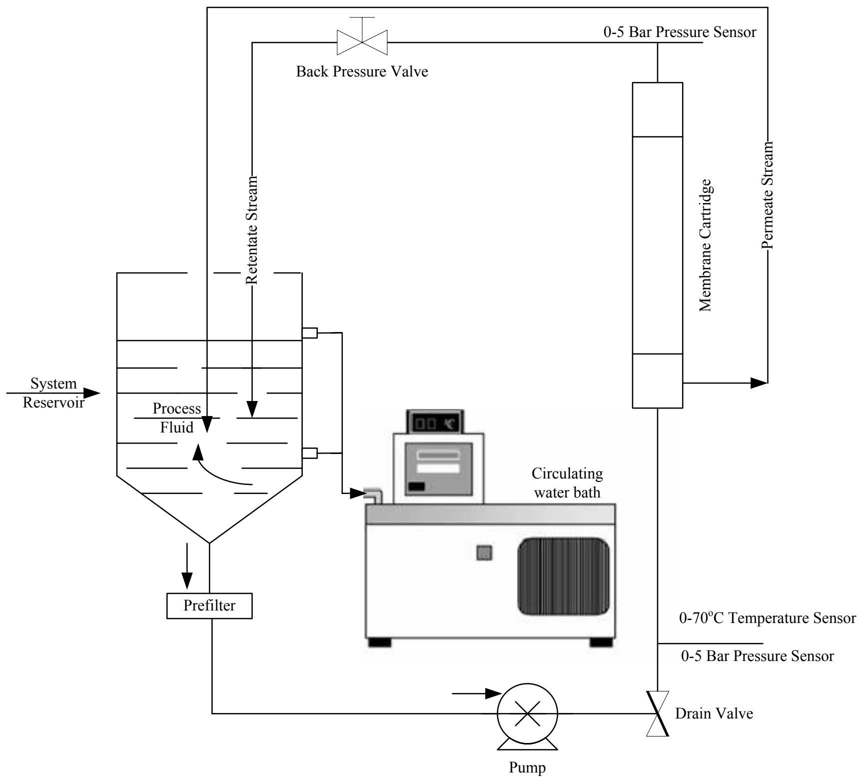
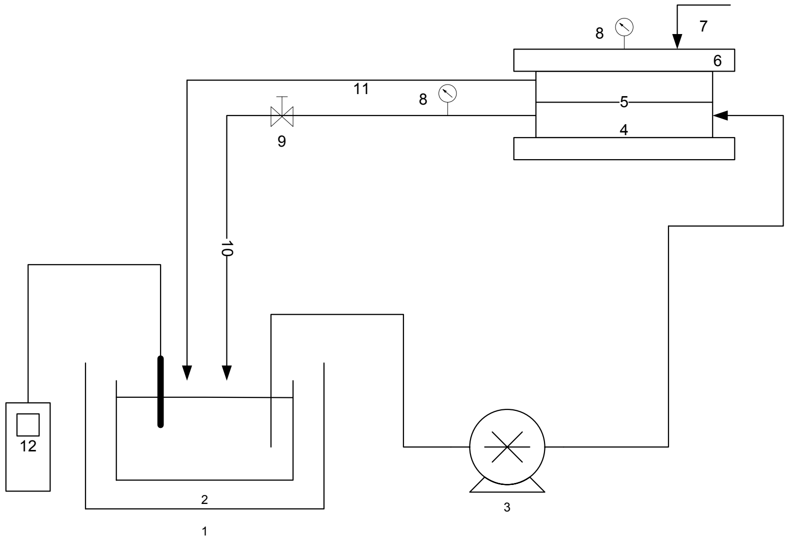


Figure 4.2: SP20 Pilot Scale Ultrafiltration System (Continuous Mode)



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. Retentate Stream
11. Permeate Stream
12. pH Meter

Figure 4.3: Schematic Diagram of Osmonics Sepa CF Membrane Cell

body. The function of the cell holder is to prevent leakages around the membrane by pressurizing the cell. Cell holder was supplied by air coming from a compressor. Throughout the experimental runs, pH of the feed solution is controlled by pH meter which was placed in the feed tank.

4.2.3 Laboratory Scale Batch Mode Ultrafiltration System

Batch mode ultrafiltration experiments were carried out on a lab-scale Model 8400 dead-end stirred membrane cell manufactured by Amicon-Millipore. Equipment has a cell capacity of 400ml. and its effective membrane area is 41.8cm^2. Schematic view of the stirred cell is illustrated in Figure 4.4. 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. Pressure should not exceed 75psi (0.01Pa).

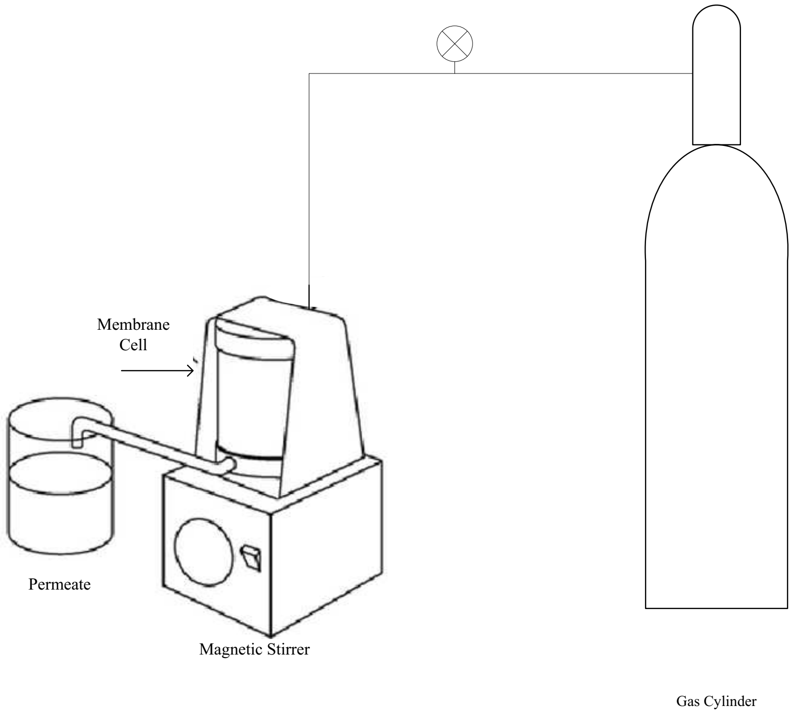


Figure 4.4: Schematic of Model 8050 Stirred Cell

4.2.4 Membrane Specifications

All commercial ultrafiltration membranes have a characteristic, called molecular weight cut-off (MWCO), which corresponds to the minimum molecular mass of a substance that can be retained by the membrane in practice. Specifications of the membranes used in three different ultrafiltration systems are given in Table 4.1.

Table 4.1: Specifications of the Membranes

System	Membrane	MWCO (Da)	Material	Recommended pH Range
Sepa CF	HG01	5000	Polyethersulfone	0.5-13
Sepa CF	HG19	20000-3000	Polyethersulfone	0.5-13
Sepa CF	HG09	20000-3000	Polyethersulfone	0.5-13
Sepa CF	AG08	10000-3000	Polyamide	1-11
SP 20	S10Y10	10 000	Regenareted Cellulose	3-11
M8400 Stirred Cell	PL-10	10 000	Regenareted Cellulose	3-11

4.3 Ultrafiltration Experiments

4.3.1 Sample Preparation

Feed solutions were prepared prior to ultrafiltration experiments. For pilot scale system 5L, for continuous mode laboratory scale system 2L and for batch mode system 50ml. feed solution were sufficient. The desired amounts of PEI and metal salts were separately dissolved in ultrapure water. When PEI dissolves in water, pH of the solution becomes about 10. In order to prevent precipitation of metals, pH of PEI solution was adjusted by adding HNO_3 and $NaOH$. Then metal solution was mixed with PEI solution and stirred at 250-300 rpm for at least 2 hours to make sure that complexation equilibria between metal ions and PEI was established. Experiments with longer mixing times showed that 2 hours was enough to achieve complexation equilibria [98]. The pH of the solutions was adjusted to desired values during the mixing period and during the experimental run.

In the preparation of salt containing solutions, same procedure was applied: metal and PEI solutions were prepared separately and then mixed at optimum pH value. Predetermined amount of $NaNO_3$ was added to the metal-PEI solution and stirred at 250-300 rpm for overnight.

4.3.2 Membrane Cleaning Procedure

All the membranes used in membrane filtration experiments were cleaned before and after each experimental run. Membranes were cleaned by applying in place 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 5L. of 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, and temperature was adjusted to 45 $^\circ$C. Thirdly, system was drained and flushed with osmosized water. After that, 3 ml/l HNO_3 60% (v/v) solution was pumped through the system for 15min. Finally, system wad drained again and flushed with osmosized water, untill the pH of the permeate stream appeared to be in neutral pH range.

4.4 Analytical Methods

4.4.1 Atomic Absorption Spectrophotometry (AAS)

Philips PU9200X atomic absorption spectrophotometry(AAS) was used in order to determine concentrations of cadmium, nickel and zinc in permeate and feed solutions.

For the analyses, acetylene-air flame AAS (FAAS) was used: Metal ions in the sample were atomized by nebulizer and air-acetylene flame. Background correction was achieved by means of deuterium lamp. At the beginning of each analysis, calibration of the instrument was performed by blank and standard solutions. Details of analysis procedure is given in Appendix A. Typical calibration curve for cadmium, zinc and nickel obtained during the analysis are depicted in Figure A.1, Figure A.2 and Figure A.3 in Appendix A.

In each measurement, samples were sucked three times and for each suction absorbance signal and corresponding concentration value in calibration curve were obtained. Average of the three signals and corresponding values of concentration was recorded to be the measured concentration of the sample.

4.4.1.1 Analysis of Polymer Containing Solutions

In the previous studies, it was found that, presence of PEI results in decrease in atomic absorption signals and as a consequence increase in PEI concentration in samples causes a decrease in measured metal concentrations [276]. This adverse effect of PEI on absorption signals should be taken into account while analyzing the samples taken from the feed stream, since these samples contain free PEI and/or PEI-metal complexes. For the samples taken from the permeate stream no extra treatment was needed to get accurate signals, since TOC analysis showed that PEI can be completely retained by the membranes selected for this study and permeate streams were free from PEI macromolecules.

In order to get rid of the adverse effect of PEI present in the feed samples, following approach was recommended for the correction of analysis results and to get accurate concentration values [98, 276]. According to the proposed approach, in order to reduce the effect of PEI, its concentration in the samples should be reduced by dilution to acceptable limits for detection of metals by AAS. Then, standard solutions containing same amount of PEI as in the diluted samples should be prepared in addition to the preparation of standard solutions without PEI. Then, the standard solutions of metals containing PEI were calibrated and absorbance of samples containing PEI with unknown concentrations of metals were measured and the concentrations were determined using these calibration curves.

Another important point that should be considered for the analysis of samples containing high amounts of salt is, during the suction of samples through the flame by the nebulizer, excess salt may cause clogging in nebulizer unit and because of the clogging effect flame may extinguished. In order to minimize the negative effects of salt concentrations, samples were diluted to acceptable limits for detection of metals by AAS.

4.4.2 Conductivity Measurements

Conductivities of the samples were measured by Jenway 4020 Conductivity meter. Prior to conductivity measurements, samples were nested in water bath which was adjusted to 25 °C. After temperature adjustment, conductivities of the samples taken from permeate and retentate streams were measured.

4.4.3 TOC Analysis

Total organic carbon (TOC) content of samples taken from feed and permeate streams were detected by Shimadzu 5000A TOC Analyzer in order to test the permeability of polymer through the membranes. In TOC measurements, high temperature burning method was applied to estimate total inorganic and organic carbon content of the samples.

4.4.4 Dynamic and Static Light Scattering Analysis

Stock solutions containing predetermined amounts of polymer and salt were prepared with Milli-Q water with R≈ % 18 MΩ·cm. 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 DLS/SLS experiments, samples were diluted and then filtered using a 0.4-mm filter, 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 10 different angles in the range of $60^\circ \leq \theta \leq 150^\circ$ and at 25 °C. For each angle three different measurements were performed and subsequently averaged. The data were normalized to absolute scale by using toluene as a reference material. For polyethleneimine (PEI) solutions the refractive index increment of the solution is taken as $(d_n/d_c = 0.2998 cm^3/g)$ which was determined in previous studies [253].

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 and form factor plots.

The average molecular weight, radius of gyration, hydrodynamic radius and second virial coefficient of the samples are calculated via Zimm plots where $(q^2 + Kc)$ is plotted versus Kc/R according to Equation 2.4.

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 (Mw) 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 5

RESULTS AND DISCUSSIONS

5.1 Conductivity Measurements

Besides the possible effects of salt concentration, the valency of the anions released by the dissolution of salts were thought to be an important parameter in ionic strength experiments. Therefore two different salts;1) $NaNO_3$, having monovalent anionic group and 2) Na_2SO_4, having divalent anionic group were selected and, in order to visualize the relationship between the conductivities of these salts in varying concentrations, conductivity profiles were obtained (Figure 5.1).

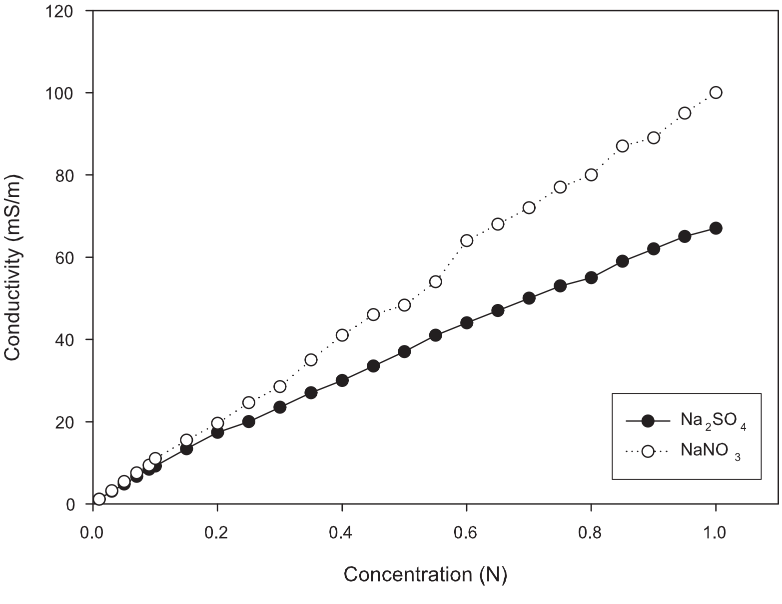


Figure 5.1: Conductivity Measurements of $NaNO_3$ and Na_2SO_4 at 25 °C

As it can be seen from Figure 5.1, when the salt concentration in solution is less than 0.25N, dissolution of either $NaNO_3$ or Na_2SO_4 causes tantamount increase in the conductivity of the solution. This equality in the conductivity values at low concentrations reveals that, in order to observe the effect of valency of anionic groups studies should be made at low salt concentrations ($< 0.25N$), to reduce the errors that may possibly occur due to the conductivity differences.

After examining the effect of salt type and concentration on the conductivity of different salt solutions, influence of pH and metal/polymer ratio on the conductivity of single component solutions containing different types of metals were investigated. In Table 5.1, conductivities of nickel containing solutions at different pH and loading values were given. The results in this table is a representative of other single component solutions containing same amounts of Zn and Cd at same acidity level.

The data presented in Table 5.1 reveal that, conductivities of the samples were slightly affected by the changes in metal/polymer ratio and pH. At the same pH level, increase in the metal/polymer ratio causes an increase in the conductivity of the solution, because the relative amount of free metal ions as compared to macromolecules increases. Same effect was also observed by the decrease of pH; excess H^+ ions increases the conductivity of the solution.

By looking at the results of conductivity measurements, it can be concluded that, interaction of free metal ions in the solution and membrane was minimum, uncomplexed free ions can pass through the membranes. For lower loadings, conductivities in permeate side was slightly decreased due to the reduction of ion concentrations in permeate side because of binding of ions by the polymer in the feed side.

In order to observe the effect of salt concentration on the conductivity of the solutions and on free metal ion-membrane interactions, conductivity measurements were performed for representative samples containing Cd^{2+} and varying amounts of $NaNO_3$. Results were given in Table 5.2 through Table 5.5.

As seen from the data in Tables 5.2- 5.5, with the addition of $NaNO_3$, depending on the salt concentration, 100-500 times increase was recorded in conductivities. Besides such a drastic effect of salt concentration, it is not meaningful to talk about the effect

Table 5.1: Conductivities of Single Component Ni Mixtures

Loading=0.05 pH 6

Time (min.)	Feed Conductivity at 25°C (mS/m)	Permeate Conductivity at 25°C (mS/m)
60	0.11	0.12
90	0.18	0.13
180	0.17	0.14
240	0.17	0.13

Loading=0.05 pH 5

Time (min.)	Feed Conductivity at 25°C (mS/m)	Permeate Conductivity at 25°C (mS/m)
60	0.20	0.14
90	0.19	0.15
180	0.20	0.14
240	0.19	0.14

Loading=1 pH 6

Time (min.)	Feed Conductivity at 25°C (mS/m)	Permeate Conductivity at 25°C (mS/m)
60	0.27	0.22
90	0.25	0.23
180	0.25	0.24
240	0.25	0.23

Loading=1 pH 5

Time (min.)	Feed Conductivity at 25°C (mS/m)	Permeate Conductivity at 25°C (mS/m)
60	0.33	0.24
90	0.31	0.20
180	0.29	0.32
240	0.34	0.27

Table 5.2: Conductivity of Cd Solutions in the Presence and Absence of 0.1N $NaNO_3$

Cd (No $NaNO_3$)	Loading=0.05	pH 6
Time (min.)	Feed Conductivity at 25 °C (mS/m)	Permeate Conductivity at 25 °C (mS/m)
60	0.21	0.18
90	0.23	0.20
180	0.30	0.27
240	0.34	0.28

Cd (No $NaNO_3$)	Loading=0.7	pH 5
Time (min.)	Feed Conductivity at 25 °C (mS/m)	Permeate Conductivity at 25 °C (mS/m)
60	0.28	0.36
90	0.34	0.34
180	0.33	0.34
240	0.34	0.35

Cd + 0.1N $NaNO_3$	Loading=0.05	pH 6
Time (min.)	Feed Conductivity at 25 °C (mS/m)	Permeate Conductivity at 25 °C (mS/m)
60	10.25	9.38
90	9.67	9.42
180	9.66	9.50
240	9.71	9.53

Cd + 0.1N $NaNO_3$	Loading=1	pH 6
Time (min.)	Feed Conductivity at 25 °C (mS/m)	Permeate Conductivity at 25 °C (mS/m)
60	10.15	9.39
90	9.33	9.23
180	9.23	9.33
240	9.12	9.15

Table 5.3: Conductivity of Cd Solutions in the Presence of 0.25N $NaNO_3$

Cd + 0.25N $NaNO_3$	Loading=0.1	pH 6
Time (min.)	Feed Conductivity at 25°C (mS/m)	Permeate Conductivity at 25°C (mS/m)
60	20.3	19.7
90	21.2	20.3
180	20.6	20.1
240	20.0	20.0

Cd + 0.25N $NaNO_3$	Loading=1	pH 5
Time (min.)	Feed Conductivity at 25°C (mS/m)	Permeate Conductivity at 25°C (mS/m)
60	21.5	20.7
90	21.8	21.3
180	20.2	20.4
240	20.0	19.8

Table 5.4: Conductivity of Cd Solutions in the Presence of 0.5N $NaNO_3$

Cd + 0.5N $NaNO_3$	Loading=0.05	pH 6.5
Time (min.)	Feed Conductivity at 25°C (mS/m)	Permeate Conductivity at 25°C (mS/m)
60	42.0	42.0
90	42.0	42.0
180	42.0	42.0
240	42.0	42.0

Cd + 0.5N $NaNO_3$	Loading=1	pH 6.5
Time (min.)	Feed Conductivity at 25°C (mS/m)	Permeate Conductivity at 25°C (mS/m)
60	43.0	43.0
90	43.0	43.0
180	43.0	43.0
240	43.0	43.0

Table 5.5: Conductivity of Cd Solutions in the Presence of 1N $NaNO_3$

Cd + 1N $NaNO_3$	Loading=0.01	pH 6
Time (min.)	Feed Conductivity at 25 °C (mS/m)	Permeate Conductivity at 25 °C (mS/m)
60	93.7	85.9
90	86.9	86.3
180	87.3	86.5
240	87.1	86.5

Cd + 1N $NaNO_3$	Loading=0.7	pH 6
Time (min.)	Feed Conductivity at 25 °C (mS/m)	Permeate Conductivity at 25 °C (mS/m)
60	93.7	85.9
90	90.1	86.3
180	88.2	86.5
240	87.1	84.2

of pH and/or metal/polymer ratio on conductivity in the presence of salt. It is also important to note that, conductivities of permeate and feed streams did not show significant differences which means interaction of free metal ions in the solution and membrane was negligible, uncomplexed free ions can pass through the membrane and counterbalance the conductivities on both sides of the membrane.

5.2 Characterization of PEI by DLS/SLS Methods

The data obtained by static and dynamic light scattering measurements were processed by utilizing the governing equations of Zimm method. The typical Zimm plots of the PEI solutions, calculated by ALV-5000 & 60X0 software is given in Appendix B and parameters extracted from Zimm plots were listed in Table 5.6.

The data in Table 5.6 indicate that, solution pH has no significant effect on the hydrodynamic radius (R_H) of PEI. On the contrary, radius of gyration (R_g) tends to decrease with decreasing pH. Molecular weight of PEI macromolecules was estimated to be 7.9x10^3 which was slightly higher than the values stated by the supplier (in the specification sheet of PEI, average molecular weight was reported to be 6x10^3). Positive second virial coefficients (A_2) indicates the repulsion between

Table 5.6: Zimm Plot Data for PEI/Water Solutions at Different pH Values

Sample	$R_g(nm)$	$R_H(nm)$	R_g/R_H	A_2 $(dm^3.mol/g^2)$	Mw (g/mol)
PEI (pH 6)	$75 \pm 7.3\%$	$57 \pm 8.3\%$	1.3	1.63x10^{-5}	7.9x10^4
PEI (pH 5)	$56 \pm 8.3\%$	$55 \pm 10.1\%$	1.1	7.99x10^{-6}	7.9x10^4
PEI (pH 4)	$49 \pm 6.7\%$	$55 \pm 7.7\%$	0.88	7.99x10^{-6}	7.9x10^4

molecules. Hydrodynamic radius of PEI which was estimated to be 57nm at pH 6 and 55nm at pH 5 and pH 4 are in agreement with the values reported in the study of Bastardo [253] such that; R_g was found to be between 50-60nm in the pH range of $5 < pH < 10$.

To comment on the impacts of parameters like; R_g, R_H and A_2 on PEI conformation, preferential consideration should be given to understand the physical meanings of these parameters. For instance, 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. R_H characterizes hydrodynamic interactions and indicates how deeply a particle is drained by the solvent: a deep draining causes a reduction in R_H [238]. In the light of this definitions, it can be said that, decrease in pH did not cause extra draining on PEI molecules and as a consequence R_H values stay almost constant. Conversely, R_g tends to decrease with the decrease in pH which indicates that, PEI molecules became more tidy at low pH values.

The direct combination of radius of gyration and hydrodynamic radius leads to useful dimensionless parameter designated as R_g/R_H. By this parameter, structure of the molecule can be predicted. It was stated that, the polydispersity causes an increase of R_g/R_H whereas branching leading to a decrease. For randomly branched chains both effects balanced out. In Table 5.7, R_g/R_H values of typical molecular structures were given [277].

When the R_g/R_H values found for PEI molecules at different pHs (Table 5.6) were compared with the ones presented in Table 5.7, it can be said that, at pH 6 and pH 5

Table 5.7: R_g/R_H Values of Typical Molecular Structures

R_g/R_H	Molecular Structure
$(3/5)^{1/2} = 0.775$	Uniform non draining sphere
$1.0 - 1.3$	Hyperbranched polymer cluster
1.504	Linear coil chain

PEI molecules posses the hyperbranched structure. However at pH 4, conformation of PEI molecule was predicted to lie between uniform sphere and hyperbranched chain.

5.2.1 Effect of Ionic Strength on Conformation of PEI

In order to have a general idea about the salt effect on the conformation of PEI molecules, DLS/SLS measurements were performed for PEI solutions containing varying amounts of $NaNO_3$ salt. Experiments were performed at pH 6 and at 25°C. R_g, R_H and 2^{nd} Virial Coefficient of the samples were estimated and tabulated in Table 5.8.

Table 5.8: Zimm Plot Data for PEI/$NaNO_3$ Solutions

Sample	$R_g(nm)$	$R_H(nm)$	$A_2(dm^3.mol/g^2)$
PEI (No $NaNO_3$)	$5 \pm 9.6\%$	$57 \pm 5.7\%$	1.6x10^{-5}
PEI + 0.1N $NaNO_3$	$72 \pm 8.5\%$	$43 \pm 8.6\%$	5.1x10^{-7}
PEI + 0.25N $NaNO_3$	$57 \pm 7.6\%$	$41 \pm 9.6\%$	1.1x10^{-6}
PEI + 0.5N $NaNO_3$	$48 \pm 9.8\%$	$39 \pm 5.9\%$	1.4x10^{-6}

As compared to the values obtained in the absence of $NaNO_3$ (Table 5.6), decrease in radius of gyration, hydrodynamic radius and 2^{nd} virial coefficient was observed by the addition of $NaNO_3$ (Table 5.8). This phenomena may be explained as follows; an association, defined as the reversible formation of physical bonds between chemical groups, occurs due to intra and intermolecular forces. In case of intramolecular association polymer coils become more compact. Since the polymer molecules become more compact by intra-molecular association, 2^{nd} virial coefficient decreases with the addition of $NaNO_3$, but remains positive indicating the repulsion between molecules [278].

R_g/R_H of 1.38 and 1.24 for PEI solutions containing 0.25 and 0.5N $NaNO_3$ respectively proves that PEI molecules persist hyperbranched conformation even at high ionic strength.

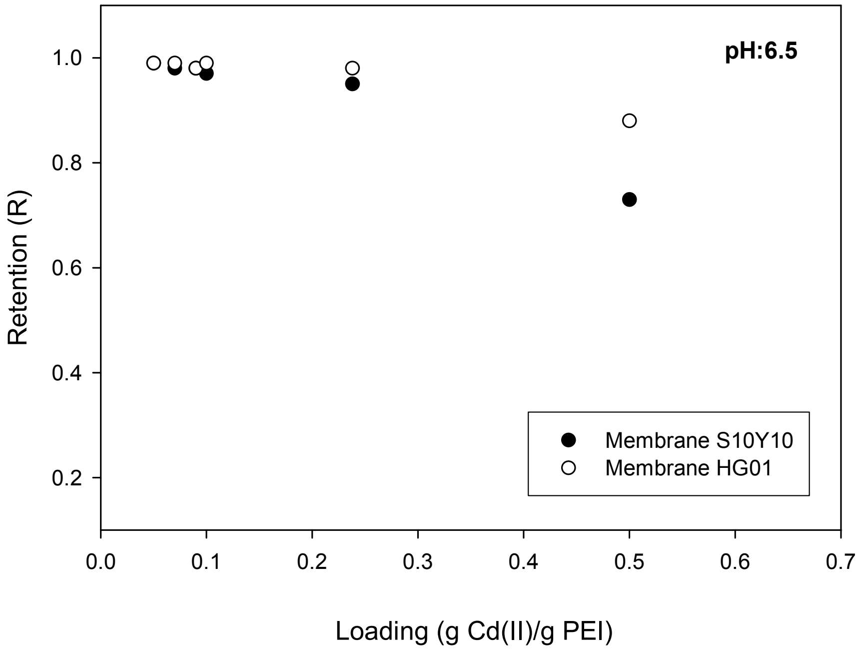
5.3 PEUF Experiments

5.3.1 Selection of Membrane Material and Configuration

In order to select suitable membrane for the operation, membranes with different material and configurations were employed in pilot-scale and laboratory scale ultrafiltration system. In pilot-scale system spiral wound regenerated cellulose membrane (S10Y10) having a molecular weight cut-off of 10000Da and effective area of $0.93m^2$ and in laboratory scale system flat sheet membranes having a molecular weight cut-off of 5000Da and effective area of $155cm^2$ and made of polysulfone (HG01) was used. Performance of the membranes were compared by observing the retention profile of cadmium in different pH and loading values in both laboratory and pilot scale systems (Figure 5.2). Data tables for Figure 5.2 were given in Appendix C.

As it can be observed from Figure 5.2, retention values are somewhat lower in pilot scale system as compared to lab-scale system especially at high loading values (i.e., higher free ion concentrations). Differences between retention profiles obtained in two different systems may be due to the different characteristics of the membranes employed. Membrane used in the pilot-scale system is a spiral wound cellulosic ultrafiltration membrane whereas HG01 (membrane employed in lab-scale system) is reported to be used in both nanofiltration and ultrafiltration applications and it is known that nanofiltration membranes may be charged.

In the previous studies, membrane HG01 was characterized by observing the salt rejection performance of the membrane. Salt rejection of HG01 is found to be in order of: $R(Na_2SO_4) > R(NaCl) > R(CaCl_2)$, which is typical for a negatively charged



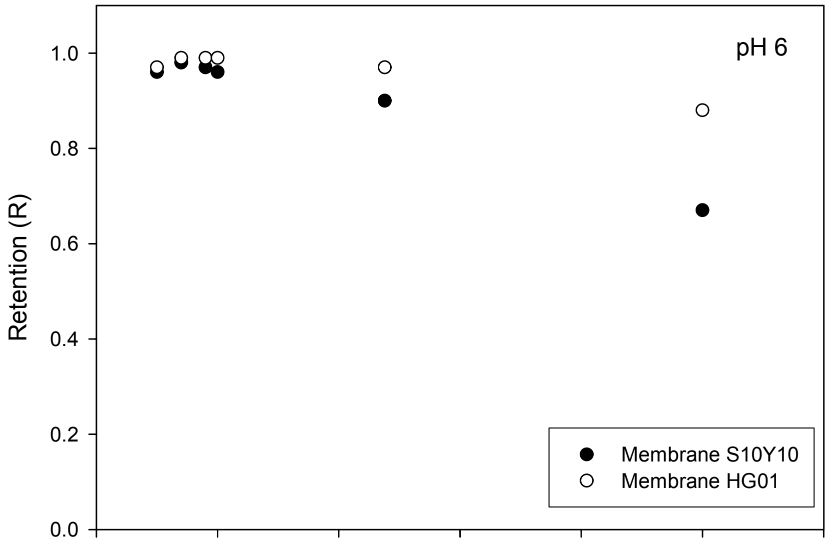


Figure 5.2: Retention Profiles of Cd^{2+} in Pilot Scale (Membrane S10Y10) and Lab Scale (Membrane HG01) Systems at pH 6.5 and 6

membrane [90].

Sample solutions in this study were prepared by $NaOH$, HNO_3, $NaNO_3$, $Cd(NO_3)_2.4H_2O$ and PEI. Therefore unbonded ions that were present in the solution were likely to be Na^+, Cd^{2+} , OH^- and $(NO_3)^-$. Because the membrane HG01 may posses a negatively charged surface, cations could be pulled by the membrane and the concentration of the cationic materials may become higher in the membrane phase. This adsorptive behavior of membrane HG01 may result in the higher retention values. In order to test this suggestion and examine the reproducibility of results, experiments were repeated four times within the period of four weeks and results were depicted in Figure 5.3.

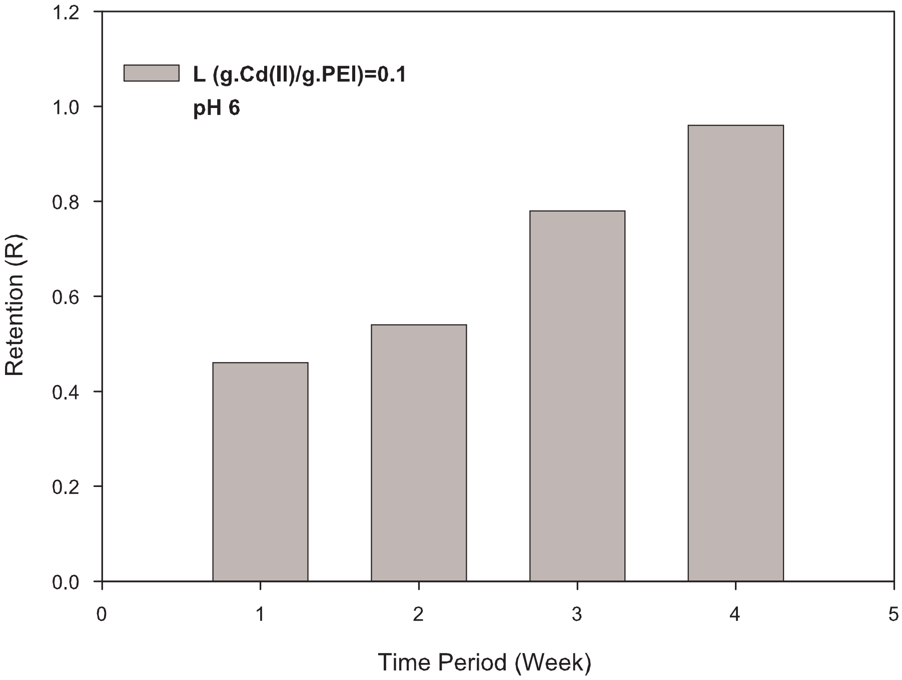


Figure 5.3: Performance of the Membrane HG01

As depicted in Figure 5.3, because of the adsorptive nature of membrane HG01, retention increases by the time and as a consequence of poor reproducibility, no reliable data can be taken from the experiments performed by using membrane HG01. To improve the reproducibility of the results, the membrane was washed with 0.1 M $NaOH$ and then with distilled water after each run, till the pH of the circulating water reaches neutral pH range. By applying this cleaning procedure after each experimental run, fouling effects were minimized and hence retention drop was observed (Figure 5.4) but considerable improvement in reproducibility can not be achieved.

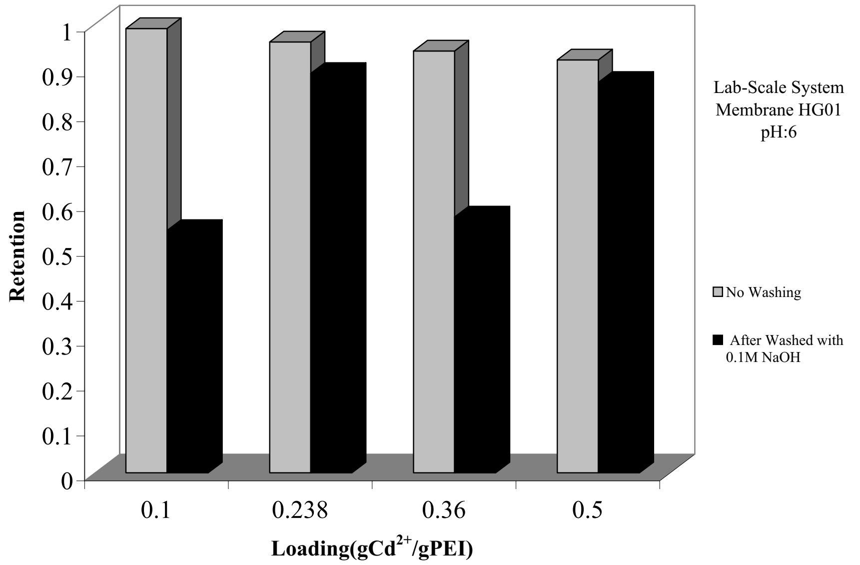


Figure 5.4: Effect of Membrane Cleaning on Retention in Lab-scale System

In order test the performance of other flat sheet membranes, characterization experiments were performed. Since the permeate water flux and molecular weight cut-off of the membranes are the important parameters in membrane selection, as a first step, fluxes of the membranes having different MWCO were measured (Table 5.9).

Table 5.9: Specifications of Sepa CF Flat Sheet Membranes

Membrane	Molecular Weight Cut-Off	Permeate Water Flux ($l./m^2.h$)
HG01	5000Da	9.68
HG19	20 000-3000 Da	96.78
HG09	20 000-3000 Da	10.75
AG08	10 000-3000 Da	446.65

Among the membranes given in Table 5.9, AG08 gives the highest permeate water flux. As far as the flux data was concerned, performance of AG08 and HG19 seem to be high, however in order to test the eligibility of the membranes for this study, in addition to flux measurements, polymer retention tests were made. Extent of PEI retention was examined by TOC analysis and results were presented in Table 5.10.

Table 5.10: Results of TOC Analysis

Membrane	TOC of feed stream (ppm)	TOC of permeate stream (ppm)
HG19	2615.1	111.15
HG09	2478.6	3.289
AG08	2552.1	3.30

The results showed that HG19 is not suitable for the experiments, because low molecular weight PEI fractions may pass through the membrane. On the other hand, HG09 and AG08 show promising performance for the rejection of polymer. In order to test the performance of membrane AG08, experiments were performed in lab scale system with solutions containing Cd^{2+} and varying amounts of PEI and obtained results were compared with the data taken from the pilot scale system (Figure 5.5 and Figure 5.6).

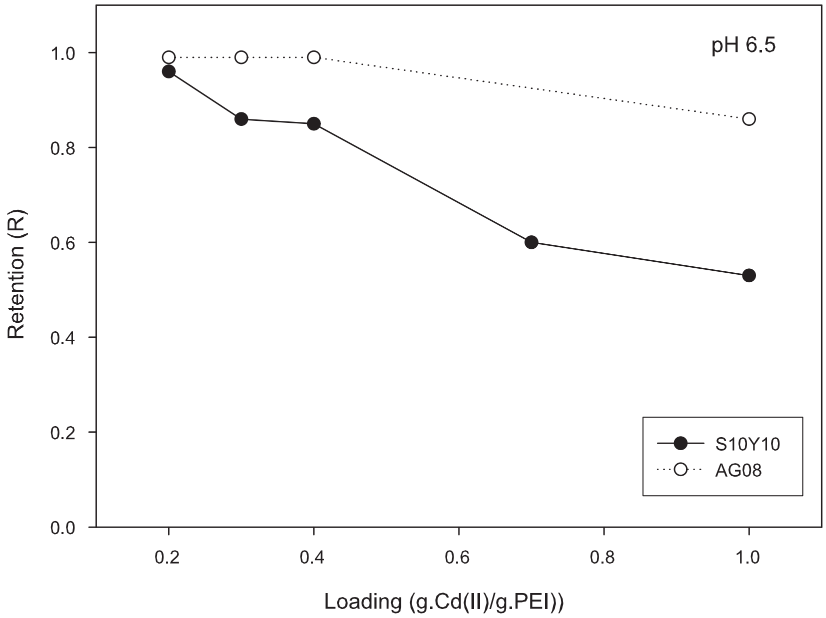


Figure 5.5: Retention Profiles of Cd^{2+} in Pilot Scale (Membrane S10Y10) and Lab Scale (Membrane AG08) Systems at pH 6.5

As it can be seen from Figure 5.5 and Figure 5.6, even at high loading values (i.e., L=0.5, 1) extent of retentions was high for membrane AG08, which reveals that,

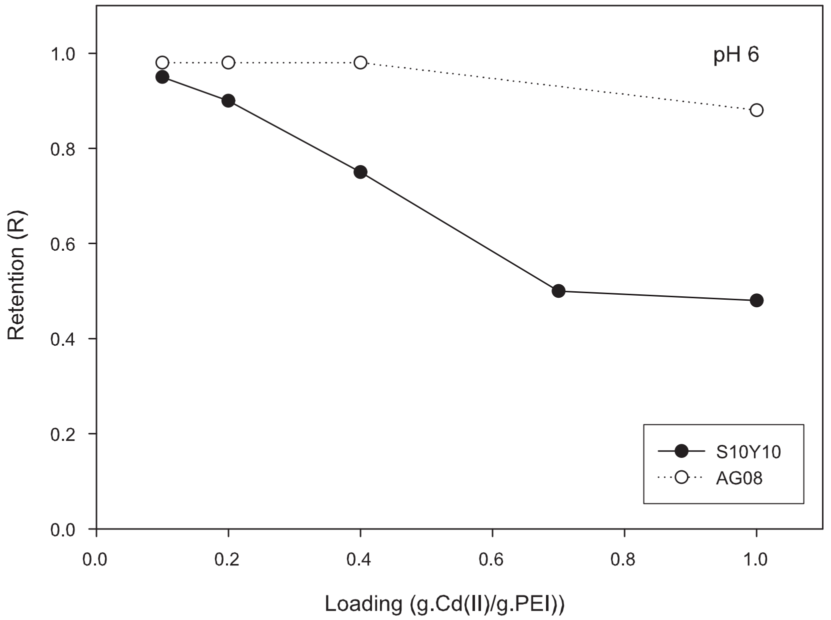


Figure 5.6: Retention Profiles of Cd^{2+} in Pilot Scale (Membrane S10Y10) and Lab Scale (Membrane AG08) Systems at pH 6

membrane AG08 has tendency to adsorb the solutes in feed solutions. Because of this adsorption tendency and poor reproducibility of the results obtained from the experiments performed with AG08, for the rest of the study pilot scale system and membrane S10Y10 which was made of regenerated cellulose was used.

5.3.2 Pilot Scale PEUF Experiments

In pilot scale PEUF experiments to ensure the time period required to reach the steady state, starting from the 15^{th} minute representative samples were taken from both permeate and feed streams in different time intervals. Concentration of the solutions and corresponding retention and flux values were presented in Table 5.11, for two typical runs. Rest of the representative unsteady and steady state data for different experimental runs were given in Appendix D.

Only small fluctuations were observed in both feed and permeate concentrations as a function of time. But R values were observed to stay constant after 1.5 hour of operation, indicating that steady state can be reached within 90 minutes. As also demonstrated in this table, permeate fluxes were constant throughout the

Table 5.11: Unsteady State Data for PEUF Experiments

Loading= Cd^{2+}/PEI=0.05 pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux $lt./m^2.h.$
15	14.7	0.39	0.97	9.87
30	14.6	0.42	0.97	9.87
60	14.3	0.40	0.97	9.87
90	14.3	0.34	0.98	9.87
120	14.3	0.35	0.98	9.87
150	14.3	0.33	0.98	9.87
180	14.3	0.33	0.98	9.87
210	14.3	0.33	0.98	9.87
240	14.3	0.33	0.98	9.87

Loading= Cd^{2+}/PEI=0.7 pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux $lt./m^2.h.$
15	15.6	6.80	0.56	10.75
30	15.3	6.66	0.56	10.75
60	14.9	6.50	0.56	10.75
90	15.1	6.00	0.60	10.75
120	15.0	6.00	0.60	10.75
150	15.0	6.00	0.60	10.75
180	15.0	6.00	0.60	10.75
210	15.0	6.00	0.60	10.75
240	15.0	6.00	0.60	10.75

experimental runs. This situation is valid for all experimental runs regardless of the solution composition (i.e., single, binary and ternary component solutions) and salt concentration.

The reproducibility of experiments has been examined by multiple measurements. As a representative example, time dependent retention data for Cd^{2+} solution, was given in Table 5.12. The reliability of the data reported is ensured by the satisfactory agreement of the experimental results obtained in different dates.

If the molecular mass of polymer is too high, this may results in a high viscosity of the

Table 5.12: Reproducibility of the Retention Data Obtained from Pilot Scale System

Date	Loading	pH	Retention
11.03.2006	0.1	6	0.95
18.05.2006	0.1	6	0.97
07.06.2006	0.1	6	0.97

solution when such a polymer is added to it and as a consequence permeate flux may decrease with increasing polymer concentration in feed solution. Table 5.13 shows the loading and corresponding permeate flux values for the representative samples containing nickel ions and varying amounts of PEI.

Table 5.13: Effect of PEI Concentration on Permeate Flux (Δ P=6kPa, pH 6)

Loading (g.Ni(II)/g.PEI)	Permeate Flux $lt./m^2.h$
0.05	9.45
0.1	9.68
0.2	9.68
0.5	10.11
1	12.13

As it can be seen from Table 5.13, for the studied range of polymer concentration ($0.05 < L < 1$), permeate flux was slightly reduced by the increase in polymer concentration. However, those flux changes are relatively insignificant. Same trend was also observed in the other experiments performed with solutions containing single, binary, tertiary components of Cd, Ni and Zn ions both in the absence and presence of salt (Refer to the tables in Appendix D).

This result also indicates that there is no significant change in viscosity because of the increase in polymer concentration, which is consistent with the fact that; the viscosity value of branched PEI is almost constant over the wide range of pH 2-11 in an aqueous solution. Branched PEI does not cause the conformation change of polymer chains in aqueous solution probably due to a highly branched globular structure. This viscosity behavior is observed both for low and high molecular weight branched PEIs [168].

Steady state metal rejection results of PEUF experiments were discussed in three parts:

In the first part of the experiments, in order to evaluate and compare more completely the complexation potentiality of PEI towards divalent ions of cadmium, nickel and zinc and to investigate the impact of ionic strength on the complexation mechanism, ultrafiltration experiments were performed after the completion of complexation reaction taking place between PEI macromolecules and heavy metal ions.

In the second part, possibility of selective separation of heavy metal ions from aqueous solutions containing equimolar $Cd^{2+} - Ni^{2+}$, $Cd^{2+} - Zn^{2+}$ and $Ni^{2+} - Zn^{2+}$ metal mixtures, was investigated and the effect of increasing $NaNO_3$ concentration on the effectiveness of fractional separation was examined.

In the third part, PEUF experiments were performed with solutions containing equimolar mixtures of $Cd^{2+} - Ni^{2+} - Zn^{2+}$. Changes in the binding ability of metals in single and ternary metal mixtures were investigated.

5.4 PEUF Experiments with Single Metal Solutions

5.4.1 Effect of pH and Loading

Complexation tests for metals were made with 15 ppm metal solutions and varying polymer concentrations in the range where metal/polymer ratio remains between 0.05 and 1. Since the previous study of Uludag [188] showed that, retention is dependent on metal/polymer ratio rather than their individual concentrations, throughout the experiments, metal concentration was kept constant at 15ppm and only relative amounts of metal and polymer were changed.

It is also important to note that, for the loading values lower than 0.01 (100:1 polymer:metal concentration ratio) decrease in retention was observed probably because of the decrease in the solubility of PEI and hence inefficiency in complex formation. To ensure favorable conditions for the process in further parts of the research, a maximum of 10-fold weight excess of the polymer with respect to the amount of metal present in the feed was used.

Although complexation period of 2 hours is found to be sufficient to achieve complexation equilibria [134], PEI-metal mixtures were left for complexation for 12 hours throughout this study.

In Figure 5.7, retention of cadmium ions at different acidity levels and metal/polymer ratios are shown. Data tables for the figures showing the retention profiles of single component metal solutions are given in Appendix E.

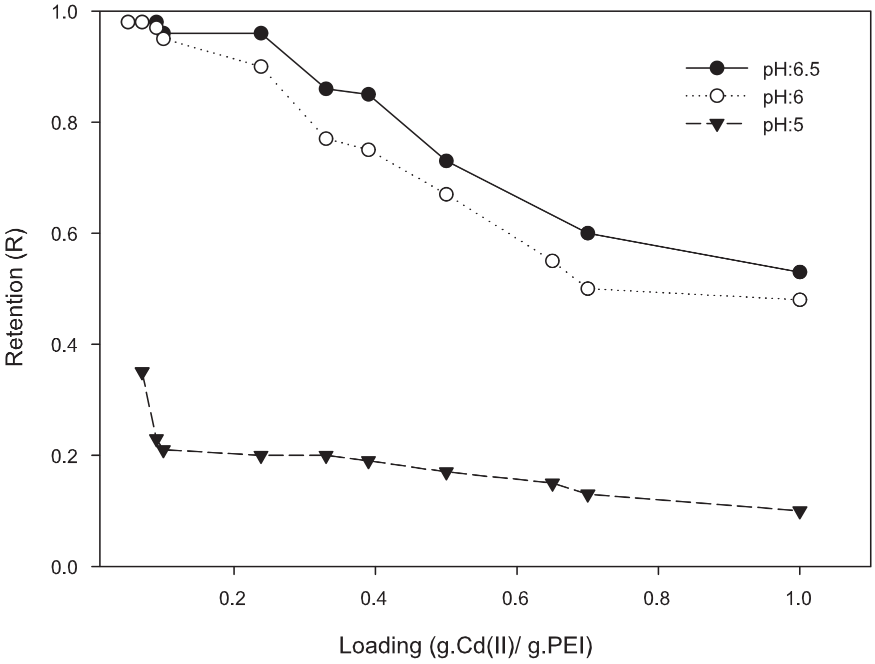


Figure 5.7: Effect of pH and Loading on the Retention Profile of Cd^{2+}

As seen from the figure, pH has very profound effect on Cd^{2+}-PEI complexation and as a consequence on the amount of Cd^{2+} retained by the membrane.

The extent of binding of Cd^{2+} by PEI at pH 6.5 and pH 6 was considerably superior to that at pH 5. At low loadings, retention values were almost same and almost equal to 1 at pH 6.5 and pH 6 which means; almost complete retention of cadmium ions can be achieved when the amount of polymer is at least 10 fold higher than the amount of metal in solution. As the metal/polymer ratio increases, effect of pH can be seen more clearly since the retention values at pH 6 becomes lower than the retention values obtained at pH 6.5. This result is consistent with the results of previous studies in which it was reported that, cadmium is highly responsive to pH alternation, and complexation reaction between cadmium and PEI is favorable at pH 6.5 [119, 134]. When pH was reduced down to pH 5, process enabled a maximum retention of only 35%. Depending on loading values, 50-70% reduction in the amount of metal rejection was recorded as a consequence of pH reduction from pH 6.5 to pH 5.

Such a strong dependence of the retention coefficients on the acidity level of the solution may result from the changes in the binding ability of PEI at different pHs. At higher pHs, amine groups are more available and can coordinate more easily with the metal ions. It was determined that only 0.00001% of the amine groups were deprotonated at pH 3, whereas at pH 5, the value reached 0.001%, and at pH 7, it was 0.1% [189]. This means that there is a strong competition between the metal ions and protons for the electron pairs in the amine groups of PEI. This competition is favored for the metal ions at higher pH values, therefore effective binding of metal ions to the active sites of PEI molecules takes place at high pH levels.

In literature there are also other studies related with the characterization of polychetalogen-metal binding, in one of them poly(1-vinyl-2-pyrrolidone-co-hydroxyethylmethacrylate), polymer having chelation properties was reported to be effectively bind Cd(II) ions in the pH range of ($3 < pH < 7$). At pH 3, amount of cadmium retention was recorded to be 89% [279]. As compared to results of PEI-Cd^{2+} complexation tests, PEI was observed to be more sensitive than that of poly(1-vinyl-2-pyrrolidone-co-hydroxyethylmethacrylate) against the pH changes. This may be regarded as a valuable property since linking of Cd ions with PEI ligands is a reversible process, it is possible to regenerate the retentate containing PEI-Cd^{2+} complex, in order to recover the metal and complexing agent by reducing the pH down to 5 and introducing a successive ultrafiltration stage.

As far as pH effect is concerned, same trend as in the case of Cd^{2+}-PEI binding was also observed for Ni^{2+} (Figure 5.8). Binding of Ni^{2+} with PEI is favorable at pH 6.5 and pH 6 and the extent of complexation is decreased markedly when the pH of the solution is reduced down to pH 5. Depending on the amount of polymer in the solution 40-98% and 35-96% of Ni^{2+} can be retained by the membrane at pH 6.5

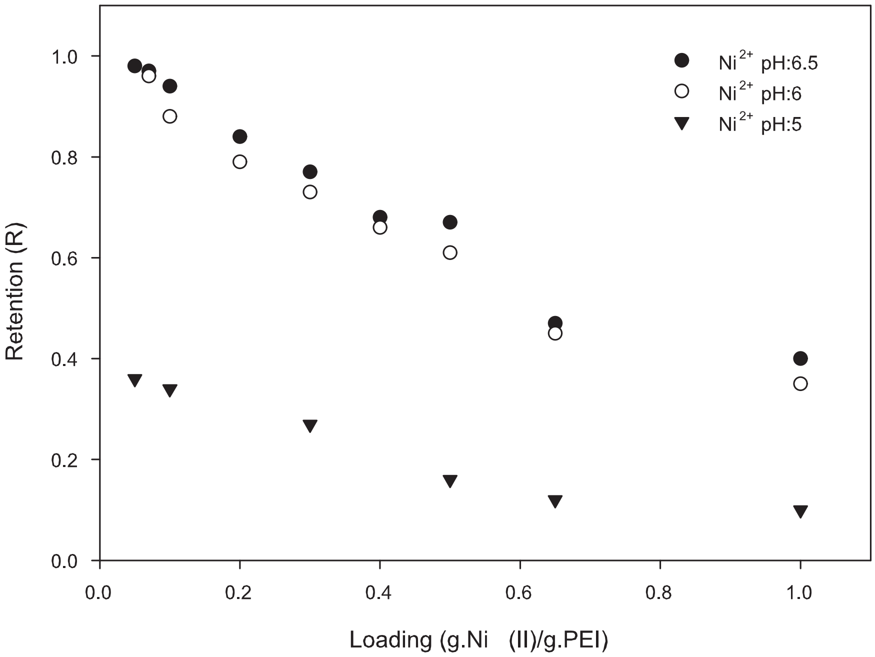


Figure 5.8: Effect of pH and Loading on the Retention Profile of Ni^{2+}

and pH 6 respectively. But when the pH is reduced to 5, because of the inhibition of binding ability of PEI due to protonation of amine groups, Ni^{2+} retention is decreased and the maximum retention was recorded to be 34%.

Same recovery ratios were also obtained in separation process performed by polyacrylate such that, in the acid medium (pH 2 and pH 4), Ni(II) retention was observed to be 10-30%. However with the increase in pH up to 8, almost complete retention can be achieved [118].

Previous studies conducted with $PEI - Ni^{2+}$ solution at pH 7, 5 and 3, showed that more than 50% and 80% retention can be achieved at pH 5 and pH 7 respectively but the chelation ability of PEI was reported to be inhibited at low pH values and only 10-15% of Ni^{2+} can be complexed with the PEI at pH 3 [223]. Few experiments were performed with Ni^{2+} at pH 7, in order to test the pH sensitiviy of $PEI - Ni^{2+}$ complexation system, results of these experiments are given in Figure 5.9.

As seen in Figure 5.9, almost same retention values were obtained at pH 7 and pH

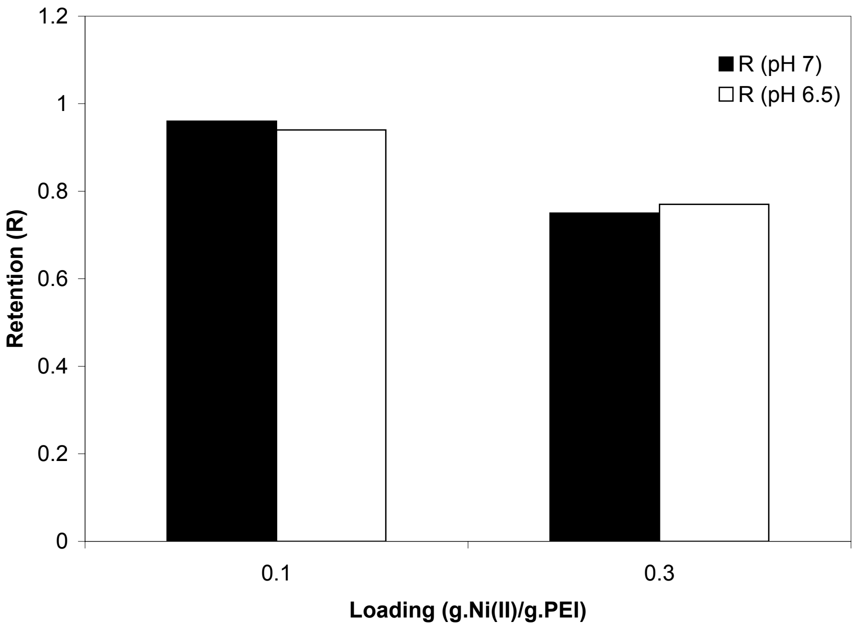


Figure 5.9: Comparison of Ni^{2+} Retention at pH 7 and pH 6.5

6.5 for the same metal/polymer ratios. Although PEI showed similar binding ability towards Ni^{2+} ions both at pH 7 and pH 6.5, for the rest of the nickel experiments and other single and binary metal experiments pH 7 was not preffered as an operational parameter, because heavy metal ions tend to form insoluble hydroxy complexes at high pH values which may render metal-polymer complexation. Especially for zinc and nickel, metal-hydroxy complexes start to form at pH 7.5 and pH 8.5, respectively. For cadmium probability of formation of cadmium-hydroxy complexes is high at pH 10 [280].

It is important to note that, very little attention has been paid to nickel(II) in the previous studies. It is probably because nickel(II) leads to electrochemically irreversible systems [137]. The results of nickel experiments with PEI showed that, Ni^{2+}-PEI complexation is a reversible process and as a consequence at high pH values Ni^{2+} can be removed from aqueous solutions. Then at low pH values it is possible to regenerate the retentate containing PEI-Ni^{2+} complex to recover the metal and complexing agent by introducing a successive ultrafiltration stage.

Binding ability of Zn^{2+} with PEI was tested in the pH range of 3-6.5 (Figure 5.10). It

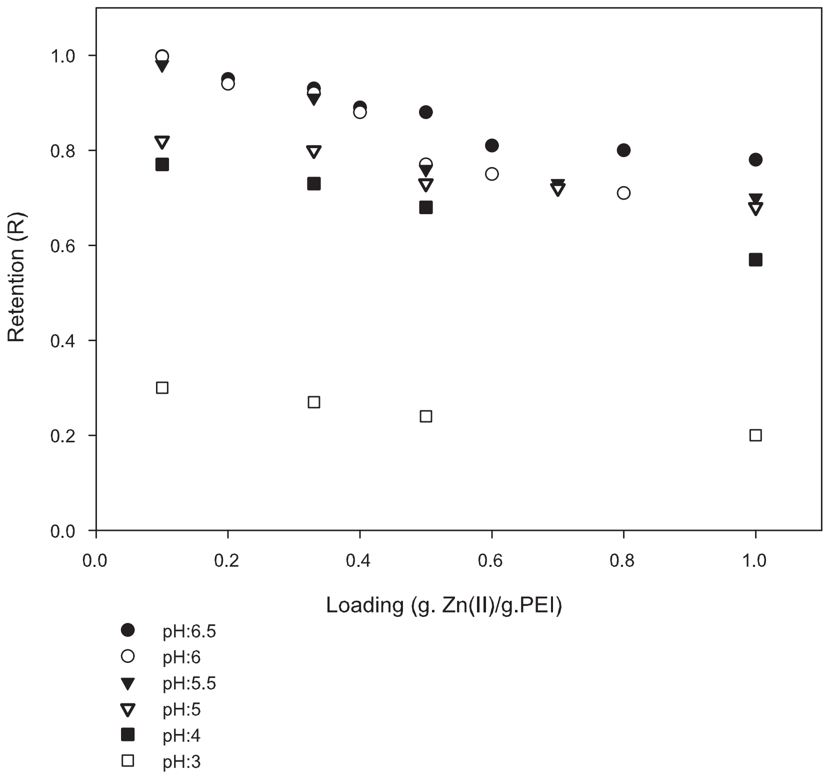


Figure 5.10: Effect of pH and Loading on the Retention Profile of Zn^{2+}

was observed that, almost complete retention can be achieved at high pH values. In addition, PEI molecules retained zinc ions effectively down to pH 4. Zn^{2+} retention slightly decreased between pH 6.5 and 4, then steep decrease (50-70%) in retention was observed at pH 3 because the protonation of amine groups leads to the release of zinc ions.

The effect of pH on zinc rejection is analogous to that of Cd^{2+} and Ni^{2+}, at pH 6.5 and 6, but in contrast to this similar behavior seen in high pH s. At pH levels of 5 and less than 5, retention profile Zn^{2+} ion is distinguished from the that of Ni^{2+} and Cd^{2+} ions in such a way that, at pH 5 neither Ni^{2+} nor Cd^{2+} ions can be retained significantly whereas 80% of Zn^{2+} retention can be achieved at that acidity level.

At pH 3, maximum of 30% Zn(II) retention can be achieved with PEI which is a quite low value as compared to 87% Zn(II) retention at same acidity level but in the presence of poly(1-vinyl-2-pyrrolidone-co-hydroxyethylmethacrylate) (P(NVP-co-HEMA)) which is a kind of polychetalogen like PEI [279]. From an engineering point of view, process optimization can be made with the aid of distinguishing properties of several metal-polychetalogen interactions, such that: If it is desired to remove zinc ions from the aqueous solutions at low pH values, it may be better to use polychetalogens like (P(NVP-co-HEMA)), which have high affinity towards zinc even at low pH values. On the other hand, if the aim is to recover both the metal ions and polymer, performing PEUF operation in the presence of polychetalogens like PEI may be a good alternative. By this way, zinc ions can be removed from the aqueous solutions at high pH values and both polymer and metal ions can be recovered by the regeneration of polymer-metal complexes at low pHs.

It is known that, in general, cadmium compounds exhibit properties similar to the corresponding zinc compounds [10], but as far as the pH effect is concerned, in the presence of PEI and at low pH values cadmium and zinc exhibit different behaviors. This distinct behavior of zinc at low pH can be explained by its amphoteric nature; zinc compounds can dissolve in both basic and acidic medium [10]. Cadmium and/or nickel ions may exist in different forms depending on the pH of the medium. For example, nickel may exist in the form of $(HNiO_2)^-$, NiO, Ni_3O_4, Ni_2O_3 [281] and cadmium may exist in the form of $(HCdO_2)^-$, CdO [281] in aqueous solutions at different pH values. But by courtesy of the amphoteric nature, zinc persists its ionic form Zn^{2+} even in highly acidic medium and as a consequence does not loose complexation ability at low pH values.

For the removal of divalent zinc ions, polyacrylate was also reported to be effectively used at high pH values. On the contrary, in acidic medium (pH 2 and pH 4), polyacrylate can retain only 20-40% of Zn(II) [118]. Polyethylene glycol and diethylaminoethyl cellulose were the other examples of polymers used in Zn(II) removal by PEUF. It was reported that, complete retention of Zn(II) can only be achieved at pH values around pH 9. At the pH values lower than pH 6.5, only 30% and 40% of Zn(II) can be retained in the presence of polyethylene glycol and diethylaminoethyl respectively [282].

By looking at the retention profiles of cadmium, nickel and zinc ions it can be concluded that PEI has high binding ability towards these metals at high pHs. This result is consistent with the data cited in literature since it is known that cations such as copper(II), silver(I), cadmium(II), nickel (II) and zinc(II), form stable amine complexes in aqueous solutions. For these metals, the metal-amine bond is significantly stronger than the metal-water bond [232]. Altough PEI has proven ability to bind metallic cations, depending on the type of metal, strength of the PEI-metal bond and influence of pH on metal-polymer binding may be different.

In order to determine the binding order of metals, retention profiles of three metals at different pH and loading values were compared (Figure 5.11). In the studied pH range binding order was found to be $Zn^{2+} > Cd^{2+} > Ni^{2+}$, which is consistent with the literature. In a previous study, measurements have been made to investigate the binding of divalent metal ions of Cu, Ni, Co and Zn by PEI, and it was found that the order of binding is $Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$ at lower loading ratios, but higher free ion concentrations reverse the situation because of the steep rise in binding for Zn^{2+}: The Zn^{2+} ion is bound much more strongly than any other metal ion at high loading values [283]. In other studies, for nickel, zinc and copper binding with PEI, the order of binding is found to be $Zn^{2+} > Ni^{2+} > Cu^{2+} >$ at pH 3.5 [144] and for the uptake of heavy metals from synthetic aqueous solutions using modified PEI-silica gels, the binding order of the metals was reported to be Zn>Cd>Ni [284].

As seen from Figure 5.11, predominance of zinc retention over nickel and cadmium retentions was most clearly observed at pH 5. This is expected since, PEI-Zn^{2+} interaction was favorable over those of PEI-Cd^{2+} and PEI-Ni^{2+} interactions.

Together with the results of single component metal experiments, binding order of metals found in literature point out the significant binding ability of zinc over cadmium and nickel. In order to find out the possible reasons of favorable binding of Zn ions over that of Ni and Cd, and the distinctions in the pH dependency of metals in the complexation reactions, it is important to analyze the properties of both PEI and metal ions that may play important roles in complex formation.

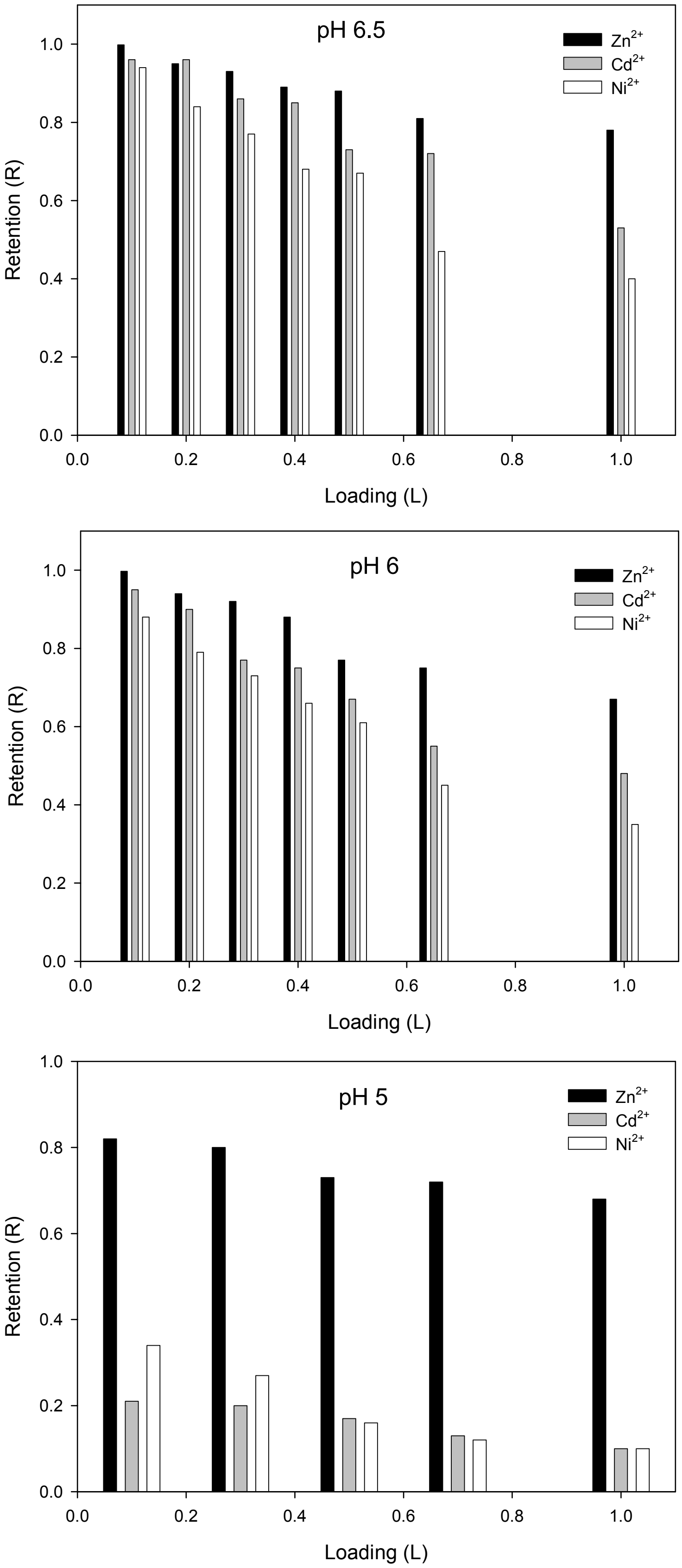


Figure 5.11: Binding Order of Metals in Single Component Metal Solutions

As a first step, it is better to analyze the properties of PEI that are probably important in complex formation. It was reported that, for polymeric amines like PEI, the microstructure of the polymer is not operative in complex formation and they are much less sensitive ligands to form complexes demanding specific configuration (i.e., planar or tetrahedral) [168]. Therefore it was assumed that the hexagonal crystal structures of zinc and cadmium and cubic face centered structure of nickel does not play a role in determining the binding mechanism of metal ions with PEI.

The effect of pH on the conformational changes were investigated by static and dynamic light scattering as mentioned in Section 5.2. It was found that decrease in pH level did not change the hydrodynamic radius of the PEI. However, with the decrease of pH from pH 6 to pH 4, PEI molecules tend to loose the hyperbranched nature and became more rigid. This conformational change in PEI molecules may be regarded as one of the reasons of low affinity of the molecules towards several metal ions at low pH values.

In addition to the properties of polymer molecules, contribution of the properties of metals to the binding mechanism may also be important. One of the important features of metallic species related with the formation of bonds is the electronegativity value which is defined as a measure of the ability of an atom or molecule to attract electrons in the context of a chemical bond. Since the PEI molecules have amine functional groups possesing nitrogen as electron donating species, the binding between PEI and metal ions is established via the interaction of nitrogen with the metallic ions. Electronegativities of the species which exist in the process solutions were given in Table 5.14 [285].

Table 5.14: Electronegativities of the Elements

Species	Electronegativity (Pauling Scale)
N	3.04
H	2.20
Ni	1.91
Cd	1.69
Zn	1.65

From Table 5.14, it can be calculated that difference between the electronegativities of the target metal ions (Cd^{2+}, Ni^{2+}, Zn^{2+}) and nitrogen, which constitutes the active site of the PEI molecules for metal binding, is largest for Zn-N pair and lowest for Ni-N. Since it is known that, large difference between the electronegativities of the elements contributing the complex formation indicates the strength of a bond [232], it can be concluded that the strength of the bond formed between nickel and nitrogen is much more lower as compared to that of zinc and cadmium. This clue helps us to explain the binding order of target metals in this study.

5.4.2 Effect of Ionic Strength

In experiments which were performed in order to observe the effect of ionic strength on the retention, it was decided to use two different salts; $NaNO_3$, having monovalent anionic group and Na_2SO_4, having divalent anionic group. The aim was to observe the effect of counter anion valency in addition to the effects of salt concentration. Metal rejection experiments were performed at pH 6, in the presence of 0.25N Na_2SO_4 for solutions containing 15ppm Cd^{2+} and 15ppm Ni^{2+} and, results were compared with the data obtained from the experiments performed in the presence of 0.25N $NaNO_3$ (Figure 5.12).

As it is seen from Figure 5.12, although same amount of salt was added to the solutions, lower retention of both Cd^{2+} and Ni^{2+} was obtained in the presence of Na_2SO_4 as compared to the values obtained in the presence of $NaNO_3$. Figure 5.1, demonstrate that, by the addition of either 0.25N Na_2SO_4 or 0.25N $NaNO_3$, conductivity of the solutions became almost same around 20mS/m theoretically. However results presented in Figure 5.12 showed that, in addition to the degree of ionic strength of the solution, type of salt may effect the extent of metal rejection in the presence of PEI.

Salt type may affect the metal retention by changing the polymer conformation and/or by causing the formation of insoluble metal complexes. During the experiments performed with metal solutions containing Na_2SO_4, feed solution became blurry which is the indication of agglomeration of the particles in solution. This may be

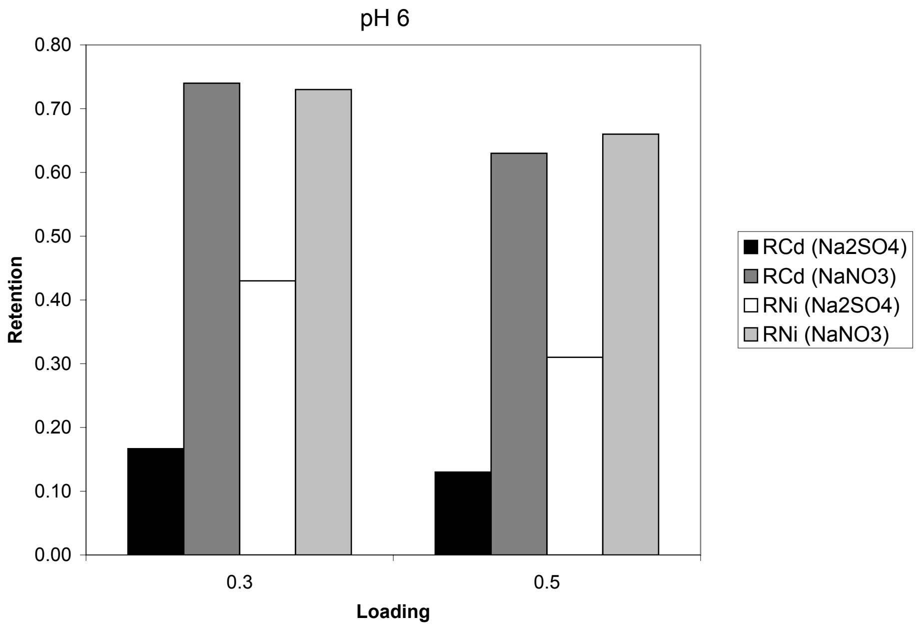


Figure 5.12: Comparison of the Retention Data Obtained in the Presence of 0.25N Na_2SO_4 and $NaNO_3$

either due to the formation of insoluble metal complexes or due to the precipitation of PEI molecules.

In order to understand the reasons of the blurry nature of the solution, conductivity tests were performed and it was observed that conductivities of the feed solutions containing 0.25N Na_2SO_4 (conductivity=31 mS/m) were higher than the conductivity values recorded for solutions containing 0.25N $NaNO_3$ (conductivity=22 mS/m) although same amount of metal ions (i.e., Ni or Cd) and PEI present in both solutions. This indicates that, no insoluble metal complexes were formed in the presence of Na_2SO_4 and relative amounts of free metal ions were high as compared to the solutions containing 0.25N $NaNO_3$.

From this result it can be concluded that, agglomeration occurred in the presence of PEI and Na_2SO_4 was not because of the formation of insoluble metal complexes. Other predicted reason of agglomeration may be the precipitation of PEI macromolecules. It can be said that; because of precipitation available sites of the macromolecule decreases and hence the extent of metal retention decreases, which also explains the high conductivity of Na_2SO_4 solutions. Because of the inhibition of polymer-metal binding, relative amount of free metal ions in the solution increases. As a consequence higher conductivity values are obtained.

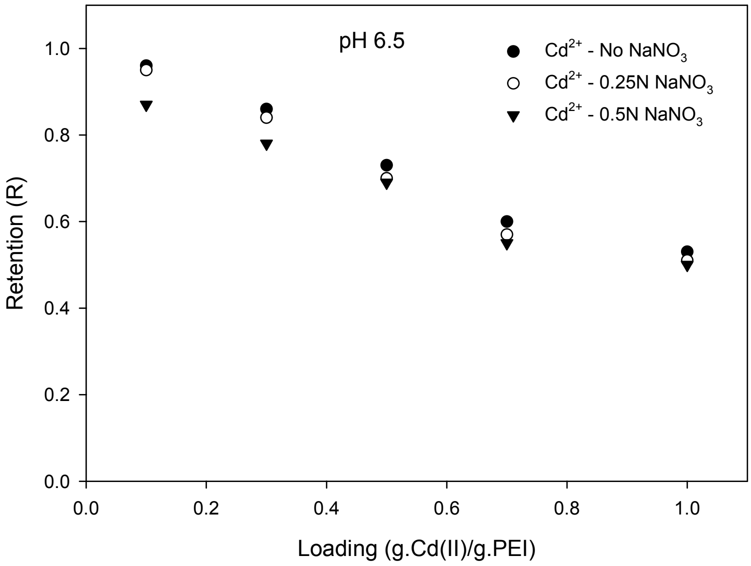
Same behaviour of PEI was also observed in the study of Juang et.al. [210]. It was found that retention of Cu ions became smaller than 0.1 with the concentation of Na_2SO_4 added exceeds about 10mM. It was also reported that, gelatin-like white aggregates form in the presence of either Na_2SO_4 or $MgSO_4$ at the salt concentration of 10 mM or higher.

The reason of PEI precipitation in the presence of Na_2SO_4 may be because of the formation of amine sulfates. It is known that PEI molecules have primary, secondary and tertiary amine groups and these groups tend to form amine-sulfate complexes and among these complexes tertiary amine-sulfate is known to be aggregated [286].

In order to observe the effect of salt concentration on the retention profiles of metals in single component metal solutions, varying amounts of $NaNO_3$ in the range between 0.1N and 1N was added into the representative samples. As it was mentioned before in Section 5.1, conductivity values corresponding to 0.5N and 1N $NaNO_3$ were approximately 50 and 100 mS/m, respectively. These values were regarded to be quite high as compared to conductivity of the solutions in the absence of $NaNO_3$. However, these values are within the reported range of conductivity of wastewaters that may be encountered in industrial applications (Table 5.15). Therefore, to create realistic experimental conditions, experiments were performed in high ionic strength medium. In addition, as the conformation of PEI molecules was found to be changed with the addition of high concentrations of $NaNO_3$, performing the PEUF experiments in high ionic strength values allowed to observe the effects of polymer conformation on the binding ability of PEI with metal ions.

Effect of ionic strength on Cd^{2+} retention was examined at pH 6.5 and pH 6 by adding increasing amount of $NaNO_3$ into the solution. Results are shown in Figure 5.13.

As depicted in this figure, at pH 6.5, where the binding ability of cadmium ions were proved to be maximum, addition of 0.25N $NaNO_3$ causes only 1-3% decrease in the



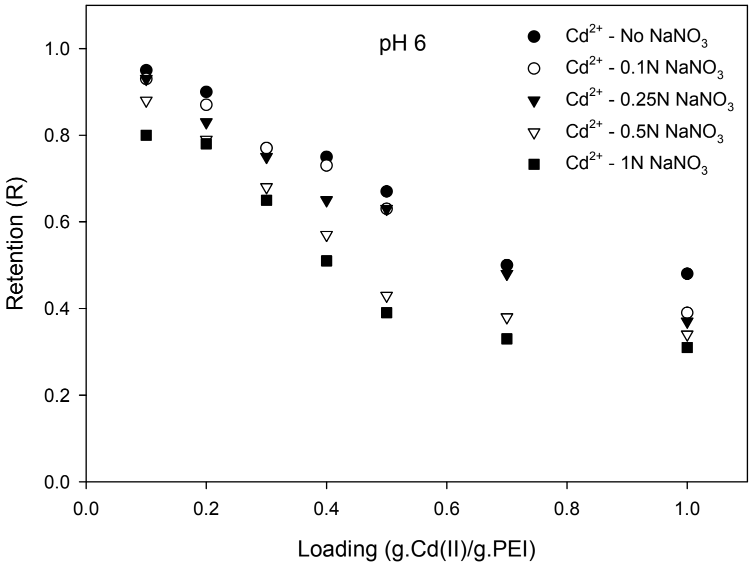


Figure 5.13: Effect of Ionic Strength on Retention of Cd^{2+} at pH 6.5 and pH 6

Table 5.15: Conductivities of Typical Wastewaters

Sample	Conductivity, mS/m	Reference
Polluted groundwater	191-578	[287]
Surface water	13.8-15.1	[288]
Water Containing Metal Ions	25.5-76.9	[289]
Industrial Electroplating Wastewater	970	[290]
Wastewater from grinding (metal)	180	[291]
Oily wastewater (metal)	510	[291]
Coating wastewater (paper)	50	[291]

retention values. By the further increase in salt concentration (0.5N $NaNO_3$) retention drop was reported to be between 3-9%. Reduction in Cd^{2+} retention amounting to 1-9% is relatively insignificant, therefore it may be concluded that, using PEI as a complexation agent in PEUF process is a good alternative for the removal of divalent cadmium ions from high ionic strength medium at high pH.

At pH 6, effect of salt addition was observed in wider concentration range lying between 0.1 and 1N $NaNO_3$ (Figure 5.13). From the figure it can be inferred that, effect of ionic strength on Cd^{2+} retention was observed to be more pronounced at pH 6 then pH 6.5 especially at high salt concentrations. This was an expected result since the PEI-Cd^{2+} complexation was proven to be more favorable at pH 6.5. Therefore the complex formed at pH 6.5 was likely to be more resistant to the salt effects.

No considerable adverse effect of salt concentration was observed in the presence of 0.1N $NaNO_3$ at pH 6, which is consistent with the results of previous study [227]. Decrease in the retention of Cd^{2+} started in the presence of 0.25N $NaNO_3$, depending on the metal/polymer ratios 2-11% reduction in retention was recorded by the addition of 0.25N $NaNO_3$. Extent of reduction in retention values were obtained to be in the range of 9-24% and 12-28% in the presence of 0.5N $NaNO_3$ and 1N $NaNO_3$, respectively.

In one of the previous studies, effect of salt concentration on the binding ability of poly(sodium 4-styrenesulfonate) with Cd^{2+} was investigated by PEUF under similar experimental conditions [292]. It was reported that $NaNO_3$ had a great influence on the retention of cadmium such that, in the absence of $NaNO_3$ cadmium ions were completely retained whereas addition of 0.4N $NaNO_3$ causes a total release of the ions by the poly(sodium 4-styrenesulfonate). Compared with the results obtained in this study, it can be inferred that polyelectrolyte-Cd^{2+} interaction is more sensitive to the changes in ionic strength than that of polychetalogen-Cd^{2+} system. In case of polychetalogen-Cd^{2+} complexation, bonds can only be broken up at high ionic strength medium.

Experiments for Ni^{2+} were performed in the presence of 0.5N $NaNO_3$ at pH 6.5 and in the presence of 0.25N and 0.5N $NaNO_3$ at pH 6 (Figure 5.14). Adverse effect of excess salt concentration on Ni^{2+} retention was observed to be more significant at pH 6 than pH 6.5.

This is parallel to our expectations, since Ni^{2+}-PEI complexation is favorable at pH 6.5, and the strength of the bond may probably be higher than the one formed at pH 6, therefore can withstand the changes in ionic strength.

At pH 6, 1-8% and 9-28% reduction in retention values were recorded in the presence of 0.25N and 0.5N $NaNO_3$, respectively. When compared with the separation process performed by using CMC (carboxy methyl cellulose) as a complexation agent, in which the ionic strength was reported to have practically no influence on metal retention regardless of the pH of the solution [150], it can be said that CMC may be effectively used for the removal of divalent Ni ions. However, use of PEI as a complexation agent may give rise to recovery of both Ni ions and PEI, due to the reversible nature of PEI-Ni^{2+} complexation reaction at different pH values and salt concentrations.

Retention profiles of divalent ions of zinc in the presence of varying amounts of $NaNO_3$ salt and different pHs were depicted in Figure 5.15 and Figure 5.16. Amoung three target metals, most drastic adverse effect of ionic strength was observed in the

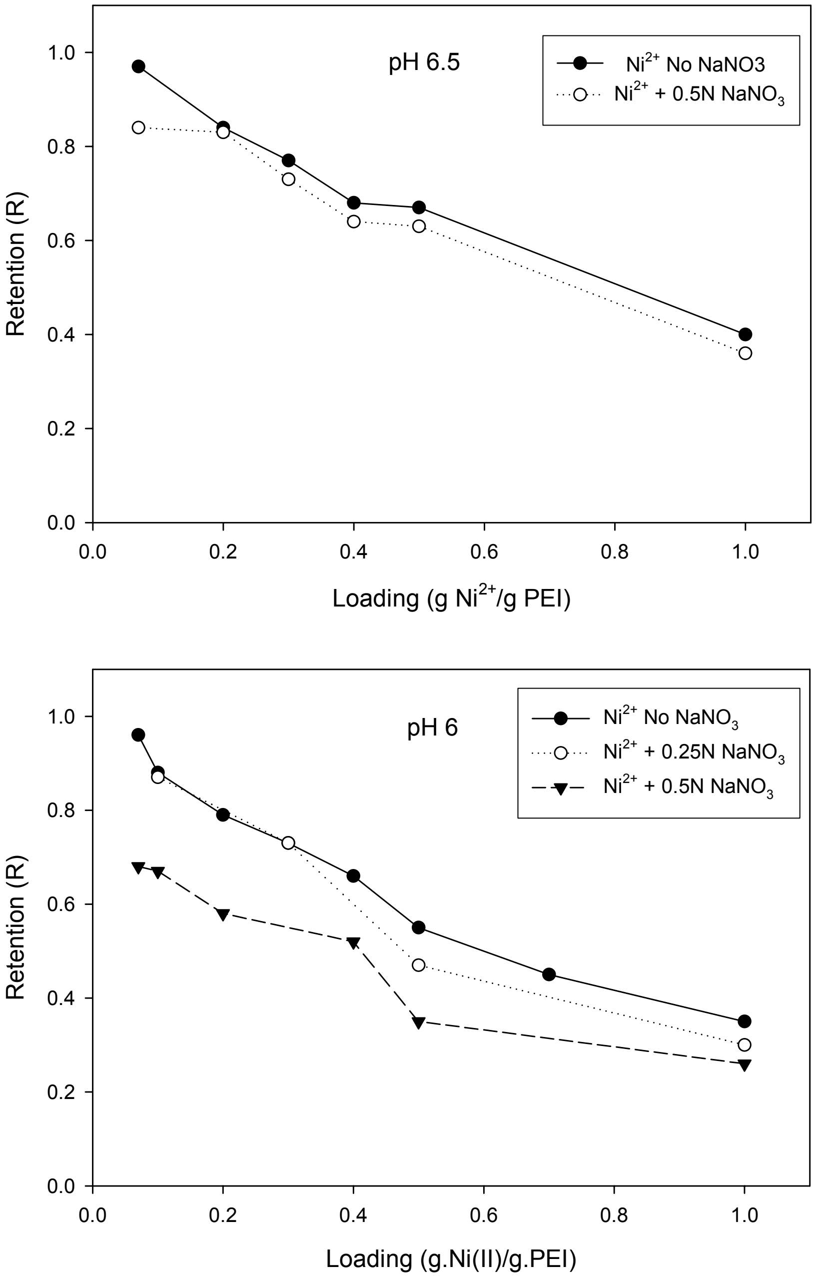


Figure 5.14: Effect of Ionic Strength on Retention of Ni^{2+} at pH 6.5 and pH 6

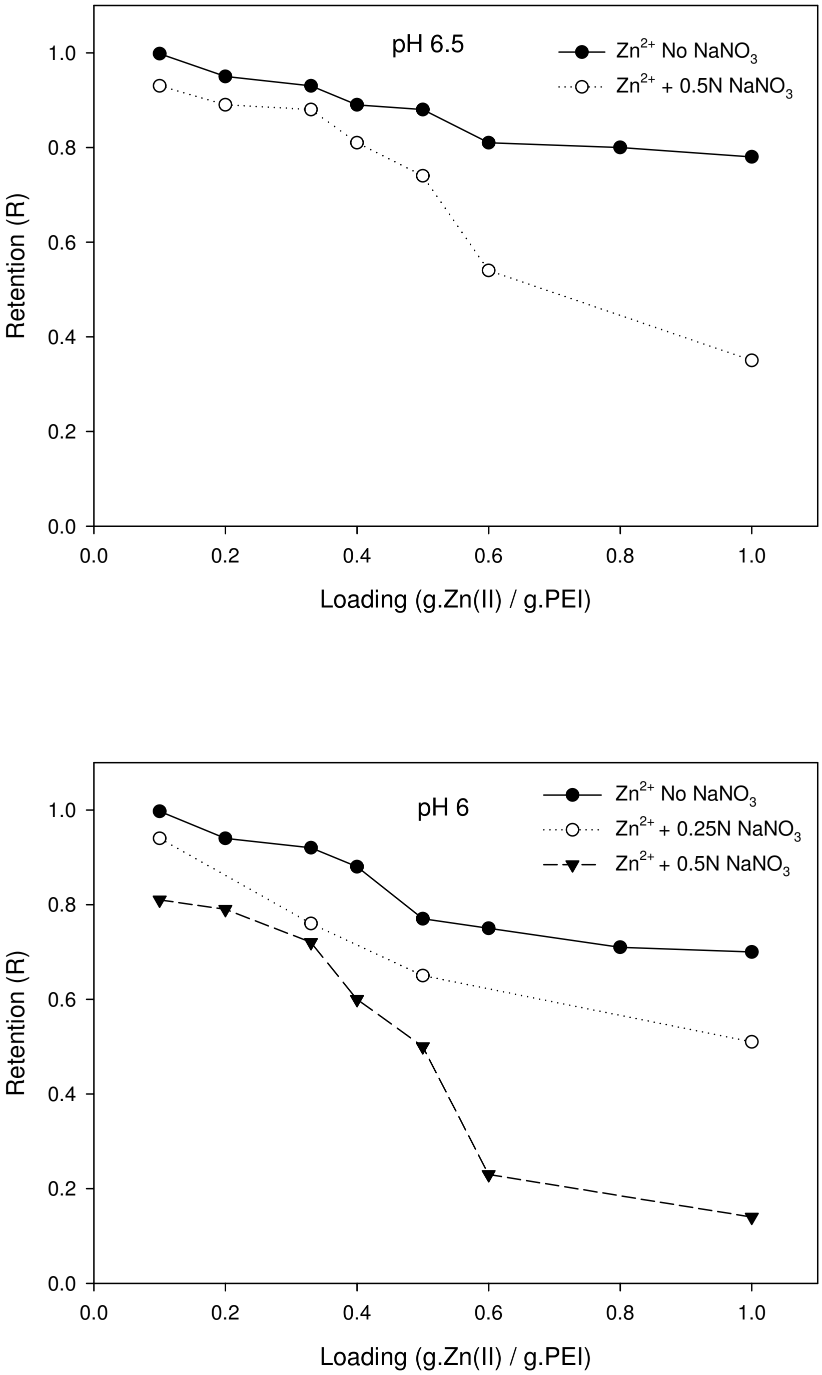


Figure 5.15: Effect of Ionic Strength on Retention of Zn^{2+} at pH 6.5 and pH 6

retention of Zn^{2+} especially at high loading values. In the presence of 0.5N $NaNO_3$ and for the loading values greater than 0.5, approximately 45% and 55% decrement occured in the retention of Zn^{2+} at pH 6.5 and pH 6, respectively.

As mentioned earlier, in the absence of $NaNO_3$, 80% of Zn^{2+} retention can be achieved at pH 5. On the other hand, by the addition of 0.5N $NaNO_3$, depending on metal/polymer ratios, 5-13% reduction in the binding ability of Zn^{2+} with PEI was observed and maximum of 77% retention could be achieved at that acidity level (Figure 5.16). It was also observed that, adverse effect of high salt concentrations on retention was not so drastic at pH 5 as compared to high pHs (i.e., pH 6.5 and pH 6). From this result it may be inferred that, for effective separation of divalent zinc ions from high ionic strength medium via the complexation with PEI, it would be better to carry out the operation at pH 5.

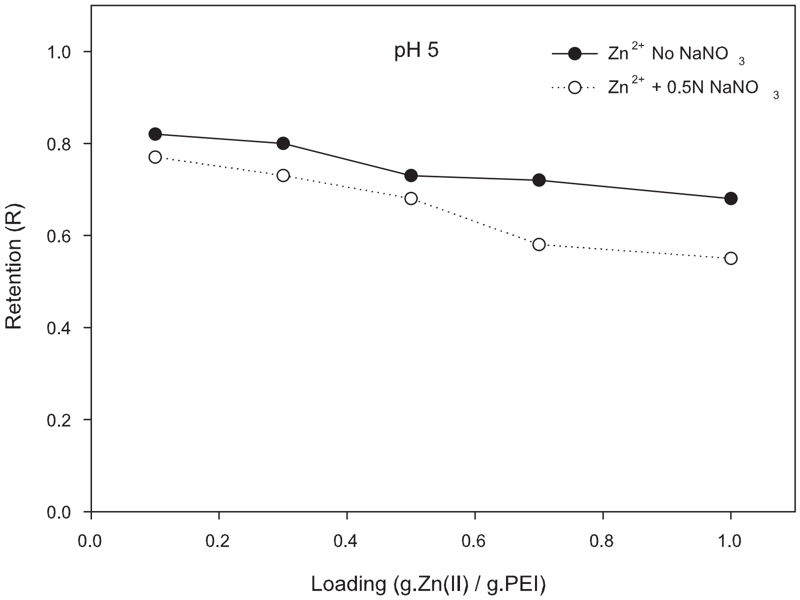


Figure 5.16: Effect of Ionic Strength on Retention of Zn^{2+} at pH 5

As a summary, it can be said that; as far as salt effect is concerned zinc is much more sensible to the changes in ionic strength, therefore while dealing with zinc containing solutions, salt concentration in the medium should be taken into account in order to estimate the process efficiency properly.

After examining the individual behaviors of each metal in high ionic strength medium, effect of ionic strength on the order of binding of metals at pH 6.5 (Figure 5.17) and pH 6 (Figure 5.18) were evaluated.

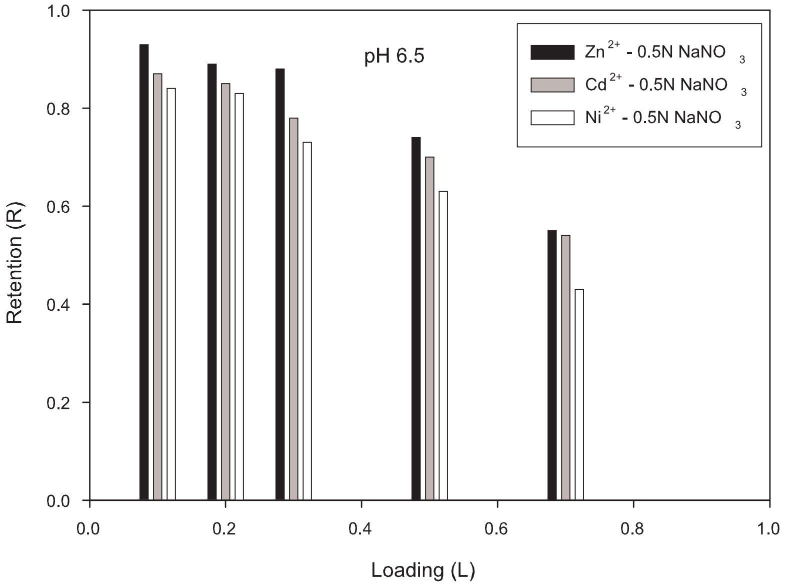


Figure 5.17: Effect of Ionic Strength on Binding order of Metals at pH 6.5

It was observed that although increase in salt concentration reduces the amount of metal bound to PEI and hence the amount rejected by the membrane, binding order remains the same both in the absence and presence of high $NaNO_3$ concentrations for the studied pH range. Zn(II) exhibited a higher rejection than Cd(II), which in turn was higher than Ni(II). This phenomenon may be explained as follows; with the addition of $NaNO_3$, due to the reduction in screening effects, polymer chains partially interwear, and macromolecules may not be described as separate globules in solution. The concentration of monomer links of polymer in solution tend to be distributed irregularly; it is larger in the globule of macromolecule than in the solution around the globule. Therefore complexes with a different stability form at the treatment of metal ions with PEI. Metal ions in the globule of macromolecules form stable complexes. At the same time, metal ions, treated with imino groups on the surface of globule, form complexes with stability close to that for low molecular amines [293]. Therefore it may be concluded that, for the metal ions which were able to penetrate into the globule of macromolecule can form stable complexes as compored to the ones remaining in

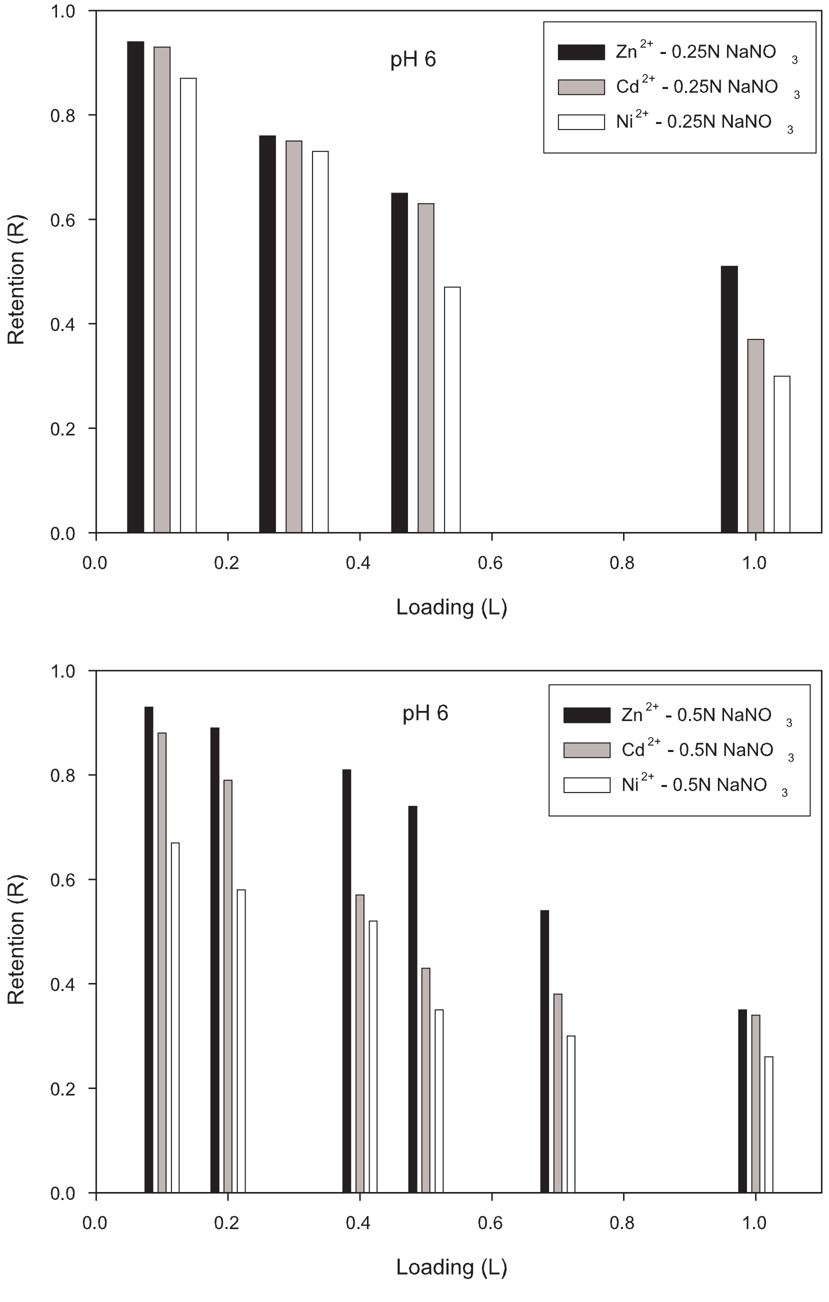


Figure 5.18: Effect of Ionic Strength on Binding order of Metals at pH 6

the surface. Based on this explanation, favorable binding of Zn^{2+} with PEI over those of Cd^{2+} and Ni^{2+} in high ionic strength medium may be probably due to the ability of zinc ions to penetrate into the globule of PEI macromolecule and hence able to form stable complexes.

5.5 Experiments with Binary Metal Solutions

In polymer enhanced ultrafiltration technique, selective separation of metals from multicomponent metal mixtures can be achieved if several metal ions form macromolecular complexes with different complexation constants.

Results of the single metal experiments showed that affinity of PEI towards the three target metals was favorable in the order of $Zn^{2+} > Cd^{2+} > Ni^{2+}$. This result gives positive expectations about the possibility of selective separation of metals from multicomponent aqueous solutions.

To test the performance of PEUF process in selective separation of target metals by using PEI as complexing agent, experiments analogous to those carried out on model solutions which contained single metal ions were performed for equimolar binary mixtures of cadmium, nickel and zinc ions. The process conditions (pH, metal/polymer ratios) were the same as stated previously. Data tables for the figures showing the retention profiles of binary component metal solutions are given in Appendix F.

5.5.1 Cd(II)-Ni(II) Binary Mixtures

5.5.1.1 Effect of pH and Loading

Cadmium-nickel pair is selected due to commercial importance of these metals especially in electroplating and Ni-Cd battery industries [9].

In Figure 5.19, retention profiles of Cd(II) and Ni(II) in equimolar binary mixture of these metals are depicted. Figure reveals that, retention of cadmium ions were favorable over nickel ion retention like it was the case for the retention behaviour of these two metals in single metal solutions.

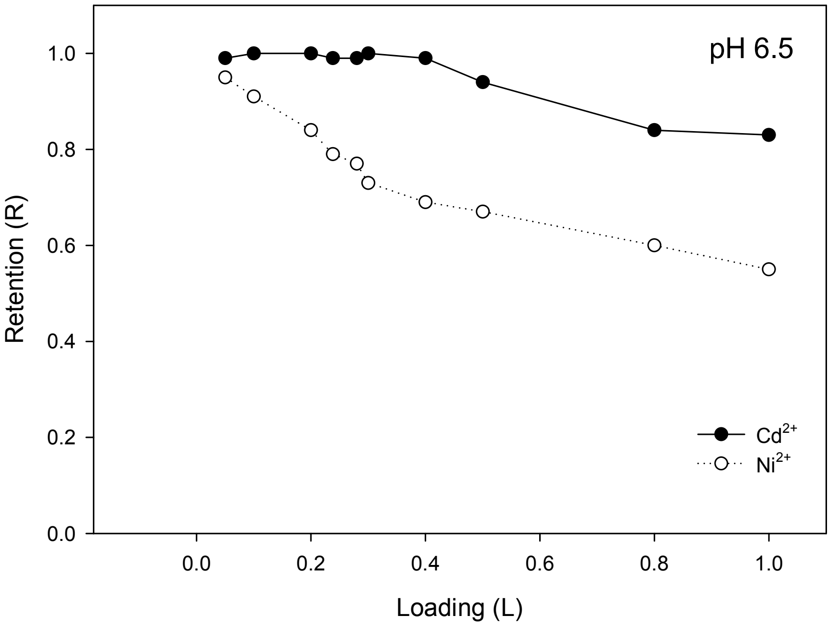
Separation process performed at pH 6.5 and pH 6 enabled 55-95% and 51-97% Ni(II) retention, respectively. Such a closeness in retention values at two different pHs indicates the ineffectiveness of pH changes on the binding ability of nickel ions with PEI in the binary mixture of considered metal pair. But for cadmium stiuation is different; when pH was reduced from pH 6.5 to pH 6, percent recoveries of cadmium falled from 83-99% to 57-99%. This result indicates that, as compared to nickel, cadmium ions are more sensitive to the pH changes.

Favourable binding of cadmium over nickel ions may be explained as follows: All metallic ions apparently form hydrates in aqueous solution, surrounding themselves with large numbers of molecules of water. The ease with which metallic ions form hydrates increases with increasing charge and with decreasing radius [232]. Since ionic radii of nickel ions (r = 0.69A) is smaller than that of cadmium ions (r = 0.92 A) [189], nickel ions tend to form hydrates more easily. Hydrolysis effects renders the Ni^{2+}-PEI complexation reaction, due to the fact that the amino groups present in PEI cannot be easily bound to hydrolyzed metal ions owing to the competitive reactions between OH ions and amino groups [117].

Selectivity factors for Cd(II)-Ni(II) binary metal mixture were calculated by the formula expressed in Equation 1.4 on page 14 for each loading value and compared with the ideal selectivity factors which were estimated by the cadmium and nickel retention data in single metal solutions in same process conditions (Table 5.16 and Table 5.17).

Table 5.16: Selectivities in Cd^{2+}-Ni^{2+} Binary Mixtures at pH 6.5

Loading	$S_{Cd/Ni}$ (pH 6.5)	$S_{Cd/Ni}^{ideal}$ (pH 6.5)
0.05	5.0	1.0
0.1	9.0	1.5
0.2	16.0	4.0
0.3	27.0	1.6
0.4	28.0	2.1
0.5	5.5	1.2
1	2.5	1.3



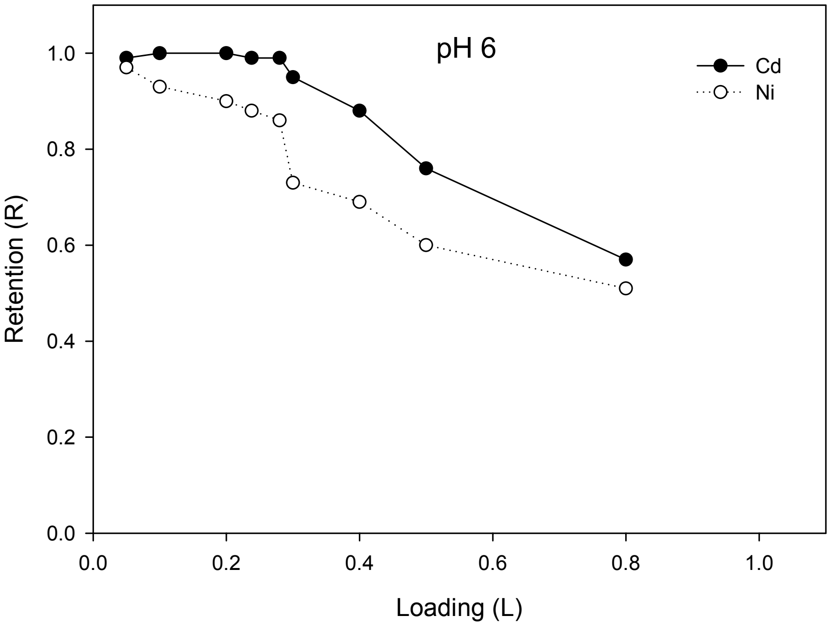


Figure 5.19: Retention Profiles of Cd^{2+} and Ni^{2+} in Binary Metal Mixtures at pH 6.5 and pH 6

Table 5.17: Selectivities in Cd^{2+}-Ni^{2+} Binary Mixtures at pH 6

Loading	$S_{Cd/Ni}$ (pH 6)	$S_{Cd/Ni}^{ideal}$ (pH 6)
0.1	7.0	2.4
0.2	10.0	2.1
0.3	5.4	1.2
0.4	2.6	1.4
0.5	1.7	1.2
0.8	1.1	1.1

Selectivity factors presented in Table 5.16 and 5.17 show that cadmium ions can be fractionated from solutions containing equimolar Cd(II)-Ni(II) mixture at high pH values and in the presence of PEI. It is also important to note that, Cd(II)-PEI complexation is favorable over that of Ni(II)-PEI complexation both in single and binary component mixtures. That means, when cadmium and nickel are present in same solution with equal concentrations, binding order of these metals did not change due to the interference effects at high pH values. The removal of cadmium and nickel mixture from aqueous solutions may be conducted as effectively as removal of each of these ions separately.

As far as pH effect was concerned surprising changes in the binding ability of Cd(II) and Ni(II) were observed at pH 5 (Figure 5.20). During polymer assisted ultrafiltration of single metal solutions it was observed that retention of both Cd^{2+} (Figure 5.7) and Ni^{2+} (Figure 5.8) decreases with the decrease of pH because of the protonation of PEI. But in the co existence of Cd(II) and Ni(II), reverse effect of pH was observed at pH 5; approximately 50-60% enhancement in cadmium and nickel retentions as compared to the values for single metal solutions was recorded (Table 5.18). Flatness of the retention profiles against over the increasing loading values was another unexpected behaviour observed for Cd^{2+}-Ni^{2+} pair at pH 5.

At pH 4, as seen from Figure 5.21 order of binding was changed and Ni(II) retention became favorable over Cd(II) retention. This distinguishing response of $Cd^{2+} - Ni^{2+}$ pair at different acidity levels enables to optimize the PEUF process according to desired end products, such that; if it is desired to fractionate cadmium from the

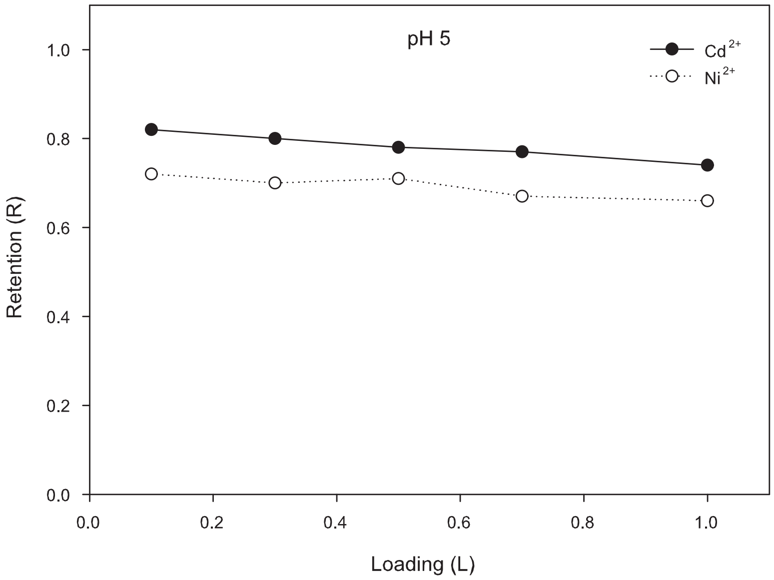


Figure 5.20: Retention Profiles of Cd^{2+} and Ni^{2+} in Binary Metal Mixtures at pH 5

Table 5.18: Comparison of Cd^{2+} and Ni^{2+} Retentions in Binary and Single Component Solutions at pH 5

Loading	R_{Cd} (Binary)	R_{Cd} (Single)	R_{Ni} (Binary)	R_{Ni} (Single)
0.1	0.82	0.21	0.72	0.34
0.3	0.80	0.20	0.70	0.27
0.5	0.78	0.17	0.71	0.18
0.7	0.77	0.11	0.67	0.12
1	0.74	0.12	0.66	0.10

solution the operation should be carried out at $pH \geq 5$ whereas pH values lower than 5 enables nickel fractionation from equimolar binary mixture of Cd(II) and Ni(II).

The enhancement in formation of bonds for PEI-Ni-Cd system with the decrease in pH, and flatness of the retention profiles at pH 5 and pH 4 may be explained as follows: PEI has a very strong heavy metal complexing ability since it contains primary, secondary and tertiary imine groups with a ratio of 1:2:1, respectively [283]. It has a spherical structure and its primary amines are exposed relatively outside due to structural limitation. Thus metal ions bind to the primary amines at the early stage of coordination. As loading increases metal ion concentration becomes higher as compared to polymer concentration and in addition decrease in the pH causes the

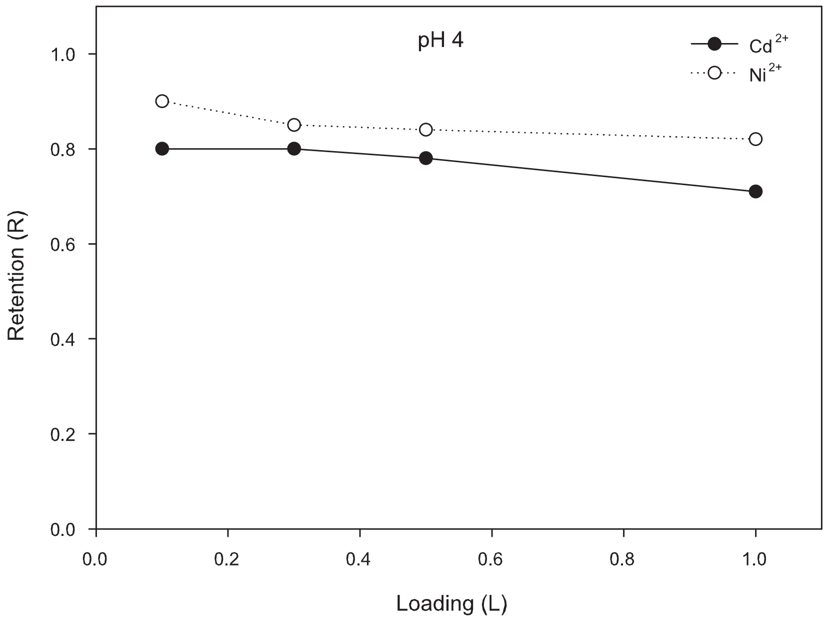


Figure 5.21: Retention Profiles of Cd^{2+} and Ni^{2+} in Binary Metal Mixtures at pH 4

protonation of the active sites of polymer and hence positive charge in the polymer matrix will increase and swelling of PEI will occur with increasing metal ion binding which makes available new sites for attachment of metal ions. As the metal ion concentration increases before reaching the critical ratio, nearly all available sites in the polymer structure was filled and uptake of metal ions by PEI approaches plateau [294]. Therefore rather than gradual decrease in retention with the increasing loading values, relatively flat segments were observed in the profiles.

Based on the data presented in Figure 5.20 and Figure 5.21, selectivity factors were calculated and presented in Tables 5.19 and 5.20. It is important to note that, contrary to the values recorded at high pHs, the selectivities were quite low, which indicates that efficiency of fractional separation was decreased with the decrease in pH.

5.5.1.2 Effect of Ionic Strength

In order to see the effects of ionic strength of the medium on the fractional separation efficiency of PEUF process for Cd^{2+}-Ni^{2+} pair, varying amounts of $NaNO_3$ was added to the equimolar Cd(II)-Ni(II) mixture and retention profiles were obtained at pH 6.5, 6 and 5 (Figure 5.22).

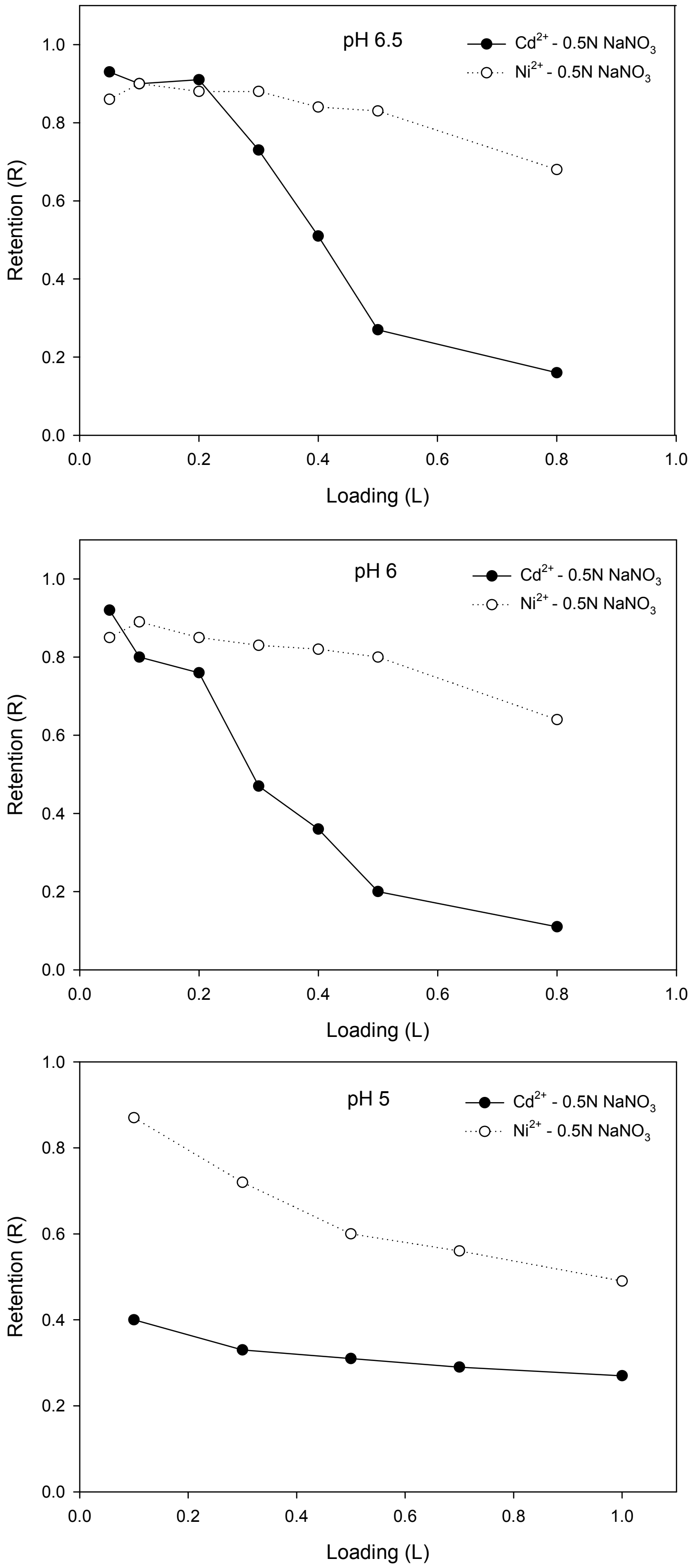


Figure 5.22: Effect of Ionic Strength on the Retention Profiles of Cd^{2+} and Ni^{2+} in Binary Metal Mixtures at pH 6.5, 6 and 5

Table 5.19: Selectivities in Cd^{2+}-Ni^{2+} Binary Mixtures at pH 5

Loading	$S_{Cd/Ni}$ (pH 5)	$S^{ideal}_{Cd/Ni}$ (pH 5)
0.1	1.6	1.2
0.3	1.5	1.1
0.5	1.3	1.1
0.7	1.4	1.1
1	1.3	1.0

Table 5.20: Selectivities in Cd^{2+}-Ni^{2+} Binary Mixtures at pH 4

Loading	$S_{Ni/Cd}$ (pH 4)
0.1	2.0
0.3	1.3
0.5	1.4
1	1.6

As the retention profiles of Cd^{2+}-Ni^{2+} pair in the absence (Figure 5.19) and in the presence of 0.5N $NaNO_3$ (Figure 5.22) were compared it can be observed that addition of salt enhanced the Ni^{2+}-PEI binding while depressing the Cd^{2+}-PEI binding. Depending on the metal/polymer ratios 9-68% reduction in the Cd^{2+} retention was recorded on the contrary to the 9-15% increment in Ni^{2+} retention at pH 6.5. Same behaviour was also observed at pH 6 and pH 5, in average 40% and 47% decrement in Cd^{2+} retention, 11% and 17% increment in Ni^{2+} retention were achieved at pH 6 and pH 5, respectively. From these results it can be concluded that, the addition of high amount of salt gives rise to the favorable separation of nickel over cadmium from their equimolar binary mixtures.

To analyze the possible reasons of the dual effect of salt concentration on the binding ability of cadmium and nickel ions with PEI, it is important to have an idea about the conformational changes of both PEI and metal ions. As discussed in Section 5.2, dynamic/static light scattering experiments showed that PEI molecules tend to aggregate and become smaller in the presence of high salt concentrations. Because of the aggregation of PEI particles, active sites of the macromolecule may be buried and by this way ability to form metal complexes was inhibited. In addition, excess amount of Na^{+} ions coming from the dissociation of salt may also cause a deformation of the ions and hence changes the binding ability of the ions to PEI macromolecules which became also smaller in high ionic strength medium.

Although target metals selected for this study were all belong to Group B of the periodic table and therefore eligible for deformation, degree of deformation of the ions of these metals may be different from each other. For example in the case of Cd^{2+} - Ni^{2+} pair, nickel ions tend to deform more easily then cadmium ions in the presence of distorting medium. Therefore when high amount of salt was added to the solution, distorting medium appeared in the presence of excess Na^{+} ions deform the symmetrical structure of nickel ions. Deformed nickel ions can penetrate into the PEI macromolecule and can reach the active sites more easily than cadmium ions and hence nickel binding becomes favorable over cadmium binding in high ionic strength medium.

Selectivities of Ni^{2+} over Cd^{2+} were calculated for each metal/polymer ratio and they are tabulated in Table 5.21. As it is evident from the selectivity values, in high ionic strength medium nickel ions can be fractionated from the solutions containing equimolar binary mixture of Ni^{2+} and Cd^{2+}.

Table 5.21: Selectivities in Cd^{2+}-Ni^{2+} Binary Mixtures in the Presence of 0.5N $NaNO_3$

Loading	$S_{Ni/Cd}$ (pH 6.5)	$S_{Ni/Cd}$ (pH 6)	$S_{Ni/Cd}$ (pH5)
0.1	1.0	1.8	4.6
0.3	2.3	3.1	2.4
0.4	3.1	3.6	-
0.5	4.3	4.0	1.7
0.7	-	-	1.6
0.8	2.6	2.5	-
1	-	-	1.4

As a concluding remark for the solutions containing binary mixture of cadmium and nickel ions it may be said that, at high pH values, Cd^{2+} could be effectively recovered from the solution, whereas at low pH values and in the presence of high amount of $NaNO_3$, stiuation was reversed and in that case Ni^{2+} ions can be fractionated from the solution. Therefore, it may be recommended that while dealing with solutions containing both Ni and Cd, special attention should be given to the pH and ionic strength of the solution in order to optimize the fractionation process.

5.5.2 Cd(II)-Zn(II) Binary Mixtures

Separation of cadmium from zinc was reported to be the most tedious of the fractional separations because of their similar properties [295]. Several extractants, such as Cyanex 923, Aliquat 336, D2EHPA(di-2ethyl-hexyl phosphoric acid), LIX84, etc., are used for the extraction of cadmium and zinc [296–299]. The systems, such as Zn-Cd-Co-Ni [300], Zn- Cd [301] and Zn-Cd-Hg [302, 303] also have been investigated for separation of cadmium and zinc by using D2EHPA, carboxylic acid, and caprylic acid as extractants. Although a good deal of work has been reported for the liquid-liquid extraction of cadmium and zinc, the number of studies concerning the separation of cadmium and zinc by membrane techniques are scarce.

5.5.2.1 Effect of pH and Loading

The present work examines the possibility of fractional separation of cadmium and zinc ions from dilute equimolar binary component solutions of these metals. Loading versus retention values of Cd^{2+} and Zn^{2+} were plotted at different pH values to see the retention profiles and order of binding of ions (Figure 5.23 and Figure 5.24).

As seen from Figure 5.23, same extent of retention was obtained both for cadmium and zinc in the pH range between 5.5 and 6.5. Because of the similar properties of the ions, binding abilities did not show differences at high pH values and approximately same amount of cadmium and zinc ions were retained by the membrane. Selectivities of zinc over cadmium were calculated at pH 6.5, 6 and 5, and compared with the ideal selectivity values which were calculated by the Cd^{2+} and Zn^{2+} retention data obtained in PEUF experiments with single component metal solutions (Table 5.22 and Table 5.23) .

Data presented in Table 5.22 show that, in single metal solutions of zinc and cadmium, binding ability of Zn^{2+} was favorable over Cd^{2+} binding, therefore zinc retention

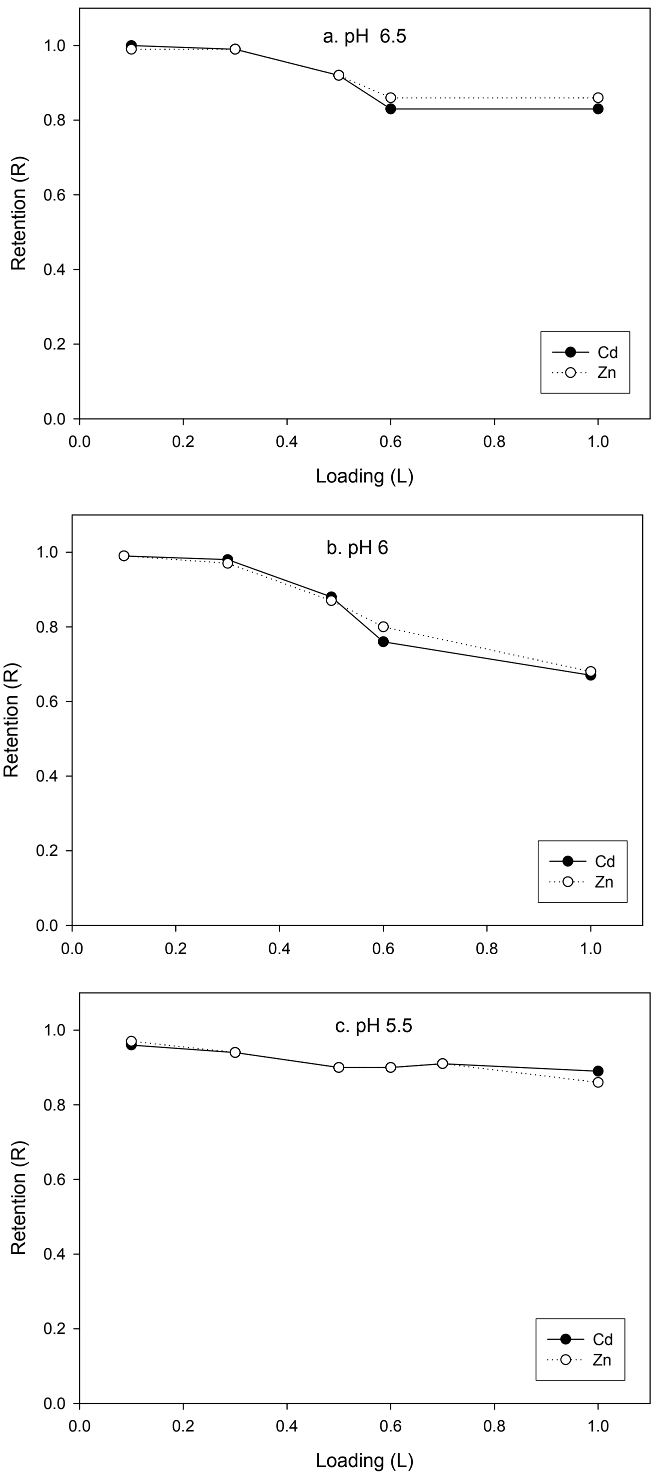


Figure 5.23: Retention Profiles of Cd^{2+} and Zn^{2+} in Binary Metal Mixtures at a. pH 6.5 b. pH 6 c. pH 5.5

Table 5.22: Selectivities in Cd^{2+}-Zn^{2+} Binary Mixtures at pH 6.5

Loading	$S_{Zn/Cd}$ (pH 6.5)	$S^{ideal}_{Zn/Cd}$(pH 6.5)
0.3	1.0	2.0
0.5	1.0	2.3
0.6	1.1	1.5
0.8	1.3	2.0
0.8	1.1	2.1

Table 5.23: Selectivities in Cd^{2+}-Zn^{2+} Binary Mixtures at pH 6

Loading	$S_{Zn/Cd}$ (pH 6)	$S^{ideal}_{Zn/Cd}$(pH 6)
0.3	0.7	2.9
0.5	0.9	1.4
0.6	1.2	1.8
1	1.0	1.8

values were higher than retention values of cadmium. Hence ideal selectivity of zinc over cadmium appeared to be higher than 1. But when cadmium and zinc both exist in the same solution, because of the similar properties of cadmium and zinc, competition between these ions results in the same extent of retention of the ions. Therefore selectivities obtained for binary metal mixture solutions were approximately 1.

In order to investigate the possibility of fractional separation of Zn^{2+} and Cd^{2+} at low pHs, similar PEUF experiments were performed at pH 5 and pH 4, and retention profiles are plotted (Figure 5.24).

As seen from Figure 5.24, selective separation of Cd^{2+} from Zn^{2+} can not be achieved at pH 5 because approximately same amounts of both metal ions were retained by the membrane. It is interesting to note that, as compared with the retention values of the obtained in single metal solutions, 52-68% enhancement in cadmium retention and in average 5% increase in zinc retention was recorded in equimolar binary mixture of the metals at pH 5. Following suggestion can be made from these results. If the aim of the operation is to remove zinc and cadmium ions from the solution at the same time, coexistance of the ions in same solution does not reduce the process efficiency.

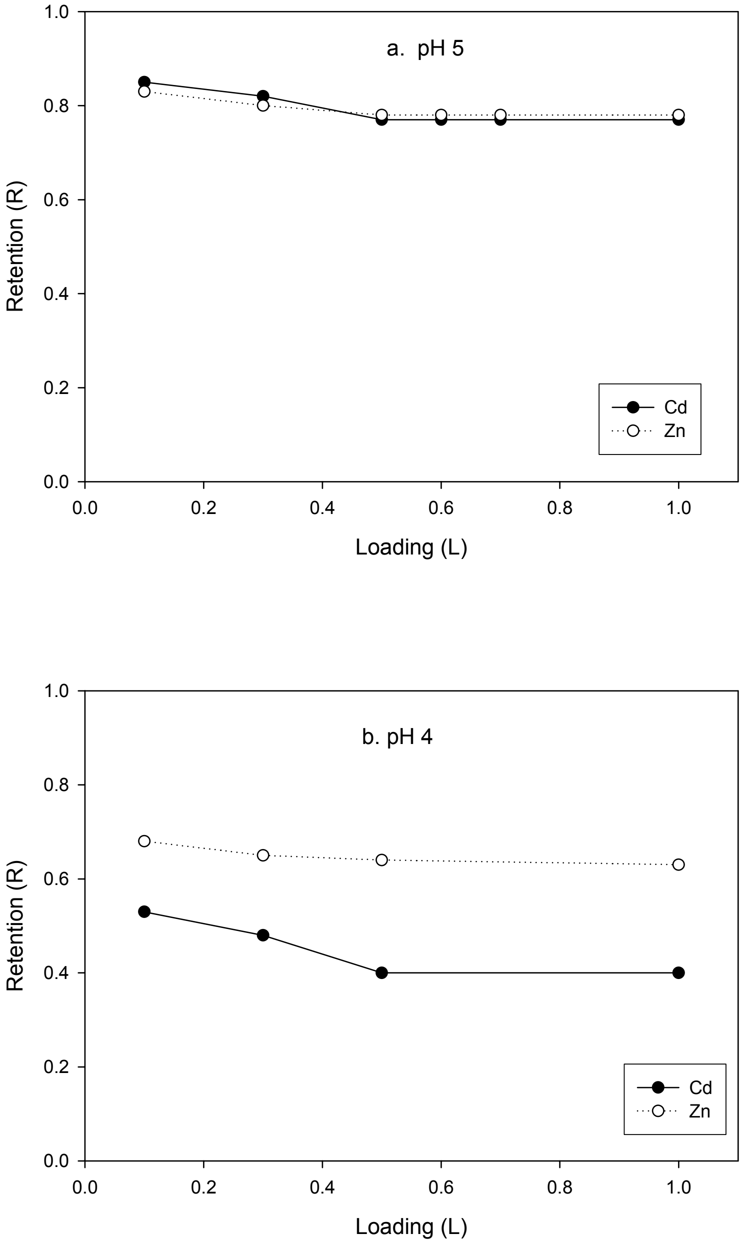


Figure 5.24: Retention Profiles of Cd^{2+} and Zn^{2+} in Binary Metal Mixtures at a.pH 5 b.pH 4

On the contrary if it is desired to fractionate zinc ions from the solution containing cadmium and zinc or vise versa, it is not possible to do that at pH 5 by using PEI as a complexing agent.

Disparity between the retention profiles of Cd^{2+} and Zn^{2+} was observed when pH was reduced down to pH 4. At this acidity level, in average 45% of cadmium and 65% zinc were able to complexed by PEI and hence retained by the membrane (Figure 5.24).

Statistical discrepancy in Cd^{2+} and Zn^{2+} retentions were more clearly observed by looking at the selectivities which were calculated and presented in Table 5.24.

Table 5.24: Selectivities in Cd^{2+}-Zn^{2+} Binary Mixtures at pH 5 and 4

Loading	$S_{Zn/Cd}$ (pH 5)	$S_{Zn/Cd}^{ideal}$ (pH 5)	$S_{Zn/Cd}$ (pH 4)
0.1	0.9	4.4	1.5
0.3	0.9	4.0	1.5
0.5	1.0	3.1	1.7
0.7	1.0	3.1	-
1	1.0	2.8	1.6

At pH 5, depending on the metal/polymer ratio zinc retention was recorded to be 4-7 times greater than cadmium retention in the single metal mixtures of these metal ions, therefore ideal selectivities were found to be between 2.8 and 4.4. But in the presence of cadmium, binding of zinc with PEI was no more favorable over that of cadmium binding and unity in the selectivity values were obtained indicating equal retention. Selective separation can only be achieved at pH 4, but not with the complete retention of either zinc or cadmium ions.

It is known that, in any periodic group the stability of the hydrates is greatest for the smallest ions, while the number of water molecules normally held is greatest for the large ions [232]. Cadmium and zinc are both belong to group IIB and cadmium have greater ionic radii as compared to zinc (r_{Cd} = 0.92A, r_{Zn} = 0.74A), therefore cadmium ions assumed to held greater amount of water molecules as compared to zinc and as a consequence binding ability of zinc ions were expected to be higher than that of cadmium. However, this suggestion seems to be valid only at low pH values, such that; at pH 5 and pH 4, Zn^{2+} retention become favorable over Cd^{2+} retention, on the contrary, at high pH values extent of retention for both metals appear to be same.

5.5.2.2 Effect of Ionic Strength

In order to see the effect of ionic strength on the separation efficiency of Cd^{2+} and Zn^{2+}, 0.5N $NaNO_3$ was added into the solution and retention profiles are drawn at different pHs (Figure 5.25).

As it is can be seen in Figure 5.25, at pH 6.5, almost complete retention of both Cd^{2+} and Zn^{2+} can be achieved in the presence of 0.5N $NaNO_3$ for low loading values. When compared to the retention profiles of cadmium and zinc in binary component mixture and in the absence of $NaNO_3$ (Figure 5.23), it can be concluded that, ionic strength has no adverse effect on the binding ability of cadmium and zinc under these conditions, since both of the metal ions can be retained by the membrane. This gives rise to remove both Cd(II) and Zn(II) from the binary component solutions even at high ionic strength, however selective separation can not be achieved at the same condition.

On the other hand, adverse effect of high salt concentration can be clearly observed at pH 5.5. More than 90% retention of both metals can be achieved at pH 5.5 when there is no $NaNO_3$ in solution, but by the addition of 0.5N $NaNO_3$ maximum of only 59% retention of Zn^{2+} and 43% of Cd^{2+} could be achieved. By the reduction of pH down to pH 4, further decrease in recovery ratios were observed and it was recorded that only 28-56% of Zn^{2+} and 10-25% of Cd^{2+} can be retained by the membrane.

Based on the retention data obtained at pH 5.5 and pH 4, selectivities were calculated and presented in Table 5.25.

By looking at the data tabulated in Table 5.25, it can be said that selective separation can be achieved in favor of zinc ions, since the selectivity values of zinc over cadmium were appeared to be greater than 1. However, low amount of zinc can be fractionated because extent of retention of metals were low. Therefore it can be concluded that, in the presence of 0.5N $NaNO_3$, both cadmium and zinc ions could be effectively

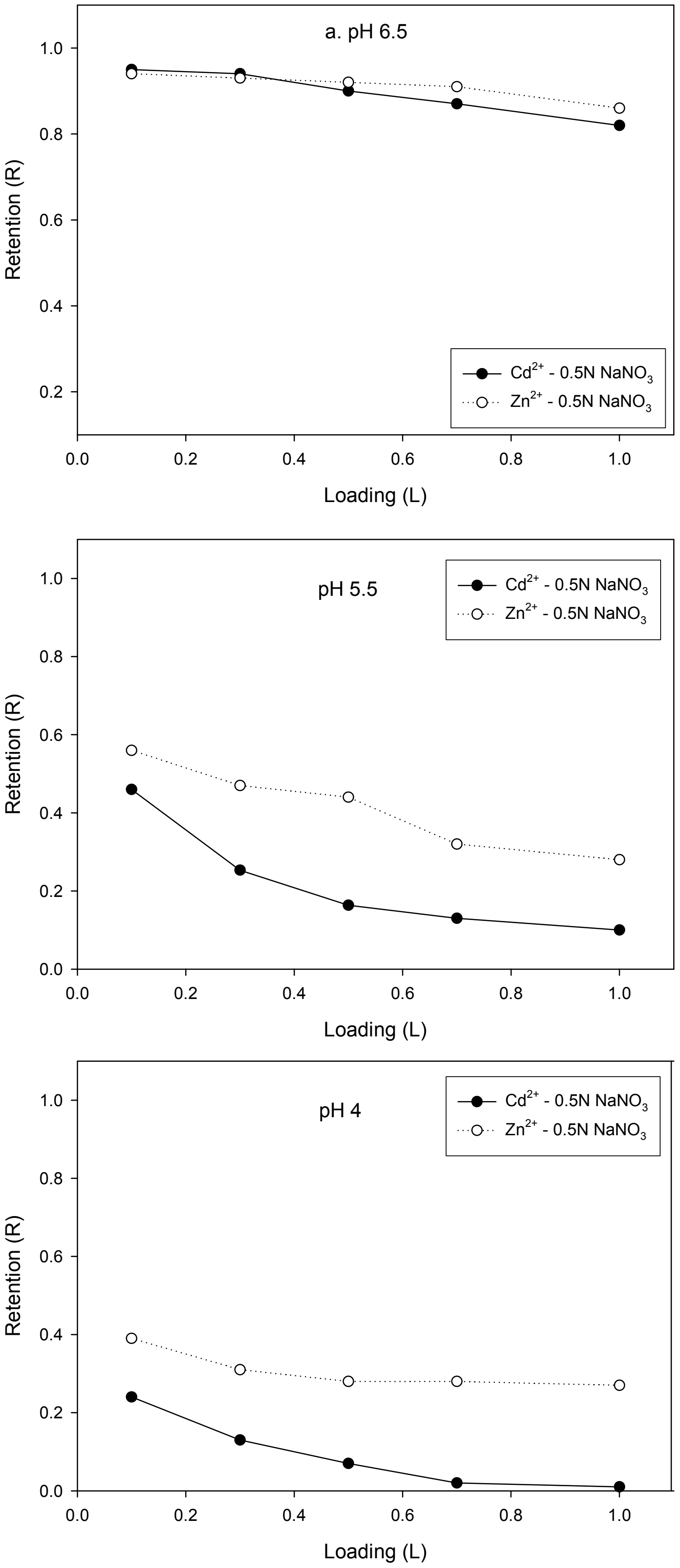


Figure 5.25: Effect of Ionic Strength on the Retention Profiles of Cd^{2+} and Zn^{2+} in Binary Metal Mixtures at pH 6.5, pH 5.5 and pH 4

Table 5.25: Selectivities in Cd^{2+}-Zn^{2+} Binary Mixtures in the Presence of 0.5N $NaNO_3$

Loading	$S_{Zn/Cd}$ (pH 5.5)	$S_{Zn/Cd}$ (pH 4)
0.1	1.2	1.2
0.3	1.3	1.4
0.5	1.3	1.5
0.7	1.4	1.3
1	1.4	1.3

removed from the solution at high pH values, fractionation of zinc can only be achieved in acidic medium but fractionation may not end up with the high recovery of zinc.

5.5.3 Ni(II)-Zn(II) Binary Mixtures

5.5.3.1 Effect of pH and Loading

Last metal pair of interest was Ni^{2+} and Zn^{2+}. PEUF experiments were performed at pH 6 and pH 5 for this metal pair and retention profiles obtained at the end of the experiments are depicted in Figure 5.26.

At pH 6, affinity of PEI towards both of the metals was almost same, therefore almost same degree of retention was obtained both for Ni^{2+} and Zn^{2+}. As compared to the retention values obtained in single metal solutions of these metals (Table 5.26), 5-34% enhancement in Ni^{2+} retention and approximately 10% enhancement in Zn^{2+} retention was observed in equimolar binary mixture of these ions.

Table 5.26: Comparison of Ni(II) and Zn(II) Retentions in Binary and Single Component Solutions at pH 6

Loading	R_{Ni}(Binary)	R_{Ni}(Single)	R_{Zn}(Binary)	R_{Zn}(Single)
0.1	0.93	0.88	1.00	0.997
0.3	0.92	0.73	0.99	0.92
0.5	0.91	0.63	0.95	0.77
1	0.89	0.21	0.90	0.67

Same behaviour is also observed at pH 5, such that; as compared to the retention

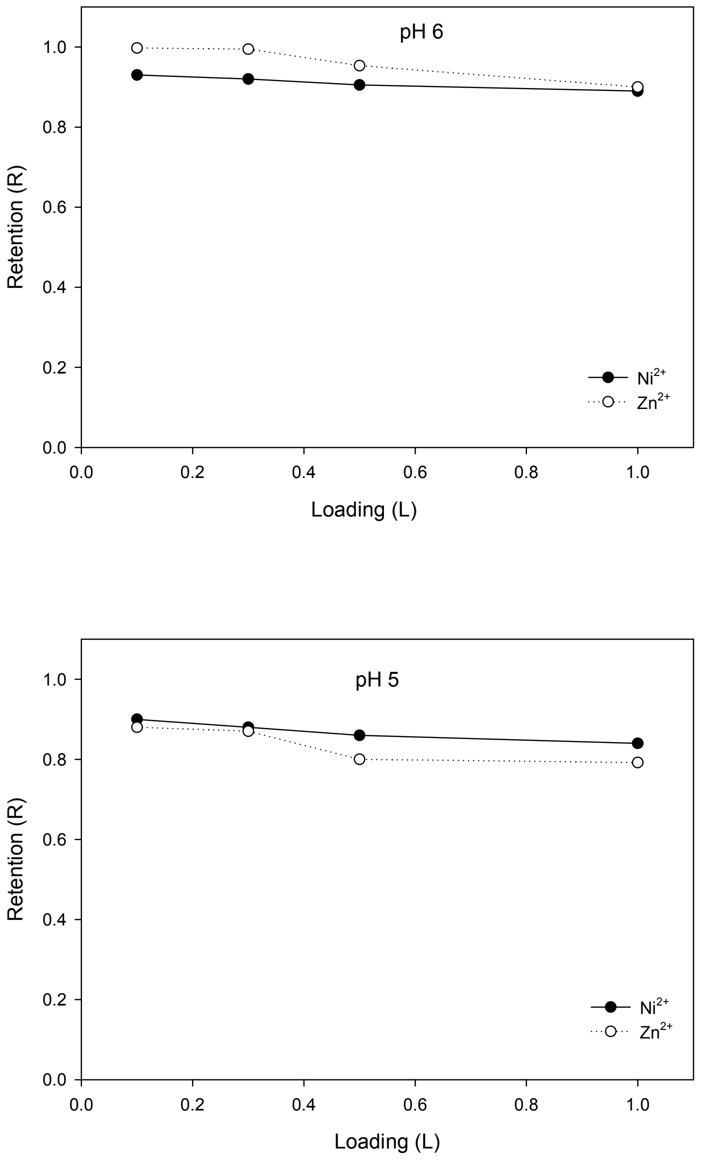


Figure 5.26: Retention Profiles of Ni^{2+} and Zn^{2+} in Binary Metal Mixtures at pH 6 and pH 5

values obtained in single metal solutions of these metals, 56-74% enhancement in Ni^{2+} retention and in average 7% enhancement in Zn^{2+} retention was observed in equimolar binary mixture of these ions (Table 5.27).

Table 5.27: Comparison of Ni^{2+} and Zn^{2+} Retentions in Binary and Single Component Solutions at pH 5

Loading	R_{Ni}(Binary)	R_{Ni}(Single)	R_{Zn}(Binary)	R_{Zn}(Single)
0.1	0.90	0.34	0.88	0.8
0.3	0.88	0.27	0.87	0.81
0.5	0.86	0.16	0.80	
1	0.84	0.12	0.79	0.69

It can be concluded that, when both Ni^{2+} and Zn^{2+} exist in the same solution, because of the interference effects, extent of metal-complexation increases therefore both of the metals can be retained by the membrane and as a consequence selective separation can not be achieved. The results of binary metal experiments showed that, when zinc is present in the solution, regardless of the type of the other metal in binary metal solution, interference effects dominate and degree of binding of both metals increases as in the case of Ni^{2+} - Zn^{2+} and Cd^{2+} - Zn^{2+}. Fractional separation of either Ni^{2+} or Cd^{2+} ions is difficult in the presence of zinc.

5.5.3.2 Effect of Ionic Strength

In order to observe the possible effects of salt concentration on the selective separation of Ni^{2+} and Zn^{2+}, 0.5N $NaNO_3$ was added into the solution and retention profiles were drawn accordingly. Effect of ionic strength was observed at pH 6 and pH 5 (Figure 5.27).

It is important to note that, by the addition of excess amount of salt, selective separation of Ni^{2+} over Zn^{2+} can be achieved at pH 6 and to a little extent at pH 5 (Figure 5.27). Too much salt probably reduced the interaction between nickel and zinc ions and diminished the interference effects. And in addition to that, as mentioned before, PEI macromolecules shrinks in high ionic strength medium, and because of the shrinking effect active sites of the macromolecule available for metal

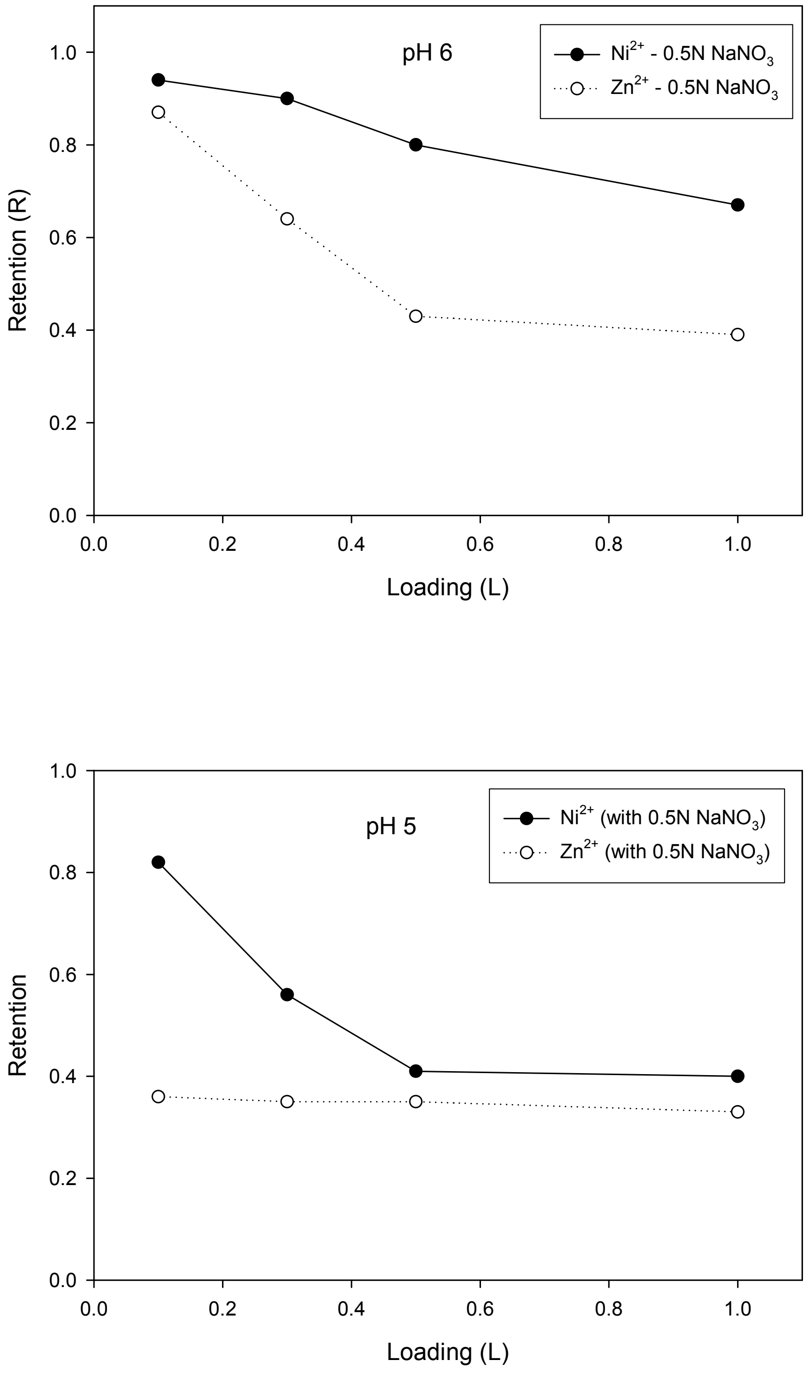


Figure 5.27: Effect of Ionic Strength on the Retention Profiles of Ni^{2+} and Zn^{2+} in Binary Metal Mixtures at pH 6 and pH 5

binding are buried. Since nickel ions have tendency to deform in the presence of high amounts of counter ions, by the courtesy of the deformation ability, nickel ions may penetrate into the active sites of the PEI molecules which was buried by the presence of excess $NaNO_3$. Therefore Ni^{2+} retention became favorable over Zn^{2+} retention in the presence of high $NaNO_3$ concentrations.

Selectivities calculated for Ni^{2+} - Zn^{2+} solutions in the presence of 0.5N $NaNO_3$ are given in Table 5.28. Results in this table reveal that, fractional separation of Ni^{2+} over Zn^{2+} can be achieved at pH 6 in the presence of high amounts of salt. 67-94% of Ni^{2+} and 39-87% of Zn^{2+} can be recovered at pH 6. On the other hand, by the decrease in pH down to pH 5, fractionation efficiency was reduced, and only 40-82% of Ni^{2+} and in average 34% of Zn^{2+} can be removed from the aqueous solution.

Table 5.28: Selectivities in Ni^{2+}-Zn^{2+} Binary Mixtures in the Presence of 0.5N $NaNO_3$

Loading	$S_{Ni/Zn}$ (pH 6)	$S_{Ni/Zn}$ (pH 5)
0.1	2.2	3.6
0.3	3.6	1.5
0.5	2.9	1.1
1	1.8	1.1

5.6 PEUF Experiments with Ternary Mixtures of Cd(II)-Ni(II)-Zn(II)

PEUF experiments with the solutions containing equimolar mixtures of Cd^{2+}-Ni^{2+}-Zn^{2+} were carried out at pH 6.5 and pH 5, with varying metal/polymer ratios in the range between 0.1 and 1. Results are shown in Figure 5.28 and Figure 5.29. Data tables for the figures showing the retention profiles of ternary component metal solutions are given in Appendix F.

Figure 5.28 reveals that, at pH 6.5, divalent ions of zinc and cadmium show similar affinities towards PEI and as a consequence same amounts of Cd^{2+} and Zn^{2+} were able to complexed with PEI and hence retained by the membrane. Fractional

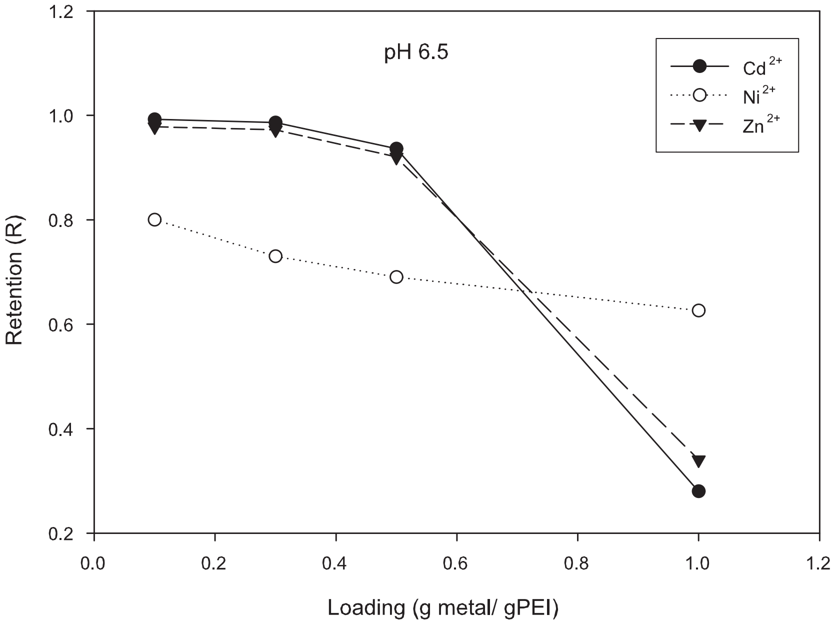


Figure 5.28: Effect pH and Loading on the Retention Profiles of Metals in Ternary Cd^{2+}-Ni^{2+}-Zn^{2+} Mixtures at pH 6.5

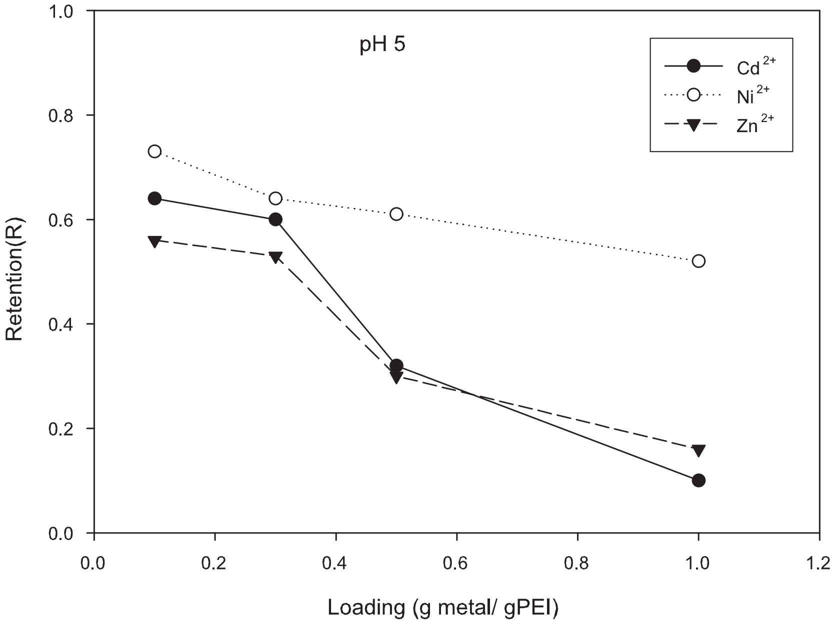


Figure 5.29: Effect pH and Loading on the Retention Profiles of Metals in Ternary Cd^{2+}-Ni^{2+}-Zn^{2+} Mixtures at pH 5

separation of Cd^{2+}-Zn^{2+} pair over Ni^{2+} can be achieved from the multicomponent mixture of Cd^{2+}-Ni^{2+}-Zn^{2+}. Depending on the metal/polymer ratios, 28-99% of cadmium-zinc ion pair can be fractionated, and 62-80% of nickel ions can be removed from the solution.

As it can be seen from Figure 5.28, at pH 6.5, degree of binding decreases in the order of $Cd^{2+} \geq Zn^{2+} > Ni^{2+}$, but at pH 5 situation was reversed because of the steep rise in the binding of Ni^{2+}, and binding order at that acidity level was found to be in the order of $Ni^{2+} > Cd^{2+} \geq Zn^{2+}$ (Figure 5.29). By the courtesy of increased binding ability of nickel ions, 52-72% of Ni^{2+} can be fractionated from the ternary metal solution of cadmium, nickel and zinc.

It can be concluded that, in the presence of zinc ions, it is difficult to fractionate zinc or its counterpart in binary metal solutions, because of the interference effects of zinc. But in the ternary metal mixtures of Cd^{2+}, Ni^{2+} and Zn^{2+}, cadmium-zinc pair showed similar binding properties and by this way they were distinguished from Ni^{2+}. This difference between the behaviour of nickel and cadmium-zinc pair, gives rise to the selective separation of nickel from ternary mixtures of these metals.

5.7 Estimation of Binding Constants by Continuous Mode PEUF Operation

Based on the Equation 3.35 on page 56, apparent binding constants of target metals with PEI were estimated. Sample calculation for the estimation of K_{app} for PEI-metal complexation reaction is given in Appendix G.

The apparent binding constants obtained in this study, together with those reported in the literature, are compiled in Table 5.29.

Table 5.29: Apparent Complexation Constants of Metal Ions with PEI

Metal/pH	n	LogK(This Study)	LogK(Ref)	Method/Reference
Ni^{2+} pH:6	2	7.09	7.61	UV-Visible Spectrometry [182]
Cd^{2+} pH:6	2	7.27	7.84	Two phase potentiometry [196]
Zn^{2+} pH:6	2	10.41	11.1	Potentiometric titration [168]

As it is evident from Table 5.29, there is a good agreement between the apparent complexation constants estimated in this study and the ones cited in the literature although parameters like pH, molecular weight of PEI may be different. For instance, PEI used in the study of Canizares et.al. [182] has a molecular weight of 25000Da and that of used in potentiometric study was 30000 [168].

It is important to note that, the metal-PEI complex formation constants estimated from the equations proposed in this study are conditional and affected by pH, actual metal concentration in aqueous solutions and salt concentration. These apparent complex formation constants are thus valid only for the conditions of the experiments. Generalization of such calculations on complexation by PEI in real waste waters would therefore require a large data set representing all the conditions of interest (pH, ionic strength, and ion composition) or a model that can account for such variations.

5.7.1 Effect of pH and Ionic Strength

Apparent binding constants of metal ions were calculated at predetermined values of L = 0.1, [PEI] = 5x10^{-3} M, n = 2 and at different pH values. Results were presented in Table 5.30. Although pH did not remain explicitly in governing equation (Eqn. 3.35), different K_{app} values at different acidity levels exhibit the effect of pH on the degree of binding and as a consequence on the apparent binding constants.

Table 5.30: Effect of pH on Apparent Complexation Constants of Metal Ions

Metal	pH	logK
Cd	6.5	6.17
Cd	6	6.06
Cd	5	4.06
Ni	6.5	5.98
Ni	6	5.64
Ni	5	4.38
Zn	6.5	7.49
Zn	6	7.32
Zn	5.5	6.48
Zn	5	5.42
Zn	4	5.27
Zn	3	4.29

As it can be seen from Table 5.30, apparent binding constant of Zn^{2+} was higher than that of Cd^{2+}, which in turn was higher than that of Ni^{2+}. In addition, adverse effect of pH reduction can also be observed in apparent binding constants, which confirmed the results of PEUF experiments.

Same as pH, salt concentration did not remain explicitly in governing equation of binding constants (Eqn. 3.35). But adverse effect of ionic strength on the binding ability of cadmium, nickel and zinc ions and hence on the binding constants can be observed from the data presented in Table 5.31.

Table 5.31: Effect of Salt Concentration on Apparent Complexation Constants of Metal Ions (Calculations were made at predetermined values of L = 0.1, [PEI] = $5x10^{-3}$, n = 2)

Metal	pH	Salt Concentration	logK
Cd	6	0.1N $NaNO_3$	5.90
Cd	6.5	0.25N $NaNO_3$	6.17
Cd	6	0.25N $NaNO_3$	5.90
Cd	5	0.25N $NaNO_3$	4.31
Cd	6.5	0.5N $NaNO_3$	5.59
Cd	6	0.5N $NaNO_3$	5.48
Cd	6	1N $NaNO_3$	5.30
Ni	6	0.25N $NaNO_3$	5.59
Ni	6.5	0.5N $NaNO_3$	5.48
Ni	6	0.5N $NaNO_3$	5.03
Zn	6.5	0.5N $NaNO_3$	5.90
Zn	6	0.5N $NaNO_3$	5.39
Zn	6	0.25N $NaNO_3$	5.98

5.7.2 Effect of Mode of PEUF Operation on the Estimation of K_{app} Values

As mentioned before, in most of the PEUF studies, batch systems are employed [125, 126]. In these studies, the binding properties were documented in retention profiles, which are plots of the retention (R) versus the filtration factor (Z) [189]. Z is defined as the ratio of the volume of the filtrate and the volume of the cell solution.

Since in most of the PEUF studies, batch systems were employed, there is vast amount of data related with the complexation ability of several metal ions with different polyelectrolytes and/or polychetalogens. If a connection between the batch and continuous data can be established, by looking at the data obtained from batch studies performance of continuous mode of operations should be predicted.

In order to build-up a connection between batch and continuous mode studies, first of all, for the selected loading and pH values, retention values of cadmium, nickel and zinc ions were determined by the PEUF experiments performed in batch mode by the dead end stirred membrane cell, details of which was given in Section 4.2.3 of Chapter 4. Unsteady state data obtained during the experimental runs in batch mode system are given in Appendix H.

As it was mentioned earlier, metal/polymer ratio does not remain constant through out the batch processes because permeate stream was continuously withdrawn from the membrane cell and causing a decrease in metal concentration and relative increase in polymer concentration in feed solution. In order to calculate the instant loading value in membrane cell, several models have been developed [127]. But, for the sake of simplicity, it was assumed that changes in the relative amounts of metal and polymer concentrations did not affect the loading value in batch mode experiments performed in this study. Since the experiments were performed for dilute metal mixtures containing low amount of polymer, assumption of ineffectiveness of changes in metal concentration on loading was considered to be reasonable and the unsteady data presented in Appendix H verify the validity of this assumption.

By substituting the loading, total polymer concentration and retention values obtained in batch mode experiments into Equation 3.35, apparent complexation constants of cadmium, nickel and zinc were calculated and compared with the ones obtained by continuous mode PEUF experiments. Results are presented in Table 5.32.

As it can be seen from Table 5.32, almost same apparent binding constants are obtained both in batch and continuous mode operations. Therefore it can be concluded that, for dilute metal solutions containing relatively low amounts of polymer, by looking at the apparent constants calculated for batch systems, we may have an idea about the performance of PEUF systems operating in continuous mode and with the same conditions as batch system.

Table 5.32: Comparison of K_{app} Values Obtained in Continuous and Batch PEUF Systems

pH	Metal	[PEI]	n	R	L	logK
6	Cd	5x10^{-3}	2	0.95(Continuous)	0.1	6.06
6	Cd	5x10^{-3}	2	0.98 (Batch)	0.1	6.48
5	Cd	5x10^{-3}	2	0.21(Continuous)	0.1	4.06
5	Cd	5x10^{-3}	2	0.32 (Batch)	0.1	4.33
6	Ni	5x10^{-3}	2	0.88(Continuous)	0.1	5.64
6	Ni	5x10^{-3}	2	0.86 (Batch)	0.1	5.55
5	Ni	5x10^{-3}	2	0.34(Continuous)	0.1	4.38
5	Ni	5x10^{-3}	2	0.41 (Batch)	0.1	4.52
6	Zn	5x10^{-3}	2	1.00(Continuous)	0.1	7.32
6	Zn	5x10^{-3}	2	0.99 (Batch)	0.1	6.79
5	Zn	5x10^{-3}	2	0.82(Continuous)	0.1	5.42
5	Zn	5x10^{-3}	2	0.90 (Batch)	0.1	5.73

CHAPTER 6

CONCLUSIONS

In this study, effects of ionic strength, pH and metal/polymer ratio on the performance of continuous mode PEUF process have been examined. A model for PEUF process was developed and by the proposed model, apparent binding constants of metal-PEI complexation reactions were estimated. In addition, to understand the effect of conformational changes of PEI on its complexation ability, characterization tests of PEI were performed by dynamic and static light scattering analysis methods.

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

1. PEI has high binding ability towards the divalent ions of Cd, Ni and Zn at pH 6.5 and pH 6. PEI molecules retained cadmium and nickel ions effectively down to pH 6 and zinc ions down to pH 4. That means, cadmium and nickel are more sensitive to the changes in the acidity level of the solution.
2. By the addition of $NaNO_3$, depending on the concentration of $NaNO_3$, extent of complexation between PEI and metal ions decreases and as a consequence retentions of metals tend to decrease. For Cd^{2+} and Ni^{2+}, at pH 6.5 and 6, addition of low amounts of $NaNO_3$ did not change the degree of retention, adverse effect of salt addition can be observed upon the addition of high amounts of salt (i.e., $>$0.5N $NaNO_3$). Amoung the three metals, most drastic adverse effect of ionic strength was seen on Zn^{2+} retention especially at high loading values.
3. For single component metal solutions, in the absence of $NaNO_3$, order of binding for the considered metal ions was found to be $Zn^{2+} > Cd^{2+} > Ni^{2+}$. This binding sequence did not change in high ionic strength medium although extent of binding of each metal with PEI decreases with the addition of $NaNO_3$.

4. Possibility of fractional separation of metals from binary mixtures of Cd(II)-Ni(II), Cd(II)-Zn(II) and Ni(II)-Zn(II) pairs was investigated. Results showed that, for the solutions containing equimolar mixtures of Cd(II) and Ni(II), there is no inhibiting effect of one of the examined metals on complexation of the other over the range of concentrations analysed. Thus, the removal of cadmium and nickel mixture from aqueous solutions may be conducted as effectively as removal of each of these ions separately. Cd ions can be effectively separated from Ni ions at high pH values. On the other hand, reverse case is valid at low pH values; Ni ions can be fractionated from the cadmium-nickel solutions. Salt concentration has dual effect in binary metal solutions of Cd-Ni pair; by the addition of $NaNO_3$, retention of Cd ions were reduced and that of Ni ions were enhanced. By this dual effect, Ni(II) ions can be effectively fractionated from Cd(II) ions in high ionic strength medium.

5. When both Cd(II) and Zn(II) exist in the same solution, fractional separation can not be achieved in the studied pH range ($5 < pH < 6.5$). Fractional separation of zinc ions from equimolar binary mixture of Cd-Zn pair can only be achieved at pH 4. High ionic strength medium did not hinder Cd^{2+}-PEI or Zn^{2+}-PEI complexation reactions, almost complete retention of both metals can be achieved in binary Cd-Zn metal mixture, but this complete retention did not ends up with fractional separation of Cd ions over that of Zn ions or vice versa.

6. For Ni(II) and Zn(II) pair, as in the case of Cd(II)-Zn(II) pair, fractional separation can not be achieved at pH 6 and pH 5 in the absence of salt, whereas by the addition of 0.5N $NaNO_3$, Ni^{2+} retention became favourable over Zn^{2+} retention and as a consequence nickel ions can be fractionated from the solution containing equimolar Ni(II)-Zn(II) mixture.

7. In ternary component mixtures, at pH 6.5, degree of binding decreases in the order of $Cd^{2+} \geq Zn^{2+} > Ni^{2+}$, but at pH 5 situation was reversed because of the steep rise in the binding of Ni^{2+}, and as a consequence binding order at that acidity level was found to be in the order of $Ni^{2+} > Cd^{2+} \geq Zn^{2+}$. By the

courtesy of increased binding ability, nickel ions can be fractionated from the ternary metal solution of Cd^{2+}-Ni^{2+}-Zn^{2+}.

8. Dynamic/Static light scattering experiments showed that, decrease in pH did not affect the hydrodynamic radius of PEI macromolecules. R_H of the PEI macromolecule was estimated to be 57nm at pH 6 and 55nm at pH 5 and 4. It was also found that PEI exists in hyperbranced structure in the studied pH range.

   With the increase in ionic strength, PEI molecules tend to become smaller and as a result, smaller R_H values were obtained. PEI persists its hyperbranced structure in high ionic strength medium, but because of the aggregation tendency of molecules, 2^{nd} virial coefficients tend to decrease but remains positive indicating the repulsion between the PEI molecules.

9. Based on the proposed model, binding constants were calculated and compared with the ones cited in the literature. Proximity of the apparent constants which were estimated in this study and the ones estimated by potentiometric and/or spectrometric methods, indicate that, continuous mode-PEUF method can be used to predict the apparent binding constants of metals with polymeric agents.

   For dilute metal solutions and in the presence of low PEI concentrations, approximately same apparent binding constants were obtained based on the data obtained by batch and continuous mode PEUF operations. Therefore, it can be concluded that, by looking at the apparent constants calculated for batch systems, we may have an idea about the performance of PEUF systems operating in continuous mode and with the same conditions as batch system.

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APPENDIX A

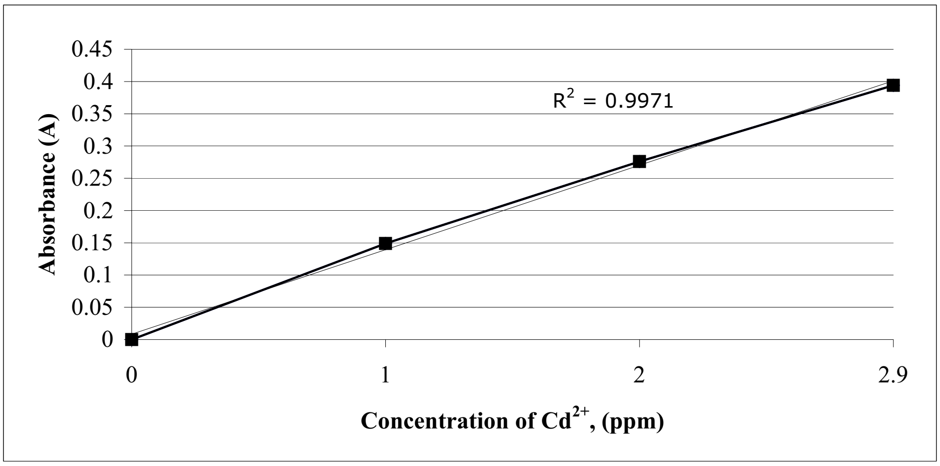
Flame-AAS Analysis Method

Flame operation employs a 50mm burner which supports air/acetylene flame used in the analysis of Cd, Ni and Zn. 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 Hallow Cathode Lamp for each element was used so that the instrument is able to sense the element and maximum current.

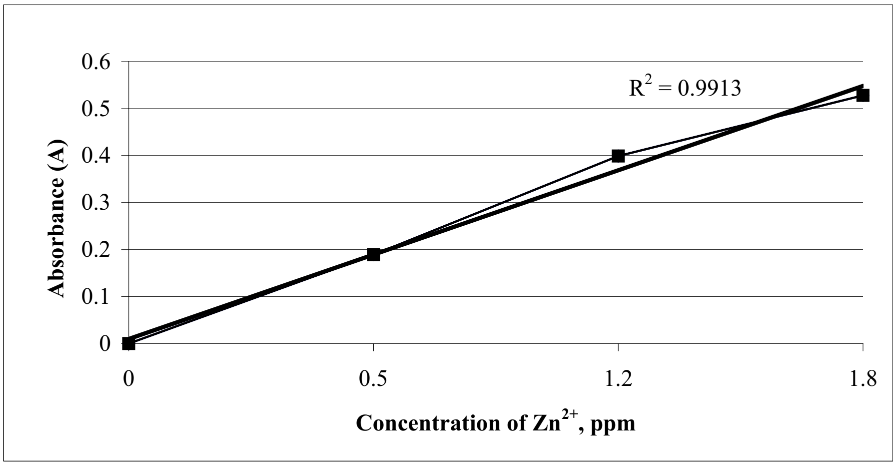
Standard samples for calibration were prepared from the atomic absorption standards for Cd, Ni and Zn according to predetermined optimum concentrations which give best signals. For the preparation of standard samples and as a blank solution ultrapure water having a specific conductance of $18.3 M\Omega cm^{-1}$ was used. Analysis of the polmer 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 cadmium, zinc and nickel obtained during the analysis were shown in Figure A.1, Figure A.2 and Figure A.3 respectively. Linear relationship was seen between concentration and absorbance in the calibration curves of the metals which means that Beer’s Law is valid within the concentration range studied in the experiments.



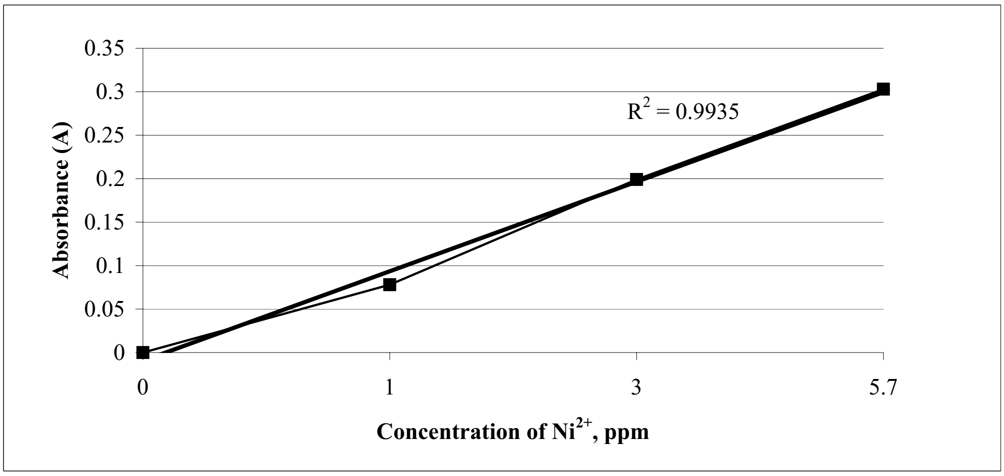
	Cd^{2+} Concentration (ppm)	Absorbance (A)
Blank	0	0
Std 1	1	0.149
Std 2	2	0.276
Std 3	2.9	0.394

Figure A.1: Calibration curve and its data obtained during F-AAS analysis of Cd^{2+}



	Zn^{2+} Concentration (ppm)	Absorbance (A)
Blank	0	0
Std 1	0.5	0.189
Std 2	1.2	0.399
Std 3	1.8	0.528

Figure A.2: Calibration curve and its data obtained during F-AAS analysis of Zn^{2+}



	Ni^{2+} Concentration (ppm)	Absorbance (A)
Blank	0	0
Std 1	1	0.078
Std 2	3	0.199
Std 3	5.7	0.303

Figure A.3: Calibration curve and its data obtained during F-AAS analysis of Ni^{2+}

APPENDIX B

Data Tables for DLS/SLS Experiments

dn/dc=0.2998x10^{-3} dm^3/g
Zimm Plot, q^2-dep:1st order, C-dep: 1st order

	Conc/(g/dm³)	Mw(app)/(g/mol)	<S²>(app)/µm²	Rg(app)/nm
Conc.=0	0	1.45E+04	5.69E-03	75.442
PEI (pH 6)	6	3.99E+03	1.51E-03	38.82
PEI (pH 6)	3.6	5.91E+03	2.43E-03	49.321
PEI (pH 6)	2.4	7.45E+03	3.18E-03	56.405
A_2: 1.632e-05 mol dm³/g² (± 3.69 %) Rg: 7.544e+01 nm (± 12.1 %)				

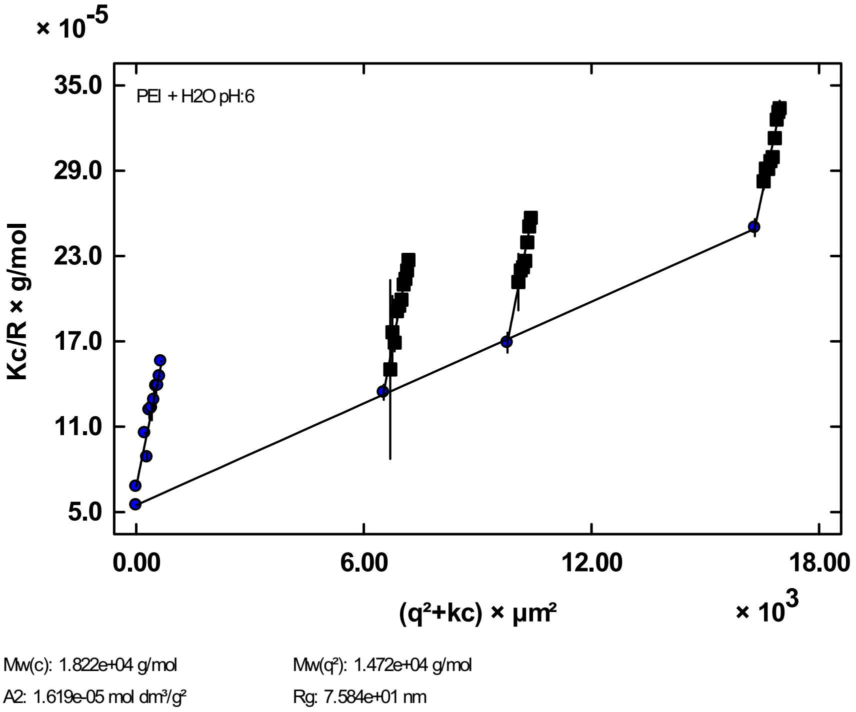
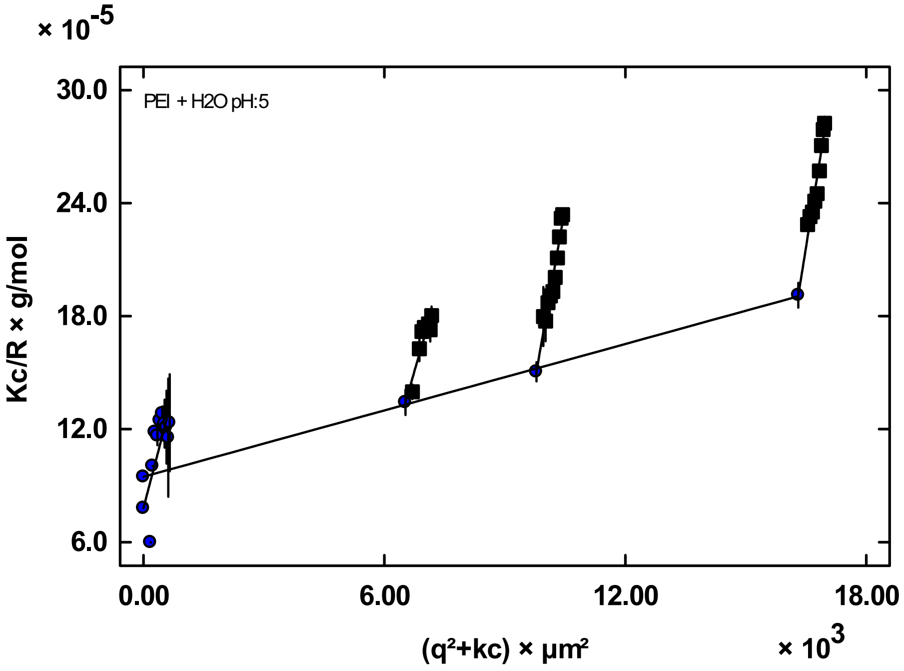


Figure B.1: Zimm Plot of PEI/Water Solution at pH 6

dn/dc=0.2998x10^{-3} dm^3/g
Zimm Plot, q^2-dep:1st order, C-dep: 1st order

	Conc/(g/dm³)	Mw(app)/(g/mol)	<S²>(app)/µm²	Rg(app)/nm
Conc.=0	0	1.28E+04	3.14E-03	56.044
PEI (pH 5)	6	5.23E+03	2.10E-03	45.868
PEI (pH 5)	3.6	6.65E+03	2.43E-03	49.287
PEI (pH 5)	2.4	7.45E+03	1.64E-03	40.497
A2: 7.985e-06 mol dm³/g² (± 5.3 %) Rg: 5.604e+01 nm (± 21.6 %)				

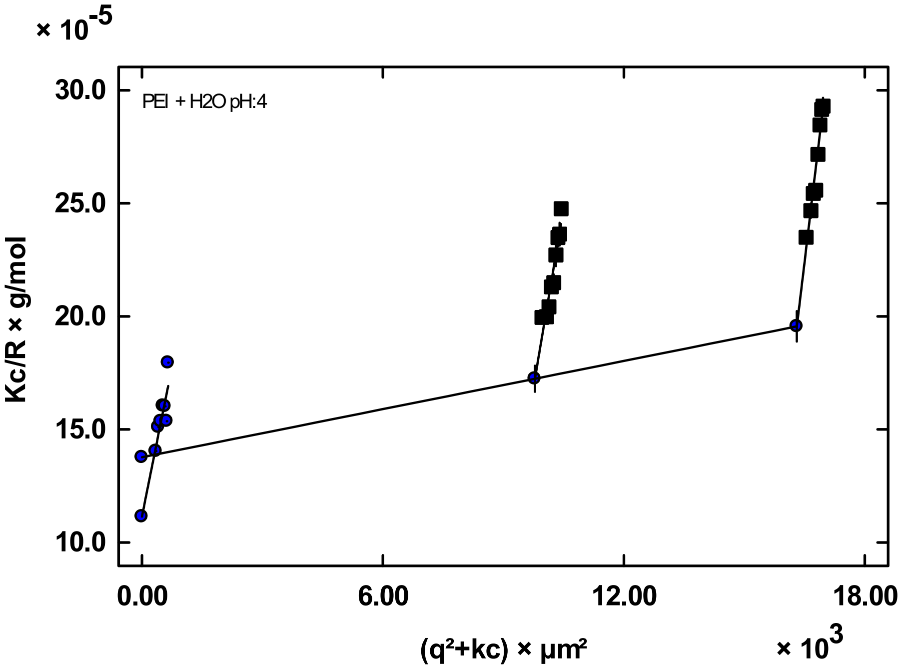


Mw(c): 1.056e+04 g/mol Mw(q²): 1.281e+04 g/mol
A2: 7.985e-06 mol dm³/g² Rg: 5.604e+01 nm

Figure B.2: Zimm Plot of PEI/Water Solution at pH 5

dn/dc=0.2998x10^{-3} dm^3/g
Zimm Plot, q^2-dep:1st order, C-dep: 1st order

	Conc/(g/dm³)	Mw(app)/(g/mol)	<S²>(app)/µm²	Rg(app)/nm
Conc.=0	0	8.98E+03	2.39E-03	48.849
PEI (pH 4)	6	5.11E+03	2.28E-03	47.717
PEI (pH 4)	3.6	5.80E+03	1.82E-03	42.714
A2: 4.826e-06 mol dm³/g² (± 0 %) Rg: 4.885e+01 nm (± 17.1 %)				



Mw(c): 7.265e+03 g/mol Mw(q²): 8.976e+03 g/mol

A2: 4.826e-06 mol dm³/g² Rg: 4.885e+01 nm

Figure B.3: Zimm Plot of PEI/Water Solution at pH 4

APPENDIX C

Data Tables for Lab-Scale Ultrafiltration Experiments

Table C.1: Values of loading and retention plotted in Figure 5.2

pH 6.5		
Loading (gCd^{2+}/gPEI)	Pilot-Scale Membrane S10Y10	Lab-Scale Membrane HG01
0.05	0.99	0.99
0.07	0.98	0.99
0.09	0.98	0.98
0.1	0.97	0.99
0.2	0.95	0.98
0.5	0.73	0.88

pH 6		
Loading (gCd^{2+}/gPEI)	Pilot-Scale Membrane S10Y10	Lab-Scale Membrane HG01
0.05	0.96	0.97
0.07	0.98	0.99
0.09	0.97	0.99
0.1	0.96	0.99
0.2	0.90	0.97
0.5	0.67	0.88

APPENDIX D

Unsteady and Steady State Data of PEUF Experiments

D.1 Experiments with Solutions Containing Cd^{2+}

Table D.1: Solution: Cd^{2+}, L=0.1, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	16.0	1.45	0.91	9.75
90	15.4	0.93	0.94	9.75
120	15.6	0.70	0.96	9.75
150	15.5	0.69	0.96	9.75
180	15.4	0.68	0.96	9.75
210	15.5	0.69	0.96	9.75
240	15.5	0.68	0.96	9.75

Table D.2: Solution: Cd^{2+}, L=0.1, pH 5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15	11.9	0.21	9.68
90	15	11.8	0.21	9.68
120	15	11.8	0.21	9.68
150	15	11.8	0.21	9.68
180	15	11.8	0.21	9.68
210	15	11.8	0.21	9.68
240	15	11.8	0.21	9.68

Table D.3: Solution: Cd^{2+}, L=0.5, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15	5.00	0.67	12.10
90	15	5.00	0.67	12.10
120	15	4.00	0.73	12.10
150	15	4.00	0.73	12.10
180	15	4.00	0.73	12.10
210	15	4.00	0.73	12.10
240	15	4.00	0.73	12.10

Table D.4: Solution: Cd^{2+}, L=0.5, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15	4.50	0.70	12.10
90	15	5.00	0.67	12.10
120	15	5.00	0.67	12.10
150	15	5.50	0.63	12.10
180	15	5.00	0.67	12.10
210	15	5.00	0.67	12.10
240	15	5.00	0.67	12.10

Table D.5: Solution: Cd^{2+}, L=0.5, pH 5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15	10.90	0.27	12.10
90	15	12.25	0.18	12.10
120	15	12.50	0.17	12.10
150	15	12.50	0.17	12.10
180	15	12.50	0.17	12.10
210	15	12.50	0.17	12.10
240	15	12.50	0.17	12.10

Table D.6: Solution: Cd^{2+}, L=1, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	13.4	6.65	0.50	12.15
90	14.0	6.65	0.53	12.15
120	14.0	6.63	0.53	12.15
150	14.3	6.66	0.53	12.15
180	14.3	6.67	0.53	12.15
210	14.4	6.70	0.53	12.15
240	14.4	6.70	0.53	12.15

Table D.7: Solution: Cd^{2+}, L=1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.2	7.40	0.51	12.15
90	15.2	7.80	0.49	12.15
120	15.2	7.85	0.48	12.15
150	15.2	7.80	0.49	12.15
180	15.2	7.87	0.48	12.15
210	15.1	7.86	0.48	12.15
240	15.3	7.89	0.48	12.15

Table D.8: Solution: Cd^{2+}, L=1, pH 5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.1	13.00	0.14	12.15
90	15.3	13.40	0.12	12.15
120	15.0	13.45	0.10	12.15
150	15.0	13.46	0.10	12.15
180	15.0	13.43	0.10	12.15
210	15.0	13.42	0.11	12.15
240	15.0	13.44	0.10	12.15

D.2 Experiments with Solutions Containing Cd^{2+}+ 0.1N $NaNO_3$

Table D.9: Solution: Cd^{2+} + 0.1N $NaNO_3$, L=0.1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15	0.98	0.94	9.72
90	15	0.96	0.94	9.72
120	15	1.02	0.93	9.72
150	15	1.02	0.93	9.72
180	15	0.99	0.93	9.72
240	15	1.00	0.93	9.72

Table D.10: Solution: Cd^{2+} + 0.1N $NaNO_3$, L=0.5, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.3	5.00	0.65	9.98
90	14.3	5.50	0.62	9.98
120	14.3	5.30	0.63	9.98
150	14.3	5.32	0.63	9.98
180	14.3	5.34	0.63	9.98
240	14.3	5.44	0.62	9.98

Table D.11: Solution: Cd^{2+} + 0.1N $NaNO_3$, L=1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.6	9.00	0.38	10.03
90	14.8	9.00	0.39	10.03
120	14.8	9.00	0.39	10.03
150	14.8	9.00	0.39	10.03
180	14.8	9.00	0.39	10.03
240	14.8	9.00	0.39	10.03

D.3 Experiments with Solutions Containing Cd^{2+} + 0.25N $NaNO_3$

Table D.12: Solution: Cd^{2+} + 0.25N $NaNO_3$, L=0.1, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.7	0.68	0.95	9.68
90	14.7	0.66	0.96	9.68
120	14.7	0.68	0.95	9.68
150	14.7	0.67	0.95	9.68
180	14.7	0.67	0.95	9.68
240	14.7	0.67	0.95	9.68

Table D.13: Solution: Cd^{2+} + 0.25N $NaNO_3$, L=0.1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15	1.00	0.93	9.68
90	15	1.00	0.93	9.68
120	15	1.00	0.93	9.68
150	15	1.00	0.93	9.68
180	15	1.00	0.93	9.68
240	15	1.00	0.93	9.68

Table D.14: Solution: Cd^{2+} + 0.25N $NaNO_3$, L=0.1, pH 5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.7	10.3	0.34	9.68
90	15.0	10.3	0.31	9.68
120	15.0	10.3	0.31	9.68
150	15.0	10.3	0.31	9.68
180	15.0	10.3	0.31	9.68
240	15.1	10.3	0.32	9.68

Table D.15: Solution: Cd^{2+} + 0.25N $NaNO_3$, L=0.5, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.6	4.50	0.69	10.23
90	14.6	4.46	0.69	10.23
120	14.6	4.38	0.70	10.23
150	14.6	4.38	0.70	10.23
180	14.6	4.38	0.70	10.23
240	14.6	4.38	0.70	10.23

Table D.16: Solution: Cd^{2+} + 0.25N $NaNO_3$, L=0.5, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.2	5.50	0.64	10.23
90	15.3	5.50	0.64	10.23
120	15.0	5.50	0.63	10.23
150	15.0	5.50	0.63	10.23
180	15.0	5.50	0.63	10.23
240	15.0	5.50	0.63	10.23

Table D.17: Solution: Cd^{2+} + 0.25N $NaNO_3$, L=0.5, pH 5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	13.20	0.12	10.23
90	15.0	13.20	0.12	10.23
120	15.0	13.20	0.12	10.23
150	15.0	13.20	0.12	10.23
180	15.0	13.20	0.12	10.23
240	15.0	13.20	0.12	10.23

Table D.18: Solution: Cd^{2+} + 0.25N $NaNO_3$, L=1, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.5	8.00	0.48	10.15
90	15.5	7.78	0.50	10.15
120	15.5	7.65	0.51	10.15
150	15.5	7.66	0.51	10.15
180	15.5	7.63	0.51	10.15
240	15.5	7.66	0.51	10.15

Table D.19: Solution: Cd^{2+} + 0.25N $NaNO_3$, L=1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.6	9.00	0.38	10.15
90	14.6	9.20	0.37	10.15
120	14.6	9.00	0.38	10.15
150	14.6	9.15	0.37	10.15
180	14.6	9.18	0.37	10.15
240	14.6	9.16	0.37	10.15

Table D.20: Solution: Cd^{2+} + 0.25N $NaNO_3$, L=1, pH 5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	11.50	0.23	10.15
90	15.0	11.50	0.23	10.15
120	15.0	11.50	0.23	10.15
150	15.0	11.50	0.23	10.15
180	15.0	11.50	0.23	10.15
240	15.0	11.50	0.23	10.15

D.4 Experiments with Solutions Containing Cd^{2+} + 0.5N $NaNO_3$

Table D.21: Solution: Cd^{2+} + 0.5N $NaNO_3$, L=0.1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.8	1.72	0.88	9.68
90	14.9	1.95	0.87	9.68
120	14.9	1.82	0.88	9.68
150	15.0	1.85	0.88	9.68
180	15.1	1.87	0.88	9.68
240	15.1	1.87	0.88	9.68

Table D.22: Solution: Cd^{2+} + 0.5N $NaNO_3$, L=0.5, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	8.66	0.42	9.88
90	15.0	8.68	0.42	9.88
120	15.0	8.58	0.43	9.88
150	15.0	8.60	0.43	9.88
180	15.0	8.55	0.43	9.88
240	15.0	8.50	0.43	9.88

Table D.23: Solution: Cd^{2+} + 0.5N $NaNO_3$, L=1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.8	10.00	0.32	9.68
90	15.1	10.00	0.34	9.68
120	15.0	9.80	0.35	9.68
150	15.0	9.90	0.34	9.68
180	15.0	9.89	0.34	9.68
240	15.0	9.88	0.34	9.68

D.5 Experiments with Solutions Containing Cd^{2+}+ 1N $NaNO_3$

Table D.24: Solution: Cd^{2+} + 1N $NaNO_3$, L=0.01, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.1	3.00	0.80	9.43
90	15.0	3.00	0.80	9.43
120	15.2	3.00	0.80	9.43
150	15.0	3.00	0.80	9.43
180	15.1	3.00	0.80	9.43
240	15.0	3.00	0.80 9.43	

Table D.25: Solution: Cd^{2+} + 1N $NaNO_3$, L=0.5, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.7	8.80	0.40	10.11
90	14.7	8.90	0.39	10.11
120	14.7	8.93	0.39	10.11
150	14.7	8.90	0.39	10.11
180	14.7	8.90	0.39	10.11
240	14.7	8.94	0.39	10.11

Table D.26: Solution: Cd^{2+} + 1N $NaNO_3$, L=0.7, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.6	9.00	0.38	10.20
90	14.6	9.50	0.35	10.20
120	14.6	9.90	0.32	10.20
150	14.6	9.80	0.33	10.20
180	14.6	9.78	0.33	10.20
240	14.6	9.79	0.33	10.20

D.6 Experiments with Solutions Containing Ni^{2+}

Table D.27: Solution: Ni^{2+}, L=0.1, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.7	0.95	0.94	9.68
90	14.8	1.06	0.93	9.68
120	15.0	0.85	0.94	9.68
180	15.1	0.84	0.94	9.68
210	15.0	0.88	0.94	9.68
240	15.0	0.86	0.94	9.68

Table D.28: Solution: Ni^{2+}, L=0.1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.1	2.09	0.86	9.68
90	15.3	2.17	0.86	9.68
120	15.3	1.83	0.88	9.68
180	15.2	1.84	0.88	9.68
210	15.3	1.77	0.88	9.68
240	15.3	1.78	0.88	9.68

Table D.29: Solution: Ni^{2+}, L=0.1, pH 5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.6	10.00	0.32	9.68
90	14.6	9.60	0.34	9.68
120	14.6	9.62	0.34	9.68
180	14.6	9.63	0.34	9.68
210	14.6	9.60	0.34	9.68
240	14.6	9.60	0.34	9.68

Table D.30: Solution: Ni^{2+}, L=0.5, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.2	4.16	0.73	9.73
90	15.2	5.22	0.66	9.73
120	15.0	4.93	0.67	9.73
180	15.0	4.96	0.67	9.73
210	15.1	4.98	0.67	9.73
240	15.1	5.02	0.67	9.73

Table D.31: Solution: Ni^{2+}, L=0.5, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.9	5.25	0.65	9.71
90	14.9	5.25	0.65	9.71
120	15.0	5.88	0.61	9.71
180	14.9	5.88	0.61	9.71
210	14.9	5.87	0.61	9.71
240	14.9	5.88	0.61	9.71

Table D.32: Solution: Ni^{2+}, L=0.5, pH 5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	13.00	0.13	9.73
90	15.0	12.50	0.17	9.73
120	15.0	12.60	0.16	9.73
180	15.0	12.40	0.17	9.73
210	15.0	12.55	0.16	9.73
240	15.0	12.58	0.16	9.73

Table D.33: Solution: Ni^{2+}, L=1, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.5	9.00	0.38	9.98
90	14.8	8.88	0.40	9.98
120	14.8	8.87	0.40	9.98
180	14.8	8.86	0.40	9.98
210	14.8	8.86	0.40	9.98
240	14.8	8.86	0.40	9.98

Table D.34: Solution: Ni^{2+}, L=1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.2	9.82	0.35	9.98
90	15.2	9.83	0.35	9.98
120	15.2	9.81	0.35	9.98
180	15.2	9.81	0.35	9.98
210	15.2	9.81	0.35	9.98
240	15.2	9.81	0.35	9.98

Table D.35: Solution: Ni^{2+}, L=1, pH 5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	13.50	0.10	9.98
90	15.0	13.50	0.10	9.98
120	15.0	13.50	0.10	9.98
180	15.0	13.50	0.10	9.98
210	15.0	13.50	0.10	9.98
240	15.0	13.50	0.10	9.98

D.7 Experiments with Solutions Containing Ni^{2+}+0.25N $NaNO_3$

Table D.36: Solution: Ni^{2+} + 0.25N $NaNO_3$, L=0.1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.2	1.90	0.88	9.68
90	15.2	2.00	0.87	9.68
120	15.2	1.90	0.88	9.68
180	15.2	2.00	0.87	9.68
210	15.2	2.00	0.87	9.68
240	15.2	2.00	0.87	9.68

Table D.37: Solution: Ni^{2+} + 0.25N $NaNO_3$, L=0.3, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	4.00	0.73	9.68
90	15.0	4.00	0.73	9.68
120	15.0	4.00	0.73	9.68
180	15.0	4.00	0.73	9.68
210	15.0	4.00	0.73	9.68
240	15.0	4.00	0.73	9.68

Table D.38: Solution: Ni^{2+} + 0.25N $NaNO_3$, L=1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.8	10.30	0.30	10.11
90	14.8	10.30	0.30	10.11
120	14.8	10.30	0.30	10.11
180	14.8	10.30	0.30	10.11
210	14.8	10.30	0.30	10.11
240	14.8	10.30	0.30	10.11

D.8 Experiments with Solutions Containing Ni^{2+}+0.5N $NaNO_3$

Table D.39: Solution: Ni^{2+} + 0.5N $NaNO_3$, L=0.07, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	2.58	0.83	9.58
90	15.0	2.58	0.83	9.58
120	15.0	2.46	0.84	9.58
180	15.0	2.45	0.84	9.58
210	15.0	2.40	0.84	9.58
240	15.0	2.43	0.84	9.58

Table D.40: Solution: Ni^{2+} + 0.5N $NaNO_3$, L=1, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	9.60	0.36	10.09
90	15.0	9.60	0.36	10.09
120	15.0	9.60	0.36	10.09
180	15.0	9.60	0.36	10.09
210	15.0	9.60	0.36	10.09
240	15.0	9.60	0.36	10.09

Table D.41: Solution: Ni^{2+} + 0.5N $NaNO_3$, L=0.07, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	5.00	0.67	9.60
90	15.0	4.80	0.68	9.60
120	15.0	4.80	0.68	9.60
180	15.0	4.80	0.68	9.60
210	15.0	4.80	0.68	9.60
240	15.0	4.80	0.68	9.60

D.9 Experiments with Solutions Containing Zn^{2+}

Table D.42: Solution: Zn^{2+}, L=0.1, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.8	0.08	0.99	9.68
90	15.0	0.08	0.99	9.68
120	14.9	0.08	0.99	9.68
180	14.9	0.08	0.99	9.68
210	14.9	0.08	0.99	9.68
240	14.9	0.08	0.99	9.68

Table D.43: Solution: Zn^{2+}, L=0.1, pH 4

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	3.5	0.77	9.68
90	15.0	3.5	0.77	9.68
120	15.0	3.5	0.77	9.68
180	15.0	3.5	0.77	9.68
210	15.0	3.5	0.77	9.68
240	15.0	3.5	0.77	9.68

Table D.44: Solution: Zn^{2+}, L=0.1, pH 3

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.3	10.5	0.31	9.68
90	15.0	10.5	0.30	9.68
120	15.0	10.5	0.30	9.68
180	15.0	10.5	0.30	9.68
210	15.0	10.5	0.30	9.68
240	15.0	10.5	0.30	9.68

Table D.45: Solution: Zn^{2+}, L=1, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.2	3.4	0.78	10.12
90	15.2	3.2	0.79	10.12
120	15.2	3.3	0.78	10.12
180	15.2	3.3	0.78	10.12
210	15.2	3.3	0.78	10.12
240	15.2	3.3	0.78	10.12

Table D.46: Solution: Zn^{2+}, L=1, pH 4

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	13.4	6.0	0.55	12.13
90	13.9	5.9	0.58	12.13
120	13.9	6.0	0.57	12.13
180	13.9	6.0	0.57	12.13
210	13.9	6.0	0.57	12.13
240	13.9	6.0	0.57	12.13

Table D.47: Solution: Zn^{2+}, L=1, pH 3

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.9	12.0	0.19	12.13
90	14.9	12.0	0.19	12.13
120	15.0	12.0	0.20	12.13
180	15.0	12.0	0.20	12.13
210	15.0	12.0	0.20	12.13
240	15.0	12.0	0.20	12.13

D.10 Experiments with Solutions Containing Zn^{2+}+0.25N$NaNO_3$

Table D.48: Solution: Zn^{2+}+0.25N $NaNO_3$, L=0.3, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	3.5	0.77	9.75
90	15.0	3.6	0.76	9.75
120	15.0	3.6	0.76	9.75
180	15.0	3.6	0.76	9.75
210	15.0	3.6	0.76	9.75
240	15.0	3.6	0.76	9.75

Table D.49: Solution: Zn^{2+}+0.25N $NaNO_3$, L=0.5, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	5.2	0.65	9.88
90	15.0	5.2	0.65	9.88
120	15.0	5.2	0.65	9.88
180	15.0	5.2	0.65	9.88
210	15.0	5.2	0.65	9.88
240	15.0	5.2	0.65	9.88

Table D.50: Solution: Zn^{2+}+0.25N $NaNO_3$, L=1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.0	7.3	0.51	9.88
90	15.0	7.3	0.51	9.88
120	15.0	7.3	0.51	9.88
180	15.0	7.3	0.51	9.88
210	15.0	7.3	0.51	9.88
240	15.0	7.3	0.51	9.88

D.11 Experiments with Solutions Containing Zn^{2+}+0.5N $NaNO_3$

Table D.51: Solution: Zn^{2+}+0.5N $NaNO_3$, L=0.1, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.8	1.06	0.93	9.68
90	14.8	1.07	0.93	9.68
120	14.8	1.06	0.93	9.68
180	14.8	1.05	0.93	9.68
210	14.8	1.06	0.93	9.68
240	14.8	1.07	0.93	9.68

Table D.52: Solution: Zn^{2+}+0.5N $NaNO_3$, L=1, pH 6.5

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	15.3	10.0	0.35	10.11
90	15.3	10.0	0.35	10.11
120	15.3	10.0	0.35	10.11
180	15.3	10.0	0.35	10.11
210	15.3	10.0	0.35	10.11
240	15.3	10.0	0.35	10.11

Table D.53: Solution: Zn^{2+}+0.5N $NaNO_3$, L=1, pH 6

Time (min.)	Feed Conc. (ppm)	Permeate Conc. (ppm)	Retention	Permeate Flux (lt/m^2.hr)
60	14.6	12.7	0.13	10.11
90	14.6	12.5	0.14	10.11
120	14.6	12.5	0.14	10.11
180	14.6	12.5	0.14	10.11
210	14.6	12.5	0.14	10.11
240	14.6	12.5	0.14	10.11

D.12 Experiments with Solutions Containing Cd^{2+}+Ni^{2+}

Table D.54: Solution: Cd^{2+}+Ni^{2+}, L=0.1, pH 6

Time(min.)	R_{Cd}	R_{Ni}	Permeate Flux (lt/m^2.hr)
60	0.99	0.91	9.65
90	0.99	0.93	9.65
120	0.99	0.93	9.65
180	0.99	0.93	9.65
210	0.99	0.93	9.65
240	0.99	0.93	9.65

Table D.55: Solution: Cd^{2+}+Ni^{2+}, L=0.7, pH 5

Time(min.)	R_{Cd}	R_{Ni}	Permeate Flux (lt/m^2.hr)
60	0.77	0.67	9.98
90	0.77	0.67	9.98
120	0.77	0.67	9.98
180	0.77	0.67	9.98
210	0.77	0.67	9.98
240	0.77	0.67	9.98

Table D.56: Solution: Cd^{2+}+Ni^{2+}, L=1, pH 5

Time(min.)	R_{Cd}	R_{Ni}	Permeate Flux (lt/m^2.hr)
60	0.74	0.66	10.09
90	0.74	0.66	10.09
120	0.74	0.66	10.09
180	0.74	0.66	10.09
210	0.74	0.66	10.09
240	0.74	0.66	10.09

D.13 Experiments with Solutions Containing Cd^{2+}+Ni^{2+}+0.5N$NaNO_3$

Table D.57: Solution: Cd^{2+}+Ni^{2+}+ 0.5N $NaNO_3$, L=0.1, pH 6

Time(min.)	R_{Cd}	R_{Ni}	Permeate Flux (lt/m^2.hr)
60	0.80	0.89	9.65
90	0.80	0.89	9.65
120	0.80	0.89	9.65
180	0.80	0.89	9.65
210	0.80	0.89	9.65
240	0.80	0.89	9.65

Table D.58: Solution: Cd^{2+}+Ni^{2+}+ 0.5N $NaNO_3$, L=0.7, pH 5

Time(min.)	R_{Cd}	R_{Ni}	Permeate Flux (lt/m^2.hr)
60	0.29	0.56	9.90
90	0.29	0.56	9.90
120	0.29	0.56	9.90
180	0.29	0.56	9.90
210	0.29	0.56	9.90
240	0.29	0.56	9.90

Table D.59: Solution: Cd^{2+}+Ni^{2+}+ 0.5N $NaNO_3$, L=1, pH 5

Time(min.)	R_{Cd}	R_{Ni}	Permeate Flux (lt/m^2.hr)
60	0.27	0.49	10.10
90	0.27	0.49	10.10
120	0.27	0.49	10.10
180	0.27	0.49	10.10
210	0.27	0.49	10.10
240	0.27	0.49	10.10

D.14 Experiments with Solutions Containing Cd^{2+}+Zn^{2+}

Table D.60: Solution: Cd^{2+}+Zn^{2+}, L=0.1, pH 6.5

Time(min.)	R_{Cd}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.99	0.99	9.66
90	0.99	0.99	9.66
120	0.99	0.99	9.66
180	0.99	0.99	9.66
210	0.99	0.99	9.66
240	0.99	0.99	9.66

Table D.61: Solution: Cd^{2+}+Zn^{2+}, L=0.1, pH 5.5

Time(min.)	R_{Cd}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.96	0.97	9.68
90	0.96	0.97	9.68
120	0.96	0.97	9.68
180	0.96	0.97	9.68
210	0.96	0.97	9.68
240	0.96	0.97	9.68

Table D.62: Solution: Cd^{2+}+Zn^{2+}, L=1, pH 5.5

Time(min.)	R_{Cd}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.89	0.86	10.07
90	0.89	0.86	10.07
120	0.89	0.86	10.07
180	0.89	0.86	10.07
210	0.89	0.86	10.07
240	0.89	0.86	10.07

D.15 Experiments with Solutions Containing Cd^{2+}+Zn^{2+}+0.5N$NaNO_3$

Table D.63: Solution: Cd^{2+}+Zn^{2+}+0.5N$NaNO_3$, L=0.5, pH 6.5

Time(min.)	R_{Cd}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.90	0.92	9.86
90	0.90	0.92	9.86
120	0.90	0.92	9.86
180	0.90	0.92	9.86
210	0.90	0.92	9.86
240	0.90	0.92	9.86

Table D.64: Solution: Cd^{2+}+Zn^{2+}+0.5N$NaNO_3$, L=0.5, pH 5.5

Time(min.)	R_{Cd}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.16	0.45	9.86
90	0.16	0.43	9.86
120	0.15	0.44	9.86
180	0.16	0.44	9.86
210	0.16	0.44	9.86
240	0.16	0.44	9.86

Table D.65: Solution: Cd^{2+}+Zn^{2+}+0.5N$NaNO_3$, L=0.5, pH 4

Time(min.)	R_{Cd}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.07	0.28	9.86
90	0.07	0.28	9.86
120	0.07	0.28	9.86
180	0.07	0.28	9.86
210	0.07	0.28	9.86
240	0.07	0.28	9.86

D.16 Experiments with Solutions Containing Ni^{2+}+Zn^{2+}

Table D.66: Solution: Ni^{2+}+Zn^{2+}, L=0.1, pH 6

Time(min.)	R_{Ni}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.90	0.99	9.69
90	0.92	0.99	9.69
120	0.93	0.99	9.69
180	0.93	0.99	9.69
210	0.93	0.99	9.69
240	0.93	0.99	9.69

Table D.67: Solution: Ni^{2+}+Zn^{2+}, L=0.1, pH 5

Time(min.)	R_{Ni}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.90	0.88	9.66
90	0.90	0.88	9.66
120	0.90	0.88	9.66
180	0.90	0.88	9.66
210	0.90	0.88	9.66
240	0.90	0.88	9.66

Table D.68: Solution: Ni^{2+}+Zn^{2+}, L=1, pH 5

Time(min.)	R_{Ni}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.84	0.79	10.13
90	0.84	0.79	10.13
120	0.84	0.79	10.13
180	0.84	0.79	10.13
210	0.84	0.79	10.13
240	0.84	0.79	10.13

D.17 Experiments with Solutions Containing Ni^{2+}+Zn^{2+}+0.5N$NaNO_3$

Table D.69: Solution: Ni^{2+}+Zn^{2+}+0.5N$NaNO_3$, L=0.1, pH 6

Time(min.)	R_{Ni}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.94	0.87	9.70
90	0.94	0.87	9.70
120	0.94	0.87	9.70
180	0.94	0.87	9.70
210	0.94	0.87	9.70
240	0.94	0.87	9.70

Table D.70: Solution: Ni^{2+}+Zn^{2+}+0.5N$NaNO_3$, L=1, pH 6

Time(min.)	R_{Ni}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.67	0.39	10.12
90	0.67	0.39	10.12
120	0.67	0.39	10.12
180	0.67	0.39	10.12
210	0.67	0.39	10.12
240	0.67	0.39	10.12

Table D.71: Solution: Ni^{2+}+Zn^{2+}+0.5N$NaNO_3$, L=1, pH 5

Time(min.)	R_{Ni}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.40	0.33	10.12
90	0.40	0.33	10.12
120	0.40	0.33	10.12
180	0.40	0.33	10.12
210	0.40	0.33	10.12
240	0.40	0.33	10.12

D.18 Experiments with Solutions Containing Cd^{2+}+Ni^{2+}+Zn^{2+}

Table D.72: Solution: Cd^{2+}+Ni^{2+}+Zn^{2+} , L=0.1, pH 6.5

Time(min.)	R_{Cd}	R_{Ni}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.99	0.80	0.98	9.65
90	0.99	0.80	0.98	9.65
120	0.99	0.80	0.98	9.65
180	0.99	0.80	0.98	9.65
210	0.99	0.80	0.98	9.65
240	0.99	0.80	0.98	9.65

Table D.73: Solution: Cd^{2+}+Ni^{2+}+Zn^{2+} , L=0.1, pH 5

Time(min.)	R_{Cd}	R_{Ni}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.64	0.73	0.6	9.65
90	0.64	0.73	0.56	9.65
120	0.64	0.73	0.56	9.65
180	0.65	0.73	0.56	9.65
210	0.65	0.73	0.56	9.65
240	0.65	0.73	0.56	9.65

Table D.74: Solution: Cd^{2+}+Ni^{2+}+Zn^{2+} , L=1, pH 6.5

Time(min.)	R_{Cd}	R_{Ni}	R_{Zn}	Permeate Flux (lt/m^2.hr)
60	0.30	0.63	0.34	10.08
90	0.28	0.63	0.34	10.08
120	0.28	0.63	0.34	10.08
180	0.28	0.63	0.34	10.08
210	0.28	0.63	0.34	10.08
240	0.28	0.63	0.34	10.08

APPENDIX E

Data Tables of PEUF Experiments with Single Component Metal Solutions

Table E.1: Values of Loading and Retention Plotted in Figure 5.7

Loading (g. Cd(II) /g.PEI)	pH 6.5	pH 6	pH 5
0.05	0.98	0.98	
0.07	0.98	0.98	0.35
0.09	0.98	0.97	0.23
0.1	0.96	0.95	0.21
0.2	0.96	0.90	0.20
0.3	0.86	0.77	0.20
0.4	0.85	0.75	0.19
0.5	0.73	0.67	0.17
0.6	0.72	0.55	0.15
0.7	0.60	0.50	0.13
1	0.53	0.48	0.10

Table E.2: Values of Loading and Retention Plotted in Figure 5.8

Loading (g. Ni(II) /g.PEI)	pH 6.5	pH 6	pH 5
0.07	0.97	-	0.96
0.1	0.94	0.88	0.34
0.2	0.84	0.79	-
0.3	0.77	0.73	0.27
0.4	0.68	0.66	-
0.5	0.67	0.61	0.16
0.7	0.47	0.45	0.12
1	0.40	0.35	0.10

Table E.3: Values of Loading and Retention Plotted in Figure 5.10

Loading (g. Zn(II) /g.PEI)	pH 6.5	pH 6	pH 5.5	pH 5	pH 4	pH 3
0.1	0.998	0.997	0.98	0.82	0.77	0.3
0.2	0.95	0.94	-	-	-	-
0.3	0.93	0.92	0.91	0.80	0.73	0.27
0.4	0.89	0.88	-	-	-	-
0.5	0.88	0.77	0.76	0.73	0.68	0.24
0.6	0.81	0.75	-	-	-	-
0.7	-	-	0.73	0.72	-	-
0.8	0.80	0.71	-	-	-	-
1	0.78	-	0.70	0.68	0.57	0.20

Table E.4: Values of Loading and Retention Plotted in Figure 5.11 (pH 6.5)

pH 6.5			
Loading	R_{Zn}	R_{Cd}	R_{Ni}
0.05	-	0.98	0.98
0.07	-	0.98	0.97
0.09	-	0.98	-
0.1	0.99	0.96	0.94
0.2	0.95	0.96	0.84
0.3	0.93	0.86	0.77
0.4	0.89	0.85	0.68
0.5	0.88	0.73	0.67
0.6	0.81	0.72	0.47
0.7	-	0.60	-
0.8	0.80	-	-
1.0	0.78	0.53	0.40

Table E.5: Values of Loading and Retention Plotted in Figure 5.11 (pH 6 and 5)

pH 6			
Loading	R_{Zn}	R_{Cd}	R_{Ni}
0.05	-	0.98	-
0.07	-	0.98	0.96
0.09	-	0.97	-
0.1	0.99	0.95	0.88
0.2	0.94	0.90	0.79
0.3	0.92	0.77	0.73
0.4	0.88	0.75	0.66
0.5	0.77	0.67	0.61
0.6	0.75	0.55	0.45
0.7	-	0.50	-
0.8	0.71	-	-
1.0	0.67	0.48	0.35

pH 5			
Loading	R_{Zn}	R_{Cd}	R_{Ni}
0.1	0.82	0.21	0.34
0.2	-	0.20	-
0.3	0.80	0.20	0.27
0.4	-	0.19	-
0.5	0.73	0.17	0.16
0.7	0.72	0.15	0.12
1.0	0.68	0.10	0.10

Table E.6: Values of Loading and Retention Plotted in Figure 5.13 (pH 6.5)

Loading (g.Cd(II)/g.PEI)	No $NaNO_3$ R_{Cd}(pH 6.5)	0.25N $NaNO_3$ R_{Cd}(pH 6.5)	0.5N $NaNO_3$ R_{Cd}(pH 6.5)
0.1	0.96	0.95	0.87
0.3	0.86	0.84	0.78
0.5	0.73	0.70	0.70
0.7	0.60	0.57	0.55
1	0.53	0.51	0.50

Table E.7: Values of Loading and Retention Plotted in Figure 5.13 (pH 6)

Loading	No $NaNO_3$ R_{Cd}(pH 6)	0.1N $NaNO_3$ R_{Cd}(pH 6)	0.25N $NaNO_3$ R_{Cd}(pH 6)	0.5N $NaNO_3$ R_{Cd}(pH 6)	1N $NaNO_3$ R_{Cd}(pH 6)
0.1	0.95	0.93	0.93	0.88	0.80
0.2	0.90	0.87	0.83	0.79	0.78
0.3	0.77	0.77	0.75	0.68	0.65
0.4	0.75	0.73	0.65	0.57	0.51
0.5	0.67	0.63	0.63	0.43	0.39
0.7	0.50	-	0.48	0.38	0.33
1	0.48	0.39	0.37	0.34	0.31

Table E.8: Values of Loading and Retention Plotted in Figure 5.14

Loading (g.Ni(II)/g.PEI)	No $NaNO_3$ R_{Ni}(pH 6.5)	0.5N $NaNO_3$ R_{Ni}(pH 6.5)
0.07	0.97	0.84
0.2	0.84	0.83
0.3	0.77	0.73
0.4	0.68	0.64
0.5	0.67	0.63
0.6	0.47	-
1	0.40	0.36

Loading (g.Ni(II)/g.PEI)	No $NaNO_3$ R_{Ni}(pH 6)	0.25N $NaNO_3$ R_{Ni}(pH 6)	0.5N $NaNO_3$ R_{Ni}(pH 6)
0.07	0.96	-	0.68
0.1	0.88	0.87	0.67
0.2	0.79	-	0.58
0.3	0.73	0.73	-
0.4	0.66	-	0.52
0.5	0.55	0.47	0.35
0.7	0.45	-	-
1	0.35	0.30	0.26

Table E.9: Values of Loading and Retention Plotted in Figure 5.15

Loading (g.Zn(II)/g.PEI)	No $NaNO_3$ R_{Zn}(pH 6.5)	0.5N $NaNO_3$ R_{Zn}(pH 6.5)
0.1	0.99	0.93
0.2	0.95	0.89
0.3	0.93	0.88
0.4	0.89	0.81
0.5	0.88	0.74
0.6	0.81	0.54
1	0.78	0.35

Loading (g.Zn(II)/g.PEI)	No $NaNO_3$ R_{Zn}(pH 6)	0.25N $NaNO_3$ R_{Zn}(pH 6)	0.5N $NaNO_3$ R_{Zn}(pH 6)
0.1	0.99	0.94	0.81
0.2	0.94	-	0.79
0.3	0.92	0.76	0.72
0.4	0.88	-	0.6
0.5	0.77	0.65	0.5
0.6	0.75	-	0.23
0.8	0.71	-	-
1	0.70	0.51	0.14

Table E.10: Values of Loading and Retention Plotted in Figure 5.16

Loading (g.Zn(II)/g.PEI)	No $NaNO_3$ R_{Zn}(pH 5)	0.5N $NaNO_3$ R_{Zn}(pH 5)
0.1	0.82	0.77
0.3	0.8	0.73
0.5	0.73	0.68
0.7	0.72	0.58
1	0.68	0.55

Table E.11: Values of Loading and Retention Plotted in Figure 5.17

In the Presence of 0.5N $NaNO_3$			
Loading	R_{Zn}(pH 6.5)	R_{Cd}(pH 6.5)	R_{Ni}(pH 6.5)
0.1	0.93	0.87	0.84
0.2	0.89	0.85	0.83
0.3	0.88	0.78	0.73
0.5	0.74	0.70	0.63
0.7	0.55	0.54	0.43

Table E.12: Values of Loading and Retention Plotted in Figure 5.18

In the Presence of 0.25N $NaNO_3$			
Loading	R_{Zn}(pH 6)	R_{Cd}(pH 6)	R_{Ni}(pH 6)
0.1	0.94	0.93	0.87
0.3	0.76	0.75	0.73
0.5	0.65	0.63	0.47
1	0.51	0.37	0.30

In the Presence of 0.5N $NaNO_3$			
Loading	R_{Zn}(pH 6)	R_{Cd}(pH 6)	R_{Ni}(pH 6)
0.1	0.93	0.88	0.67
0.2	0.89	0.79	0.58
0.4	0.81	0.57	0.52
0.5	0.74	0.43	0.35
0.7	0.54	0.38	0.30
1	0.35	0.34	0.26

APPENDIX F

Data Tables of PEUF Experiments with Multicomponent Metal Solutions

Table F.1: Values of Loading and Retention Plotted in Figure 5.19

Retentions in Binary Metal Mixture		
Loading	R_{Cd} (pH 6.5)	R_{Ni}(pH 6.5)
0.05	0.99	0.95
0.10	0.99	0.91
0.20	0.99	0.84
0.24	0.99	0.79
0.28	0.99	0.77
0.30	0.99	0.73
0.40	0.99	0.69
0.50	0.94	0.67
0.80	0.84	0.60
1.00	0.83	0.55

Retentions in Binary Metal Mixture		
Loading	R_{Cd} (pH 6)	R_{Ni}(pH 6)
0.05	0.99	0.97
0.10	0.99	0.93
0.20	0.99	0.90
0.24	0.99	0.88
0.28	0.99	0.86
0.30	0.95	0.73
0.40	0.88	0.69
0.50	0.76	0.60
0.80	0.57	0.51

Table F.2: Values of Loading and Retention Plotted in Figure 5.20

Retentions in Binary Metal Mixture		
Loading	R_{Cd} (pH 5)	R_{Ni}(pH 5)
0.1	0.82	0.72
0.3	0.80	0.70
0.5	0.78	0.71
0.7	0.77	0.67
1	0.74	0.66

Table F.3: Values of Loading and Retention Plotted in Figure 5.21

Retentions in Binary Metal Mixture		
Loading	R_{Cd} (pH 4)	R_{Ni}(pH 4)
0.1	0.80	0.90
0.3	0.80	0.85
0.5	0.78	0.84
1	0.71	0.82

Table F.4: Values of Loading and Retention Plotted in Figure 5.22

Binary Metal Mixture + 0.5N $NaNO_3$		
Loading	R_{Cd}(pH 6.5)	R_{Ni}(pH 6.5)
0.05	0.93	0.86
0.1	0.90	0.90
0.2	0.91	0.88
0.3	0.73	0.88
0.4	0.51	0.84
0.5	0.27	0.83
0.8	0.16	0.68

Retentions in Binary Metal Mixture		
Loading	R_{Cd} (pH 6)	R_{Ni}(pH 6)
0.05	0.92	0.85
0.1	0.80	0.89
0.2	0.76	0.85
0.3	0.47	0.83
0.4	0.36	0.82
0.5	0.20	0.80
0.8	0.11	0.64

Table F.5: Values of Loading and Retention Plotted in Figure 5.22 (pH 5)

Binary Metal Mixture + 0.5N $NaNO_3$		
Loading	R_{Cd}(pH 5)	R_{Ni}(pH 5)
0.1	0.40	0.87
0.3	0.33	0.72
0.5	0.31	0.60
0.7	0.29	0.56
1	0.27	0.49

Table F.6: Values of Loading and Retention Plotted in Figure 5.23

Retentions in Binary Metal Mixtures		
Loading	R_{Cd}(pH 6.5)	R_{Zn}(pH 6.5)
0.1	0.99	0.99
0.3	0.99	0.99
0.5	0.92	0.92
0.6	0.84	0.86
0.8	0.88	0.91
0.8	0.92	0.93
1	0.83	0.86

Retentions in Binary Metal Mixtures		
Loading	R_{Cd}(pH 6)	R_{Zn}(pH 6)
0.1	0.99	0.99
0.3	0.98	0.97
0.5	0.88	0.87
0.6	0.76	0.80
0.8	0.83	0.87
1	0.67	0.68

Table F.7: Values of Loading and Retention Plotted in Figure 5.24

Retentions in Binary Metal Mixtures		
Loading	R_{Cd}(pH 5)	R_{Zn}(pH 5)
0.1	0.85	0.83
0.3	0.82	0.80
0.5	0.77	0.78
0.6	0.77	0.78
0.7	0.77	0.78
1	0.77	0.78

Table F.8: Values of Loading and Retention Plotted in Figure 5.24 (pH 4)

Retentions in Binary Metal Mixtures		
Loading	R_{Cd}(pH 4)	R_{Zn}(pH 4)
0.1	0.53	0.68
0.3	0.48	0.65
0.5	0.40	0.64
1	0.40	0.63

Table F.9: Values of Loading and Retention Plotted in Figure 5.25

Binary Metal Mixture+0.5N $NaNO_3$		
Loading	R_{Cd}(pH 6.5)	R_{Zn}(pH 6.5)
0.1	0.95	0.94
0.3	0.94	0.93
0.5	0.90	0.92
0.7	0.87	0.91
1	0.82	0.86

Binary Metal Mixture + 0.5N $NaNO_3$		
Loading	R_{Cd}(pH 5.5)	R_{Zn}(pH 5.5)
0.1	0.46	0.56
0.3	0.25	0.47
0.5	0.16	0.44
0.7	0.13	0.32
1	0.10	0.28

Binary Metal Mixture + 0.5N $NaNO_3$		
Loading	R_{Cd}(pH 4)	R_{Zn}(pH 4)
0.1	0.24	0.39
0.3	0.13	0.31
0.5	0.07	0.28
0.7	0.02	0.28
1	0.01	0.27

Table F.10: Values of Loading and Retention Plotted in Figure 5.26

Retentions in Binary Metal Mixtures		
Loading	R_{Ni}(pH 6)	R_{Zn}(pH 6)
0.1	0.93	1.00
0.3	0.92	0.99
0.5	0.91	0.95
1	0.89	0.90

Table F.11: Values of Loading and Retention Plotted in Figure 5.26 (pH 5)

Retentions in Binary Metal Mixtures		
Loading	R_{Ni}(pH 5)	R_{Zn}(pH 5)
0.1	0.90	0.88
0.3	0.88	0.87
0.5	0.86	0.80
1	0.84	0.79

Table F.12: Values of Loading and Retention Plotted in Figure 5.27

Binary Metal Mixture + 0.5N $NaNO_3$		
Loading	R_{Ni}(pH 6)	R_{Zn}(pH 6)
0.1	0.94	0.87
0.3	0.9	0.64
0.5	0.8	0.43
1	0.67	0.39

Binary Metal Mixture + 0.5N $NaNO_3$		
Loading	R_{Ni}(pH 5)	R_{Zn}(pH 5)
0.1	0.82	0.36
0.3	0.56	0.35
0.5	0.41	0.35
1	0.4	0.33

Table F.13: Values of Loading and Retention Plotted in Figure 5.28

Retentions in Ternary Metal Mixtures			
Loading	R_{Cd} (pH 6.5)	R_{Ni}(pH 6.5)	R_{Zn} (pH 6.5)
0.1	0.99	0.80	0.98
0.3	0.98	0.73	0.97
0.5	0.94	0.69	0.92
1	0.28	0.63	0.34

Table F.14: Values of Loading and Retention Plotted in Figure 5.29

Retentions in Ternary Metal Mixtures			
Loading	R_{Cd} (pH 5)	R_{Ni}(pH 5)	R_{Zn} (pH 5)
0.1	0.65	0.73	0.56
0.3	0.62	0.64	0.51
0.5	0.32	0.61	0.34
1	0.06	0.52	0.16

APPENDIX G

Sample Calculation for K_{app}

Values of K_{app} were estimated by the Equation 3.35 on page 56 ,which was expressed as:

$$K_{app} = \frac{R}{(1-R)\,[PEI]_t^n\,[1-nLR]^n}$$

Estimated values of K_{app} for complexation reaction taking place between PEI and cadmium, nickel and zinc ions at different pH and loading values were given below in Table G.1

Table G.1: Estimation of Apparent Binding Constants of Metal Ions with PEI

Metal-pH	$[PEI]_t$	n	$[PEI]_t^n$	R	L	$(1-nLR)^n$	K_{app}	$logK_{app}$
Ni pH 6	1.25E-03	2	1.56E-06	0.73	0.4	1.73E-01	1.00E+07	7.00
Ni pH 6	1.00E-03	2	1.00E-06	0.63	0.5	1.37E-01	1.24E+07	7.09
Ni pH 5	1.52E-03	2	2.30E-06	0.27	0.3	6.75E-01	2.39E+05	5.38
Ni pH 5	1.00E-03	2	1.00E-06	0.16	0.5	7.06E-01	2.70E+05	5.43
Cd pH 6	7.14E-04	2	5.10E-07	0.60	0.7	2.56E-02	1.15E+08	8.06
Zn pH 6	8.33E-04	2	6.94E-07	0.82	0.6	2.56E-04	2.56E+10	10.41

APPENDIX H

Data Tables for Batch-Mode PEUF Experiments

Table H.1: Experiment with Cd^{2+} Solution (pH 6, L=0.1)

Sample taken at	Feed (Cd^{2+}),ppm	Permeate (Cd^{2+}),ppm	Retention
350ml.	14.8	0.47	0.97
300ml.		0.43	
250ml.		0.45	
200ml.		0.39	
150ml.		0.34	
100ml.		0.35	
75ml.	15.6	0.35	0.98

Table H.2: Experiment with Cd^{2+} Solution (pH 5, L=0.1)

Sample taken at	Feed (Cd^{2+}),ppm	Permeate (Cd^{2+}),ppm	Retention
350ml.	15.1	10.6	0.30
300ml.		10.2	
250ml.		10.5	
200ml.		10.4	
150ml.		10.4	
100ml.		10.5	
75ml.	15.5	10.5	0.32

Table H.3: Experiment with Ni^{2+} Solution (pH 6, L=0.1)

Sample taken at	Feed (Ni^{2+}),ppm	Permeate (Ni^{2+}),ppm	Retention
350ml.	15.3	2.3	0.85
300ml.		2.2	
250ml.		2.2	
200ml.		2.4	
150ml.		2.5	
100ml.		2.4	
75ml.	15.7	2.2	0.86

Table H.4: Experiment with Ni^{2+} Solution (pH 5, L=0.1)

Sample taken at	Feed (Ni^{2+}),ppm	Permeate (Ni^{2+}),ppm	Retention
350ml.	15.0	9.7	0.35
300ml.		9.6	
250ml.		9.7	
200ml.		9.8	
150ml.		9	
100ml.		9.3	
75ml.	15.3	9.1	0.41

Table H.5: Experiment with Zn^{2+} Solution (pH 6, L=0.1)

Sample taken at	Feed (Zn^{2+}),ppm	Permeate (Zn^{2+}),ppm	Retention
350ml.	14.7	0.1	0.99
300ml.		0.09	
250ml.		0.09	
200ml.		0.09	
150ml.		0.09	
100ml.		0.09	
75ml.	15.2	0.09	0.99

Table H.6: Experiment with Zn^{2+} Solution (pH 5, L=0.1)

Sample taken at	Feed (Zn^{2+}),ppm	Permeate (Zn^{2+}),ppm	Retention
350ml.	15.3	1.4	0.91
300ml.		1.3	
250ml.		1.3	
200ml.		1.4	
150ml.		1.5	
100ml.		1.5	
75ml.	15.6	1.5	0.90

CURRICULUM VITAE

EDUCATION

- **Ph.D.** (Chemical Engineering)
  [September 2002 – November 2006]
  Middle East Technical University, Department of Chemical Engineering, Ankara, Turkey
  Dissertation Title: Effect of Ionic Strength on the Performance of Polymer Enhanced Ultrafiltration in Heavy Metal Removal From Aqueous Solutions

- **M.Sc.** (Chemical Engineering)
  [September 1999 – July 2002]
  Middle East Technical University, Department of Chemical Engineering, Ankara, Turkey
  Dissertation Title: Removal of Heavy Metals from Industrial Wastewaters by Means of Hybrid Precipitation and Polymer Enhanced Ultrafiltration Process

- **B.Sc.** (Chemical Engineering)
  [September 1995 – June 1999]
  Middle East Technical University, Department of Chemical Engineering, Ankara, Turkey

PROFESSIONAL EXPERIENCE

- **Teaching Assistant** (Chemical Engineering)
  [October 1999 – September 2006]
  Middle East Technical University, Department of Chemical Engineering, Ankara, Turkey

ACADEMIC EXPERIENCE

- Assistantship to some undergraduate courses namely, Thermodynamics I and II, Mathematical Modelling in Chemical Engineering, Separation Processes, Chemical Engineering Laboratory

- Assistantship to graduate course namely, Transport Phenomena

- Attended to “American Institute of Chemical Engineers Spring National Meeting, AICHE” in Orlando, FL/USA in April 2006.

- Attended to “Network Young Membrains Seventh Meeting, NYM-7” in Enschede/The Netherlands in June 2005.
- Attended to “Euromembrane 2004” in Hamburg/Germany in September 2005.
- Attended to “Network Young Membrains Fifth Meeting, NYM-5” in Barcelona/Spain in October 2003.

AREAS OF EXPERTISE

- Pressure Driven Membrane Processes, Instrumental Analysis, Water Treatment

COMPUTER RELATED EXPERIENCE AND SKILLS

- **Programming Languages:** HTML
- **Operating Systems:** Windows 9X/2000/XP
- **Commercial and Research Software Packages:** Visio, Sigmaplot, Microsoft Office (Word, Excel, PowerPoint)
- **Others:** LaTeX, BibTeX, Postscript

PUBLICATIONS

Journal Articles

- S. İslamoğlu, L. Yılmaz, H.Ö. Özbelge, “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, Vol. 41, pp.3367-3385, 2006.
- S. İslamoğlu, L. Yılmaz, “Effect of ionic strength on the complexation of polyethyleneimine (PEI) with Cd^{2+} and Ni^{2+} in polymer enhanced ultrafiltration (PEUF)” , Desalination, Vol.200, pp.288-289, 2006.

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- S. İslamoğlu, L. Yılmaz, H.Ö. Özbelge “Removal and Recovery of Heavy Metals from Industrial Waste Streams by Means of a Hybrid-Precipitation and Polymer Enhanced Ultrafiltration”, Proceedings of the Spring National Meeting of American Institute of Chemical Engineers (AICHE-2006), Orlando-FL/USA, April 23-27, 2006.
- S. İslamoğlu, L. Yılmaz, “Effect of Membrane Type on the Performance of Polymer Enhanced Ultrafiltration for Removal of Cadmium”, Proceedings of Seventh Network Young Membrains Conference (NYM-7), Enschede/The Netherlands, June 22-24, pp.104-105, 2005.

- S. İslamoğlu, L. Yılmaz, H.Ö. Özbelge , “Integration of Polymer Enhanced Ultrafiltration to Removal and Recovery of Heavy Metals from Industrial Effluents”, Proceedings of Fifth Network Young Membrains Conference (NYM-5), Barcelona/Spain, October 2-3, pp. 106-107, 2003.

- S. İslamoğlu, L. Yılmaz, H.Ö. Özbelge,“Integration of Polymer Enhanced Ultrafiltration to Removal and Recovery of Heavy Metals from Industrial Effluents”, Proceedings of the 3^{rd} Chemical Engineering Conference for Collaborative Research in Eastern Mediterranean (EMCC-3), Thessaloniki/Greece, May 14-16, pp. 335, 2003.