DEVELOPMENT AND EVALUATION OF PERFORMANCE OF NEW LIGANDS FOR REMOVAL OF BORON BY POLYMER ENHANCED ULTRAFILTRATION

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ABSTRACT

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Boron is an element distributed widely in environment mainly in the form of boric acid or borate salts. Boron is an element of demand because of its use in many high technology materials. Moreover boron is an essential element for growth of plants, but may also result in toxicity when present in excessive amounts. As the range between a deficient and toxic amount of boron is very narrow, imbalances in boron nutrition are well-known.

For the removal of boron from aqueous solutions, various methods exist which are chemical coagulation, adsorption, solvent extraction and ion exchange processes. In this study, an alternative, energy efficient and easily scalable membrane based method, polymer enhanced ultrafiltration (PEUF) was developed for removal of boron from aqueous boron solutions. PEUF process consists of two steps: complexing boron with a water soluble polymer then removing the complex by ultrafiltration.

Previously, boron removal from aqueous solutions was studied in a continuous process with a commercial ligand, polyvinyl alcohol (PVA). In our study, three newly developed polymers, which are derivatives of N-methyl-D-glucamine (P1) and iminodipropylene glycol(P2 and P2G) were used as the boron complexing ligand. P1 and P2 are linear polymers, while P2G is cross linked version of P2. The pilot scale system utilized for the PEUF process accommodates a spiral wound cellulose cartridge with 10000 Da molecular weight cutoffs (MWCO). The effects of operating parameters on performance of PEUF were investigated. The experimental parameters studied are metal/polymer ratio (loading) (0.01-1), pH (7-10). Boron analyses of the samples were made by using ICP-AES. Maximum removal (retention) was 90.1 %. The permeate flux remained constant at around 20 L/m^2.hr and was not affected by the operating parameters. Decrease in loading caused the retention of boron to increase. Also at high pH values, retentions were relatively higher. Results showed that PEUF could be a successful alternative method for removal of boron.

Keywords: Polymer metal complexation, ultrafiltration, boron removal

ÖZ

BORUN POLİMER KOMPLEKSLEMELİ ULTRAFİLTRASYON İLE UZAKLAŞTIRILMASINDA YENİ KOMPLEKSLERİN GELİŞTİRİLMESİ VE PERFORMANSLARININ TAYİNİ

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Bor, doğada yaygın olarak borik asit ve borat tuzları halinde dağılmış bulunan bir elementtir. Bor, birçok yüksek teknoloji malzemesinde kullanıldığından, aranan bir elementtir. Dahası bor, bitkilerin büyümesi için gerekli bir elementtir ama aynı zamanda gereğinden fazla bulunursa bitkiler için zehirli hale gelebilir. Bitkinin beslenmesinde alt ve üst sınır çok dar olduğundan, bor beslenmesindeki dengesizlikler yaygındır.

Bor, sulardan birçok değişik yöntemle uzaklaştırılabilir; bunlar kimyasal koagulasyon, adsorplama, solvent ekstraksiyonu ve ion değiştirme yöntemleridir. Alternatif olarak, enerji açısından verimli ve kolayca boyutlandırılabilen bir membran tekniği olan polimer komplekslemeli ultrafiltrasyon (PKUF), borun çözeltilerden ayrılması için geliştirildi. PKUF tekniği iki aşamadan oluşmaktadır: boru suda çözünür bir polimer ile kompleksleme ve daha sonra kompleksi ultrafiltrasyon ile ayırma.

Daha önce, borun sıvı çözeltilerden uzaklaştırılması ticari bir polimer olan polivinil alkol (PVA) ile sürekli bir süreçte çalışılmıştı. Grubumuz tarafından, N-metil-D-glukamin (P1) ve iminodipropilen glikol (P2 ve P2G)'nin türevleri olan üç yeni geliştirilmiş polimer, kompleksleme için kullanıldı. P1 ve P2 lineerken, P2G, P2'nin çapraz bağlı halidir. Pilot boyuttaki sistemde, 10000 Da'luk spiral sarım kartuş bulunmaktadır. Operasyon parametrelerinin PKUF'un performansındaki etkileri incelenmiştir. Deneysel parametreler, metal/polimer oranı (yükleme) (0.01-1) ve pH'tır (7-10). Deney örneklerinin analizi ICP-AES ile yapılmıştır. Elde edilen maksimum ayırım % 90.1'dir. Permat akısı 20 L/m^2.hr civarında sabit kaldı ve operasyon parametreleri tarafından etkilenmedi. Yüklemedeki düşüş, ayırımın artmasına yol açtı. Buna ek olarak daha yüksek pH, daha çok ayırıma yardımcı oldu. Sonuçlar, PKUF'in borun uzaklaştırılması için başarılı bir alternatif teknik olabileceğini göstermiştir.

Anahtar Kelimeler: Polimer metal komplekslenmesi, ultrafiltrasyon, bor uzaklaştırılması

To my family

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LIST OF SYMBOLS AND ABBREVIATIONS

Avg. : Average
C : Concentration
C_f : Feed Concentration
C_p : Permeate Concentration
CEUF : Complexation Enhanced Ultrafiltration
CoEUF : Colloid Enhanced Ultrafiltration
ΔP : Pressure Difference
DRE ICP : Direct Reading Echelle Inductively Coupled Plasma
F_p : Permeate Flux
Inten. : Intensity
L : Loading
MEUF : Micellar Enhanced Ultrafiltration
MW : Molecular Weight
MWCO : Molecular Weight Cut-off
P1 : Sorbitol grafted Polyglycidyl Methacrylate
P2 : Iminodipropylene grafted Polyglycidyl
P2G : Iminodipropylene grafted Polyglycidyl (Gel Version)

PEUF	: Polymer Enhanced Ultrafiltration
R	: Retention
RF	: Radio Frequency
RO	: Reverse Osmosis
SLM	: Supported Liquid Membrane
t	: time
UF	: Ultrafiltration

CHAPTER 1

INTRODUCTION

Boron is an element found in the forms of boric acid or borate salts in nature which is extensively scattered [1]. In environment, boron concentration in the aqueous sources may differ widely depending on the source. From natural and artificial waters to brines and in dilute solutions from various processes, boron exists usually in moderately low concentrations. However, purification may be needed, in situations where the boron concentration exceeds 2 mg/L, which is the tolerable limit for some crops[2]. Boron is known to be a valuable micronutrient for plants, animals and humans and what makes boron different is its narrow concentration range between the deficiency and excess [3]. While for surface waters excess boron content is rare, well waters or springs generally contain toxic amounts, particularly near geothermal areas and earthquake faults [4]. For some crops this limit is even as small as 0.2 mg/L [4]. Additionally, according to WHO's Guides for the Quality of Drinking Water, boron concentration should not exceed 0.3 mg/L based on the NOEL (no-observed-adverse-effect-level) [1]. In most surface and ground waters boron concentration do not exceed that limit, but in the areas of borate mines and some industrial regions concentrations can reach up to 7 mg/L [5].

Being one of the eight micronutrients, boron is now identified as vital for all higher plants. As a micronutrient in plants, boron is used in various places such as: cell wall formation and stabilization, and many other physiological and metabolic reactions [8]. Boron toxicity in plants has long been accepted as a problem around the world. It is considered to be one of the most important micronutrient problems in the Central Anatolia [9]. As the range between a deficient and a toxic amount of boron is very narrow as compared to any other nutrient element, imbalances in boron nutrition are widespread [10, 11]. Many studies have shown that levels of boron below or above the optimum range cause significant changes in the activity of numerous enzymes and as a result affect the metabolism of higher plants [12]. Boron deficiency in higher plants causes harmful effects on cellular functions and physiological processes. It decreases or inhibits the growth of vegetative and reproductive plant parts, depending on the extent of Boron deficiency [13]. Boron concentration in irrigation water, which is just slightly higher than the minimum, will have adverse effects for plant growth and will accelerate decay. So the boron concentration in irrigation water should be controlled to prevent those harms.

In addition to the harms to the plants at the excess concentrations, boron has been shown to induce male reproductive impediments in laboratory animals orally exposed to boric acid and borax [5]. Studies on several laboratories have revealed numerous development and teratogenic effects. All these surveys stress the requirement of the management of the boron concentrations in water.

In nature boron is found in the forms of alkali or alkaline earth borates and boric acid [6]. Commercially the most valuable boron compounds are borax ($Na_2B_4O_7 \cdot 10H_2O$), in its decahydrate, pentahydrate, and anhydrous forms, and boric acid (H_3BO_3).

The occurrence of boron in water has two obviously distinguished sources. The first one is the mineralization of boron in silts present in the aquifer. While the second one is the ineffectual removal of boron in conventional water purification processes, particularly in the systems of urban residual water coming from borax which is found in detergents [7]. These may also the sources of boron present in drinking water as well [5].

The most frequent boron pollution takes place in magnesium chloride brines. Boron interferes with the magnesium metal in the production by electrowinning operations. The removal of boron is required in numerous processes too. Considering its high market value , boron that may be found in some brine can be economical when removed [2].

Turkey possesses approximately 60% of the world's boron reserves [14]. The borate reserves in Turkey are located in four major regions, that are Emet, Bigadiç, Kırka and Mustafakemalpaşa. All of these reserves are located around the Simav River. From the borate mines, there is a considerable amount of drainage water discharged to the Simav River. As a result Simav River, which is used for irrigation, becomes polluted with boron. The boron concentration of the river increases up to 3 mg/L after it receives the discharge streams from the mines and may increase to 7 mg/L during the irrigation season. About 33000 ha of agricultural land, which is irrigated by the river is threatened by the boron pollution which is causing a national income loss of $20x10^6$ \$ (1981 unit price). In Balıkesir plain, an annual increase of 150-280 % of boron content of the soil was found because of the irrigation of the plain with the Simav River. The river receives the drainage waters, which contain approximately 135 mg/L boron with a flow rate of 230 L/s which is equivalent to 1000 tons of boron per year or 5500 tons of boric acid per year, which is transported by the river to Marmara Sea [14].

Additionally geothermal waters with high boron concentration, cause considerable boron pollution in Western Turkey [14]. The Kızıldere geothermal field is one of the most significant geothermal energy resources of Turkey [15]. This resource produces steam suitable for electric energy production. However, it necessitates a treatment technique for its safe disposal. In Kızıldere region the waste brine is directly discharged into the nearby Büyük Menderes River. Because of the amount of the geothermal waste waters and that the river is used for irrigation, purification processes should be considered. The high boron content of about 30 mg/L makes it unlikely to be discharged. Boron concentration of the river water must be kept below 1 mg/L, which is the maximum allowable concentration for the irrigation of boron-sensitive plants. Also concentrations over 3 mg/L results in accumulation of boron in the soil.

Clearly the problem has started to become important for Turkey. Therefore the essential precautions should be taken for the prevention of the pollution before it becomes untreatable.

In the literature survey, the alternative methods for removal of boron are investigated and discussed. In this study a recently developed technique for removal and recovery of boron, polymer-enhanced ultrafiltration

(PEUF) was utilized. PEUF is a membrane process based on the complexation of a water-soluble polymeric material with a target component, which is then separated from the aqueous solution by an ultrafiltration process. In the literature survey the applications of PEUF for numerous metal ions were reviewed and it has been concluded that it can also be an applicable technique for removal and recovery of boron. In this study, PEUF was used continuously for removal of boron from the aqueous solutions while the effects of the various parameters were investigated. Non-commercial polymers were applied as binding agent for complexing boron and a pilot scale ultrafiltration system was employed for the ultrafiltration process in order to separate the boron polymer complexes.

CHAPTER 2

LITERATURE SURVEY

2.1. Alternative Methods for Removal of Boron

Different alternative processes have been developed in recent years as the toxicity of excess concentration of boron was realized by the researchers. Boron can be removed by various methods but the majority of the existing techniques have some disadvantages.

In the previous studies, the removal of boron by the following methods was proved to be ineffective [14]: conventional biological treatment and chemical coagulation with lime, ferrous and aluminum salts. Adsorption of boron by clays, soils and other minerals were also investigated broadly [16, 17, 18]. Magnesium oxide was suggested to be a potential adsorbent for boron removal, where the activity of the adsorbent was regained by heating [19]. Experiments based on adsorption of boron on metal hydroxide using activated alumina, or MgO, $Ca(OH)_2$ or a mixture of two, proved that these compounds are poor adsorbers for boron removal. Large numbers of stages were necessary to decrease the boron content to under 1 mg/L which makes the method ineffective and uneconomical [15]. The other alternative for boron removal which is flocculation-precipitation process requires physical-chemical treatments. Those treatments were mentioned not to be economical because of the significant amount of use of expensive flocculants [7].

Other extensively reported techniques for removing boron from a solution, that is evaporation-crystallization and solvent extraction processes, were declared to be efficient in high concentration streams and to be utilized more for the production of boric acid rather than its removal from aqueous streams [20, 21, 22]. One of the drawbacks of the extraction processes is the requirement of specially synthesized extractants, which are expensive and need multistage systems [2, 23, 24]. The problem for adsorption process is also present for the process of boron extraction with some water-insoluble diols, that the process requires large number of stages for an adequate removal. Solvent losses throughout the extraction processes are also an additional disadvantage [15].

The most widely used processes for removing of boron are the ion exchange processes with strong base anion exchange resins [3, 4, 14, 15, 25, 26, 27]. This process is efficient for removing boron; but all other ionic species are also removed, which is a drawback if it is wanted to remove boron selectively [14]. In ion exchange processes, the weak dissociation of boron salts demand that a strong basic ion exchanger is required, and all anions of the solution would be retained, causing very high regeneration cost [15]. Therefore a boron-specific ion exchanger is essential for the satisfactory separations. The most commonly used boron specific resin is Amberlite IRA-743 with sorbitol functional groups and this resin was stated to be forming complexes with boron and it is highly selective [1, 14, 15]. Boron sorption capacities of anionic exchange resins change with temperature, concentration and resin cross linkage [26]. The major problems that were indicated are the requirement of expensive selective resins, expensive regeneration steps and low capacity with scale up problems [3-4, 25, 27]. Also the regenerate from the system is another source of boron contamination.

2.2. Membrane Methods for Boron Removal

Removals of harmful compounds from waste streams by standard methods are mostly not economical due to the huge quantities of dilute waste water to be processed [28]. The variety of difficulties and economical drawbacks of the available methods lead the researchers to carry out new studies to develop easier and more economical methods for the management of these aqueous solutions and polluted streams. In recent years development in membrane separation methods and membranes for given separation problems are the most crucial ones [29]. Membrane separation technology can considerably decrease the waste volumes without a phase change that results in low energy demand [28]. Also, these processes are appropriate for the heat sensitive materials [30]. Membrane separation techniques, for being simple and rapid, promise that membrane processes will offer a better option over the conventional separation techniques [31].

The membrane processes, such as supported liquid membrane (SLM), reverse osmosis and electro dialysis were studied for boron removal [32-34]. Liquid membranes containing particular carrier molecules may selectively complex a single substrate that will be effectively transferred through the membrane [32]. In supported liquid membranes, the organic carrier solution is immobilized in a thin, inert, micro porous film and forms a barrier between two aqueous solutions, which are the source, and receiving phases. Industrial applications of SLM's are restricted due to the main concern about stability and lifetime of such membranes. The instability exhibits two significant problems, which were seen in the study of boron removal [32]. The first was the decrease of the flux of substrate with time, due to loss of carrier from the membrane and the second one was the most encountered leakage of membrane, because of the replacement of the organic solvent by the aqueous phases in the polymeric support. The loss of the solvent cannot be prevented and causes the breakdown of the membranes which finally results with a membrane permeable to any substrate.

An additional optional technique studied to recover boron from effluents was electrotransport through an anionic membrane [33]. For making the membranes selective for ions, ion-exchange membranes are utilized which either allows the transfer of anions or cations. Anion-exchange membranes contain positively charged groups attached to a polymer. Because of the attached charge, positively charged cations are repelled from the membrane. Studies about boron transport through ionic membranes are limited [33]. In the study, it is mentioned that in the process where the concentration of the boron species had to be continuously adjusted, the use of electrotransport through an anionic membrane would provide an interesting way to recover the boron from effluents. The yield of boron electrodialysis through anionic membranes was not easy to guess when the concentration was increased. In the electrodialysis applications, the boron removal depends on the type of the membrane, pH of the solution, degree of desalinization, boron concentration in the feed and the occurrence of ion exchange resin in the desalinating chamber [34].

An additional membrane process used for boron removal is reverse osmosis (RO) [5, 7]. In RO, the pore sizes are small and therefore the molecular sizes of the retained particles are smaller compared to the other pressure driven processes such as: ultrafiltration and microfiltration [35]. For that reason pores of RO membranes are easily plugged and retained molecules are collected next to the membrane, the resistance of the membranes to mass transfer increases and thus the applied pressure (driving force) has to be increased to force the same amount of solution per unit time through the membrane. RO is not frequently preferred for selective separation of metal ions because all other waste water components in the aqueous solution would also be less completely retained by membrane. Also the osmotic pressure in the concentrated solution would become enormously high [36]. In the reverse osmosis (RO) applications for boron removal, the most important observation was the rejection of boron depended significantly on pH. Also, it was likely to get higher with increasing pressure. Moreover as the boron concentration was lower than 35 mg/L [5, 7], rejection did not depend obviously on concentration. RO processes demanded multistage systems due to the low selectivity of the process among the ions.

2.2.1. Polymer Enhanced Ultrafiltration (PEUF)

A variety of highly toxic or valuable elements, such as certain heavy metal ions, can be removed from industrial wastewater and natural water by means of membrane processes [36]. Ultrafiltration (UF) is a pressure driven separation technique widely used for concentrating, purifying or separating macromolecules, colloids, and suspended particles from the aqueous solutions and suspensions in various industrial areas [31]. UF utilizes semipermeable membranes where the separation occurs at molecular level [37]. It is a low energy requiring process that has a high efficiency and stable performance in separating colloidal particles. The target components are separated completely; the removal occurs in accordance with the molecular dimensions to pore size of the membrane. Thus, small substances pass through the membrane, while molecules larger than the pores of membrane are retained.

Even with their advantages and adequate separation capability, there are mainly two undesired incidents that, in the UF processes, can make the intrinsic capacity of the membrane ineffective and change the basic rejection characteristics of the membrane, in that way causes the filtration characteristics to alter [38]. The first one is concentration polarization, which is an increase in the concentration of rejected species with decreasing distance from the membrane because of the affinity for rejected solutes to accumulate near the membrane surface. The other one is fouling which happens for particular solutes to interact with the membrane to some extent. These phenomena reveal the significance of the membrane cleansing and choice of the crucial operating parameters to prevent these problems [29, 31, 35-38].

The size of molecule or the particle retained by ultrafiltration is in the range of 1-100 nm [35] and usually, UF is limited to managing of pollutants with molecular weights from 300 to 300000 for the relatively large pore sizes of the membrane [28]. Nevertheless, smaller pollutants such as metal ions can be removed from the solutions by complexation enhanced ultrafiltration technique (CEUF), which is, first attaching the ionic agents to larger soluble macromolecules and then utilizing ultrafiltration process to the complexes. When UF is applied to the system, the complexes are retained; so target component is removed from the solution. For an effective process, there are particular requirements for both of the complex and the membrane. The complex should have a high selectivity, a high binding capacity, a narrow molecular weight distribution, a high water solubility and recovery [36]. On the other hand, the membrane should have a high flux and a sharp molecular weight cut-off, corresponding to the average size of the membrane pores. These are the important parameters, which influence the technical viability and the economic efficiency of the whole process.

CEUF can be classified according to the complexing agent that is utilized for binding the target compounds. Colloid Enhanced Ultrafiltration (CoEUF) is the technique in which the colloids of the metal hydroxide are employed as the complexing agents, which are broadly formed by iron and aluminum [39, 40]. The colloid-metal ion complexes are then separated from the solution by the help of an UF system according to the size of the complexes bigger than the membrane pores. The low selectivity and pH restrictions limit the applications of this method.

Micellar Enhanced Ultrafiltration (MEUF) is the next CEUF method in which ionic surfactant is mixed into the aqueous solution having the metal ions to be separated with the opposite charge. The surfactant forms highly charged aggregates called micelles which adsorb or bind the metal ions. The solution is then passed through an UF system, where the micelles and adsorbed metal ions are blocked [28, 42]. One clear disadvantage of MEUF is that it can not be employed for low concentrations of metals and also the total surfactant concentration has to be greater than the critical micellar concentration for avoidance of the solution to contain great quantity of free surfactant monomer [43].

Equally CoEUF and MEUF are separation methods utilizing two-phase systems. Possibility of homogenous aqueous phase may make CEUF more beneficial by preventing the interface mass transfer resistance. To facilitate higher efficiency and selectivity in these mentioned membrane techniques for removal of metal ions, a fast and easy process which is called as Polymer Enhanced Ultrafiltration (PEUF) has been developed. In this method a water-soluble polymer is used as the complexing agent in conjunction with ultrafiltration [44].

The PEUF technique is based on the separation of ions bound to water-soluble polymers with chelating groups from non-bound ions [45]. In the ultrafiltration process, free ions and species cross the membrane as a result of their small molecular size while the polymeric species, precursor polymer, and polymer-metal complexes, with considerably larger size than the membrane pores, are retained in the cell solution. Therefore separation of inorganic ions can be attained by the help of an ultrafiltration. The processes including the details of the technique and its application on the systems for removing metals were published in many studies and reviews [44-70, 84].

For the retention of metal ions, various polymeric reagents with chelating groups have been produced [46, 73, 74, 81]. So as to have an efficient process, the polymers as chelating agents should have great number of functional groups of the complexing agent for a high capacity, and high molecular weight which allows an easy separation while the polymer has an adequate solubility.

Generally in the earlier studies, PEUF was utilized mostly on cations at the batch mode. A membrane cell, which at the start had only the polymer, was constantly fed with a metal ion solution. Main aims of the studies were primarily to examine the synthesis and UF applications of the polymeric agents for the aimed metals and to investigate their binding capacity [44-56]. In the majority of the studies, specifically synthesized polymers were used for studying the metal binding behaviors of these special chelating groups. For all of the studies were batch processes, feed concentrations were not constant all through the experiments, so there were no results showing the effect of loading [44-59].

Even though it has significant advantages, experiments made on continuous systems were less frequent. Continuous PEUF has been applied for removal of mercury and cadmium both from single and binary mixtures [66, 67, 84]. The experimentation on continuous processes makes possible the investigation of the realistic effects of the process parameters on separation performance. Besides the continuous UF studies may clarify the possibility of the handling of the wastewater with PEUF at industrial scale.

Various recent studies have focused on the operating parameters like pH and concentration of metal to polymer ratio, (loading) [56-70]. As the pH of the solution increases, usually retention of metal cations increases as well in the acidic region up to particular pH values. In the UF of zinc, copper and nickel, an increase in alkalinity ended in an improvement in the efficiency of the separation process and an increase in the value of the metal retention coefficient [57-65].

With changing the pH values properly, it is probable to disassociate polymer-metal complexes. This fact would allow the recovery of the concentrated metal in the retentate and also the regeneration of the complexing polymer [57, 58]. The regeneration of the polymers was studied by utilizing two different techniques; electrolysis of the retentate and acidification of the retentate to a quite low pH followed by UF. Electrolytic regeneration of the used polymers from a retentate was not practical while regeneration by acidification is reasonable [59].

Although loading (metal/polymer ratio) is very effective in the retention of metal ions in PEUF operations, its effect was rarely studied. Loading is important because it is directly affecting the amount of the complexes formed [56-61]. The effect of loading on the performance of UF can be clearly examined in a continuous system [66, 67]. For the higher polymer concentration, it is expected to have a high capacity of binding in the system. Even though large excess of the complexing agent would promise the binding of the ions, it increases the viscosity and affects the ultrafiltration efficiency by decreasing the permeate flux [60]. Additionally excess amounts of polymers may cause the concentration polarization and fouling problems, which also decreases the membrane efficiency [66].

In the earlier studies of our group, continuous PEUF was employed efficiently for the removal of mercury and cadmium from multi component solutions as the effects of the operating parameters were examined [66-70]. The polymer used as the metal binding agent was polyethyleneimine which was studied in the ultrafiltration processes performed on both laboratory and pilot scale systems. Increase in pH and decrease in loading caused a high retention for both metals. A flat plateau in the retention was obtained on both pH and loading studies for a broad range of loading and pH values. So the retention was observed to stay almost at a constant value around 0.98 until the critical loading and pH values were surpassed. After that decreasing pH and increasing the loading values caused a decrease in retention for both metals. Continuous PEUF technique appears to be practical for the selective removal and recovery of cations from multicomponent systems when the critical pH and loading values were clarified and utilized.

Removal of cations with PEUF is a long studied subject and for that reason most of the suitable ligands for the removal of the important cations have been developed. Therefore, recently, the main aim in cation removal is to find the suitable operation parameters. However, removal of anions with PEUF is a new area of interest. So the major purpose is to find a suitable ligand, as opposed to cations [87-89]. Mostly investigated anions were perchlorate, arsenate, chromate and phosphate. In those studies, most of the polymers used as ligands are specially synthesized or modified ones. It was seen that both pH and loading had an effect on the retention. In addition, background of the solutions were affecting the retention. While the majority of ligands had high recovery values, some of ligands were selective to specific anions and the others were capable of removing a range of anions. It is suggested that the complexation mechanism of anions may be different from the cations mechanism. This will probably cause the parameters to affect the system in a different way.

In very few studies, PEUF was used for the removal of boron from the aqueous solutions [71, 72, 83, 85]. In the first study, a polymer with a specific structure which was synthesized by grafting N-methyl-D-glucamine (NMG) onto poly (epichlorohydrin) [71] was used. In the next study, glucoheptoamide derivatives of dendrimetric poly (amido amine) and poly (ethylene imine) were employed [72]. At the first case a dead end filtration in a low-pressure stir cell system was used while at the second case a hollow fiber system operated at the batch cross flow mode was in use [72]. Rejection coefficients were functions of pH, boron concentration, and polymer concentration. In the study carried out with NMG with the polymer concentration and boric acid concentration of 0.1 M, it was stated that no boric acid was bound to NMG. In this study it was also mentioned that for an acidic solution, the polymer-boron interaction is much weaker. In the NMG experiments, at the late stages of the filtration, the boron concentration in permeate was observed to be decreasing. The reason for this situation was explained by the occurrence of a polymer rich polarization layer (concentration polarization) on the feed side of the membrane, which increased the effective polymer concentration [71]. On the other study, again feed concentrations were not constant and for defining the performance of the separation process, volume reduction factor (VRF), which is the ratio of the volume of the contaminated water treated to the volume of the concentrate produced, is used. In this study, the boron-rich retentate was acidified and free boric acid was obtained by decomplexing from the polymer solution to produce a small volume of boron concentrate. Boron rejection coefficients for these separations were dynamic, beginning very close to unity and dropping during the course of the separation as the polymer chelating sites are filled. During the experiments some polymer was lost due to permeation and this amount is noticeably increased in acidic polymer solution. And also in this system, at sufficiently high boron and polymer concentrations, the solutions possibly formed a crosslinked gel at the membrane surface where the polymer and boron concentrations were increased due to concentration polarization [72].

In the previous investigation of our group [83, 85], a continuous process for the removal of boron was studied. The effects of operating parameters on the performance of PEUF were investigated. As a complexing agent the polymer used was a commercial polymer, polyvinyl alcohol. For this study, the parameters were loading, pH, molecular weight and degree of hydrolysis of the polymer. The results of this investigation showed that retention of boron is increasing with the increasing pH, also it was stated that at low loadings, retentions were more successful. The maximum retention was 28 % and this was obtained at the pH value of 10 while the loading was 0.01. It was stated that the process is restricted by the solubility of the ligand in water. Although significant amount of polymer was added to the system, retention did not change very much. Lastly, in this study, it was suggested to develop new ligands with OH groups distributed differently on the chains.

In the studies of Bicak [73, 74], N-methyl-D-glucamine grafted polyglycidyl methacrylate (P1) and iminodipropylene glycol grafted polyglycidyl methacrylate (P2) were used as resins for removal of boron in the aqueous medium. All these studies showed that a polymer with OH groups is a promising complexing agent for the removal of boron. Therefore in the PEUF experiments, P1 and P2 (Appendix A) were used.

The lack of studies of removal of borate ion, which is an anion, with continuous PEUF and parameter studies with different complexing agents lead to try new polymers as complexing agents. PEUF was employed in continuous mode for removal of boron while the effects of operating parameters such as pH, loading, polymer type were investigated. Non-commercial polymers P1, P2 and P2G (which is crosslinked version of P2) were produced as a complexing agent in order to survey the effects of the characteristics of the polymers on retention of boron.

2.3 Boron Chemistry

When boric acid dissolves in water, it forms borate ion according to the reaction written below [32]:

$$H_2O + B(OH)_3 \longleftrightarrow B(OH)_4^- + H^+ \qquad pK_a = 9.14 \quad <2.3.1>$$

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

$$OH^- + B(OH)_3 \longleftrightarrow B(OH)_4^- \qquad <2.3.2>$$

There is also another suggested reaction mechanism for boric acid dissolution [86].

$H_2O + B(OH)_3 \longleftrightarrow H_2BO_3^- + H_3O^+$ $pK_a = 9.14$ <2.3.3>

According to this mechanism, at relatively high pH values the following equilibrium reactions occur.

$H_2BO_3^- \longleftrightarrow HBO_3^{2-} + H^+$ $pK_a = 12.74$ <2.3.4>

$HBO_3^{2-} \longleftrightarrow BO_3^{3-} + H^+$ $pK_a = 13.80$ <2.3.5>

At high concentrations, boric acid condenses on borate ion reversibly to produce polyborate ions [90].

With increasing pH, concentration of boric acid starts to decrease. There is a large decrease of boric acid concentration from pH 6.5 to 11.5. After that point, boric acid amount becomes insignificant [86]. Moreover with increasing pH, concentration of borate ion increases gradually. While borate ion concentration is very low at acidic range, it becomes significant at basic medium. Borate ion concentration reaches its maximum value between pH 10 and 12 which can be compared with the initial boric acid concentration [86].

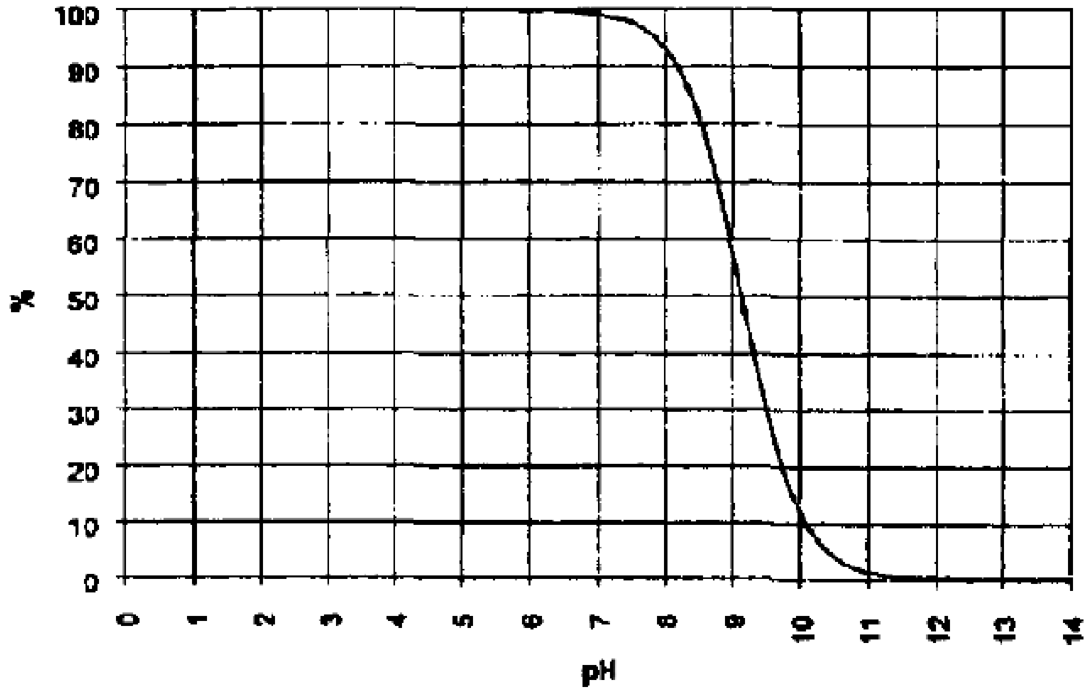

Figure 2.3.1. Percentage of boric acid with changing pH

2.3.1 Boron Complexation

Boric acid is known to make complexes with compounds containing OH groups. One of the complexes that are obtained is by the reaction of 1, 3-diols with boric acid. The product is neutral 1:1 complex (Figure 2.3.1.1) [32]. On the contrary, 1, 2 diols and carbohydrates mostly form anionic 1:1 and 1:2 complexes with the borate ion [32]. This behavior of boric acid and borate ion can also be occurring with polyhydroxy compounds. The reactions of borate ion with polyhydroxy compounds are also well known.

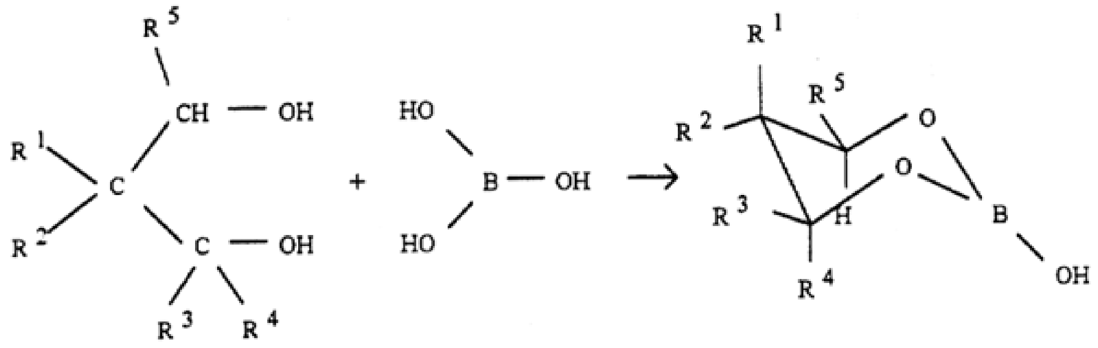

Figure 2.3.1.1. Reaction of boric acid with 1, 3 diol

The complexation reaction can be suggested as in Figure 2.3.1.2 [72]. According to these reactions borate ion can complex either in 1:1 ratio or 1:2 ratio which has a crosslinked structure.

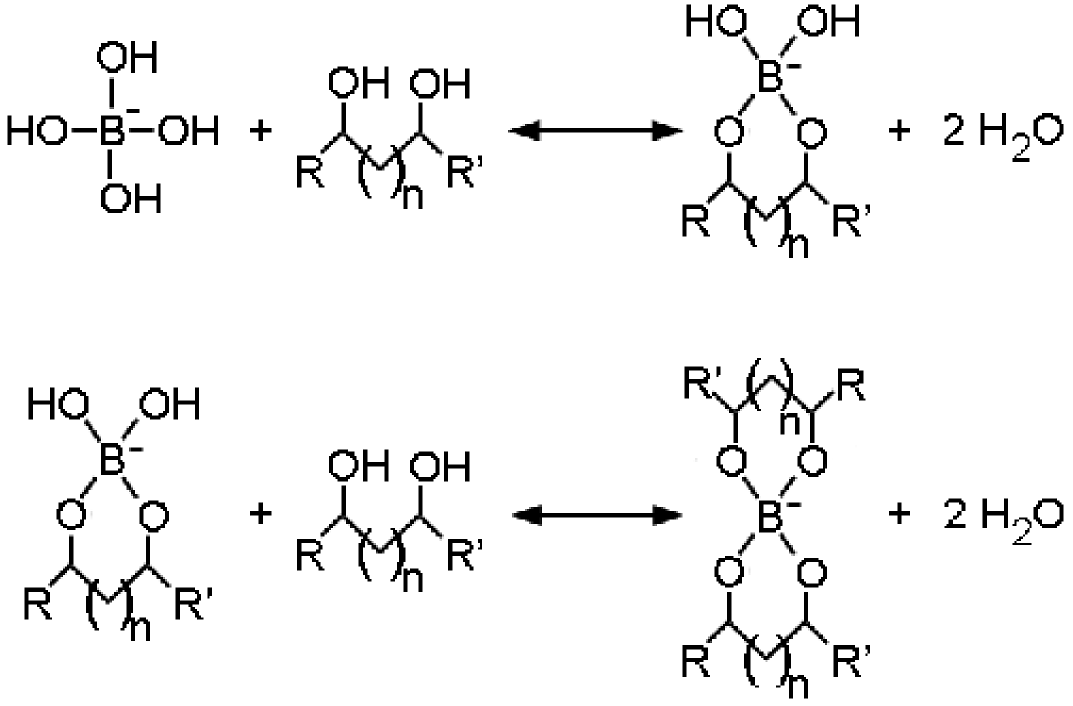

Figure 2.3.1.2. Complexation Reaction of Borate Ion

With Polyhydroxy Compounds

From the reactions <2.3.1> , <2.3.2> and <2.3.3>, it can be seen that production of borate ion is enhanced in basic medium while it is low at acidic medium. So it is unexpected to have recovery of boron at acidic pH values but polymer enhanced ultrafiltration with pH values in the basic range expected to be more suitable for removal of boron at aqueous solutions. But also according to the reaction <2.3.3> a crosslinked complexation can not occur.

CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 Materials

In the experiments P1, P2 and P2G, which is gel version P2, were used (Appendix A, Fig.A.1 & Fig.A.2). These polymers were specially synthesized according to borate ions tendency to complex with polyhydroxy compounds by Prof. Dr. Niyazi Bıçak and his research group [73, 74]. P1 is N-methyl-D-glucamine grafted polyglycidyl methacrylate and P2 is iminodipropylene grafted polyglycidyl methacrylate. Derivatives of these polymers were used as resins for removal of boron in the aqueous medium. Additional components that were used are boric acid (H_3BO_3, Merck, analytical), sodium hydroxide (Merck, analytical), nitric acid (Birpa, technical), and distilled water. All chemicals were used without auxiliary purification. The pilot scale SP20 Ultrafiltration system used for the ultrafiltration experiments has Amicon spiral wound cellulose cartridge (S10Y10) type having effective area of 0.93 m^2 and MWCO of 10000 Da.

3.2 Apparatus

The pilot scale SP20 Ultrafiltration system was used also in the previous PEUF studies for removal of boron, mercury and cadmium [66-69, 83-85]. The UF system accommodates spiral wound cellulose cartridge and consists of an integral tank, which allows processing of feed volumes from 20 liters to 1 liter (Fig. 3.2.1).

The flow is provided by a sanitary positive displacement lobe pump. The other components on the system are a prefilter, a back pressure and drain valve and pressure and temperature sensors. The system is controlled by a dedicated microprocessor, which adjusts the pump speed and back pressure valve to facilitate optimal operation conditions to be maintained. The microprocessor allows 3 levels of control, which are: manual, semi-automatic, and automatic. The system also holds the shut down set points for over pressurization, over temperature and low feed volume. The operating temperature and pressure are displayed digitally on the control panel. A circulating water bath is used for keeping the temperature constant during the experiment while pH of the solution in the tank is monitored by a pH meter during the experiments.

3.3 Ultrafiltration Experiments

As a first step, feed solutions which are going to be used in the UF system had been prepared. To carry out the experiments at a range of loading values in the specified range, polymer solutions at different concentrations for the desired loadings were prepared. Later on, the solution was mixed with specific amount of boric acid (10 ppm boron) to reach the desired loading. The mixing was performed for 3 hours at constant mixing rate of 250 rpm. pH of the solution was adjusted to desired values before it

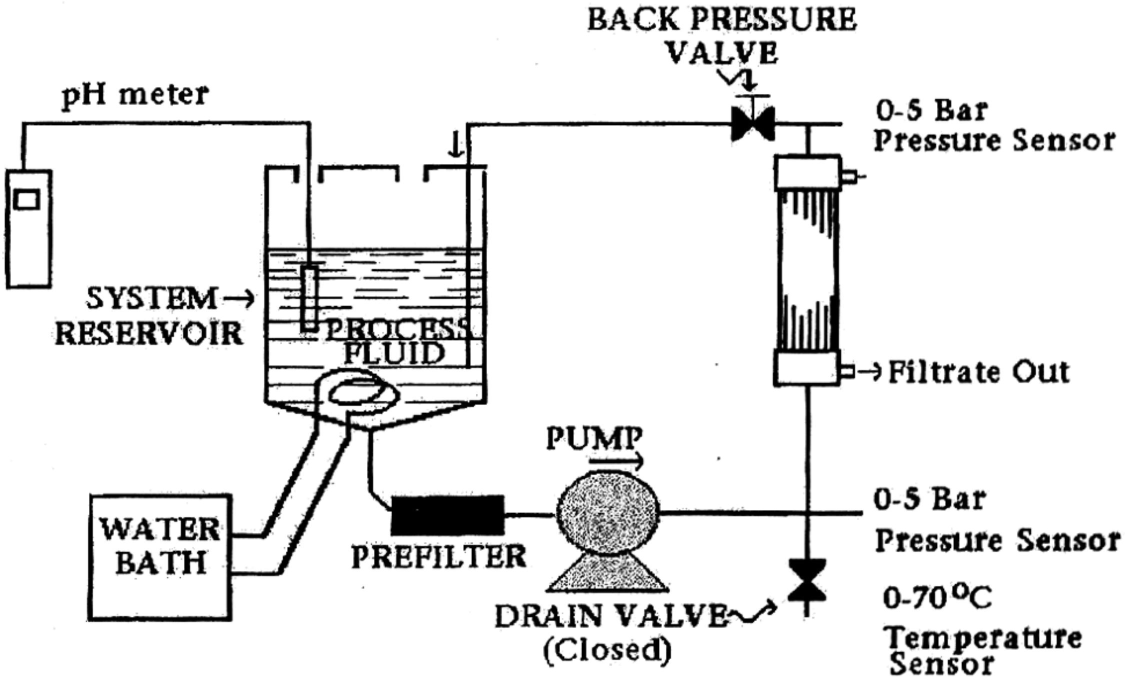

Figure 3.2.1 Pilot Scale Experimental Set-up

was mixed with boric acid and the pH was also controlled throughout the experiments. The UF system was washed by distilled water after each experiment with the intention of cleaning the system and the membrane. Also every month, 0.1 M NaOH solution was passed through the system for about one hour at 30 °C for cleaning the membrane. All of the experiments were carried out with the same membrane type at constant temperature of 20 °C ± 1 °C and constant inlet and outlet pressures of 130 kPa and 70 kPa respectively. The system was operated at semi-automatic mode to make it possible to adjust the set points during the experiments. The UF system was in a total recycle mode, which means that both the retentate and the permeate streams were returned back to the feed tank to keep the feed solution at constant concentration throughout the run. Feed circulation through the system was accomplished by the help of a pump at the set pressure values. All of the experiments were continued about 3 hours. During one run, temperature, pH, feed flow rate, pressures and the feed boron concentration (10 mg/L) were constant. Small amounts of samples were collected both from feed and permeate streams at sufficient time intervals. Volumetric flow rate of the permeate stream was measured every 30 minutes. Lastly the results were obtained by making the calculations of the flux and retention after the analyses of the samples.

3.4 Analysis

For the concentration analysis of boron, Direct Reading Echelle Inductively Coupled Plasma Optical Emission Spectrometer (DRE ICP OES) (Figure 4.3.1) was used (Leeman Labs Inc.). To perform this analysis, the DRE system uses an inductively coupled plasma (ICP) source to provide excitation energy, coupled to a direct reading echelle spectrometer to separate and measure the resultant light output [78]. The system is managed by a standard PC (Celeron 400 MHz, 128 MB RAM, Windows 98 OS). The plasma is created with argon (Ar) gas, by the help of a radio frequency (RF) generator. This generator gives enough energy to ionize the inert Ar atom. These Ar ions, once formed in plasma, are capable of absorbing adequate energy from the RF source to preserve the temperature of the plasma at a level where further ionization keeps the plasma continuously. The intensity of the light emitted in ICP is analyzed at a certain wavelength, which will be converted to meaningful data after calibrations.

<u>The ICP conditions were as follows:</u>

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

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

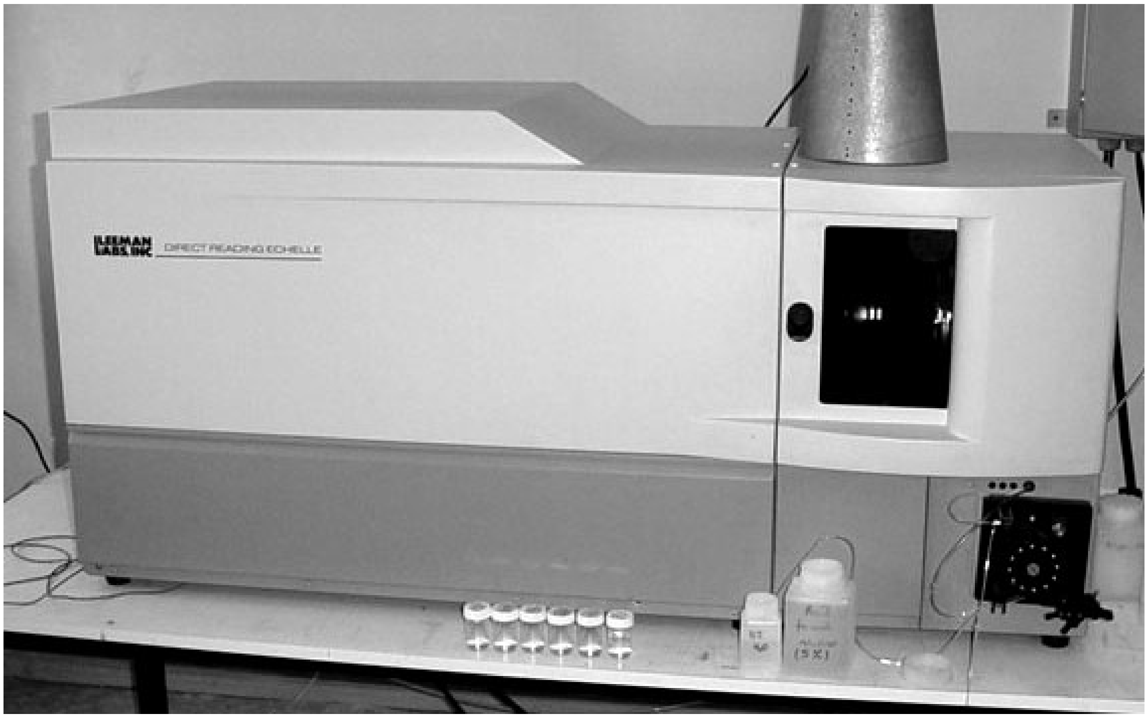

Figure 4.3.1. Direct Reading Echelle Inductively Coupled Plasma

In order to carry out analysis, first the instrument has to be calibrated. To do this, standard solutions of boric acid with different backgrounds were prepared separately for both feed and permeate solutions. Permeate standards were prepared with boric acid and distilled water while feed standards had supplementary polymer backgrounds with different loadings. These standards were scanned by ICP with three replicates of each which provide the determination of the intensity data of the standards. By the help of the intensity data, the calibration curves for both feed and permeate standards were obtained. After the calibration was performed, the analyses of samples were made. The samples were scanned and the relative average blank corrected intensities of the samples were determined. During the analysis, for preventing any blockage, system was cleaned with 0.1 M HCl after each sample reading. At the end of each analysis, the proper calculations were performed for converting the intensity data of the samples to related concentration data for determining the retention values. Detailed data and calculations of a run are given in the Appendix B.

For the measurement of the polymer concentration, samples were taken from the feed stream at the end and the start of each experiment. Later those samples were introduced to total organic carbon (TOC) device to find the carbon content of the samples. Lastly the polymer concentration was found according to the carbon ratio of the polymers. TOC modified loadings are shown in Appendix C, Table C.1 and Table C.9. A sample calculation of finding the actual loading is available at Appendix D.

CHAPTER 4

RESULTS AND DISCUSSION

The performance of an ultrafiltration process is assessed according to two major factors. These are retention of the target component and the permeate flux. Mathematical definition of retention (R) is:

$$R = 1 - \frac{C_P}{C_F} \tag{4.1}$$

Where C_P is the concentration of the target component in the permeate stream while C_F is the concentration of the target component in the feed stream.

The other important parameter, permeate flux, is defined as:

$$\text{Permeate Flux} = \frac{\text{Permeate Flow Rate}}{\text{Effective Membrane Area}} \tag{4.2}$$

In this study the experimental parameters were pH (in the range of 7-10), boron loading (g B/ g polymer) (in the range of 0.01-1), and polymer types (P1, P2, P2G).

In Table 4.1 and Appendix C, Table C1, the experimental data obtained in the UF experiments are presented. The presented data are the values of the concentration of feed and permeate, the retention values and the flux values as a function of time.

As a consequence of some experimental errors, prepared solution concentrations are different from the aimed concentrations. For the interpretation of the results, actual concentration must be known. To find the actual concentration, thus loading, samples were measured three times at TOC named device. The compared results are shown in Table C.9. Also a sample calculation of finding the actual loading is available at Appendix D. Because of having small variations between the aimed and the prepared loadings, for the analysis of the results, aimed loadings were used.

The experimental results confirm that within the runs there were small fluctuations in the concentrations, retention and the flux values. The relative standard deviations for these runs were calculated. For a chosen experiment (at $L = 0.01$, $pH = 10$ with P2G), which is shown in Table 4.1, relative standard deviations (% RSD) for permeate and feed concentrations, permeate flux and retention were calculated which are given in Appendix E,

Table E.1. These % RSD values are small enough to accept that steady state has been established.

Table 4.1. Concentration, Flux, Retention Data
Of A Sample Run

Polymer Type = P2G, Loading = 0.01, pH = 8							
F_P (L/m^{2}h)	F_{45} = 19.19 F_{60} = 20.62 F_{90} = 19.63 F_{120} = 19.20 F_{150} = 19.98 F_{180} = 19.41						
t (min)	0	60	85	110	135	160	185
C_F (mg/L)	10.12	9.70	9.66	9.54	9.49	9.44	9.44
C_P (mg/L)	-	5.06	4.99	4.94	4.87	4.80	4.83
R (%)	-	47.8	48.3	48.2	48.7	49.2	48.8
	$F_{P, Av}$ = 19.67 **$C_{F, Av}$** = 9.55 **$C_{P, Av}$** = 4.92 **R_{Av}** = 48.5						

For checking the reproducibility, a number of selected runs were repeated at the same conditions of pH, loading and polymer type. These experiments were repeated for P2G at a loading 0.01 and pH values of 7, 8, and 9. The results that are presented in Table 4.2, were compared and the relative standard deviations between these runs were calculated for both permeate flux and retention values which are given in Appendix E, Table E.2.

Again the % RSD values of the 1st and the 2nd trials showed that the UF system can reproducibly show the same performance and prove that reasonable separation of boron can be achieved by continuous PEUF. Additionally some reproducibility calculations of the analysis devices were made to see if the devices are reliable (Appendix E, Table E.3). From the results it is seen that the readings are consistent.

Table 4.2. Data of the Experiments Performed for the Reproducibility Study

	Polymer Type	Loading	pH	Permeate Flux	Retention
1st Run	P2G	0.01	9	20.25	0.514
2nd Run				19.88	0.510
1st Run	P2G	0.01	8	19.84	0.481
2nd Run				19.67	0.485
1st Run	P2G	0.01	7	20.13	0.468
2nd Run				20.20	0.465

4.1. Unsteady State Period

Before starting the UF experiments, polymer solution was mixed with boric acid and stirred for about 3 hours at the proper pH, then the solution is put into the system for ultrafiltration. From the values presented in Table C.1 it can be concluded that concentrations reach to steady state within 1 hour of ultrafiltration operation (Figure 4.1.1 & Table 4.1).

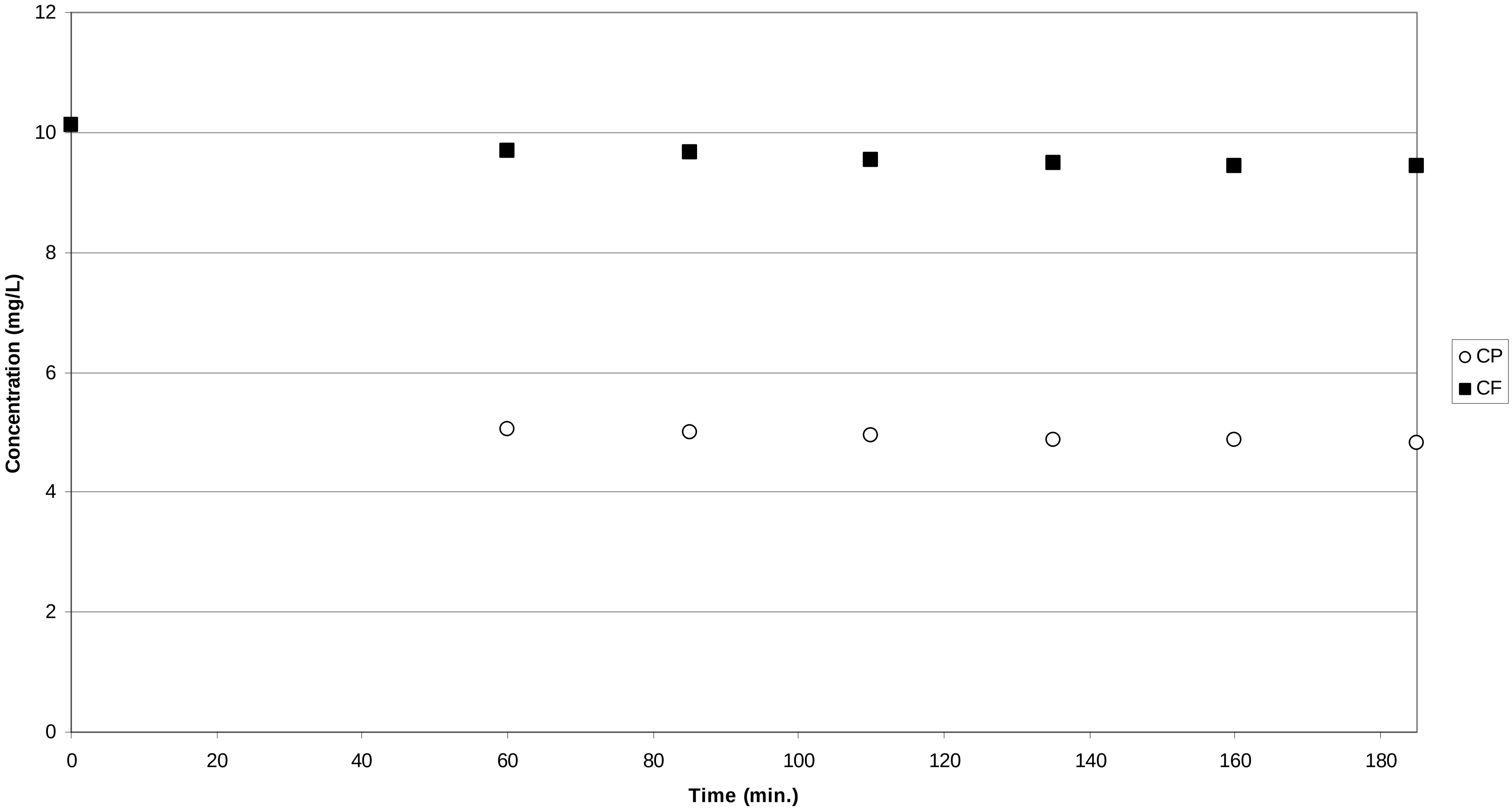

Figure 4.1.1. Concentration with Respect to Time (with P2G at pH = 8 & L = 0.01)

Consequently, complexation is probably completed in mixing stage before ultrafiltration or the complexation is completed in the early stages of ultrafiltration. So the concentrations reach to steady state in a time less than 4 hours. Also from the permeate flux values presented in Table 4.1, it can be seen that permeate flux remains constant from the very beginning of the measurements. So it can be concluded that permeate flux reach to steady state in a time less than 45 minutes. Measured values remained almost constant all through the runs at the achieved steady state permeate flux value. The relative standard deviations in each run were small enough to accept the setup, methodology, and the analysis as consistent. This result is the same with our previous study [83]. In the experiments, with high pH values and low loadings, it was seen that concentration had the tendency to reach steady state little faster.

4.2. Effects of Operating Parameters on Permeate Flux

During the experiments, the permeate flux of the UF system was measured in different operating conditions to see how these parameters are affecting the UF performance. The constancy of the permeate flux during the UF operation is one of the important thing for UF efficiency. At a constant operation pressure, if the permeate flux is decreasing to a value lower than the clear water flux; this may be the sign of gel layer formation on the membrane which plugs the membrane pores. Permeate flux values of the experiments as a function of loading are presented in Table C.3 and Fig 4.2.1 in which the loadings are in logarithmic scale.

The effect of pH, loading and polymer types were studied and it was seen that flux is independent of these variables. The flux was constant at around 20 L/m^2hr. For the experiments, synthetic solutions were used which probably helped the constancy of the flux. Independence of flux from loading proved that in the UF system there are no problems like concentration polarization, fouling and gel formation for the ranges of the polymer concentration and experimental parameters (such as ΔP and feed flow rate) used. This is probably because of the high feed flow rate, which prevents such phenomenon. In the previous studies for the removal of mercury and cadmium, the same phenomenon was observed with polyethyleneimine as the complexing polymer in the same UF system and PEUF process [60, 61]. The obtained results in the earlier and recent studies confirm the efficiency of the UF system that remains pleasingly in the range of parameters studied.

4.3. Effect of Loading on Retention of Boron

In the UF experiments, different loadings varying from 0.01 to 1 was studied to find out the binding capacities of the polymers (P1, P2, P2G). In

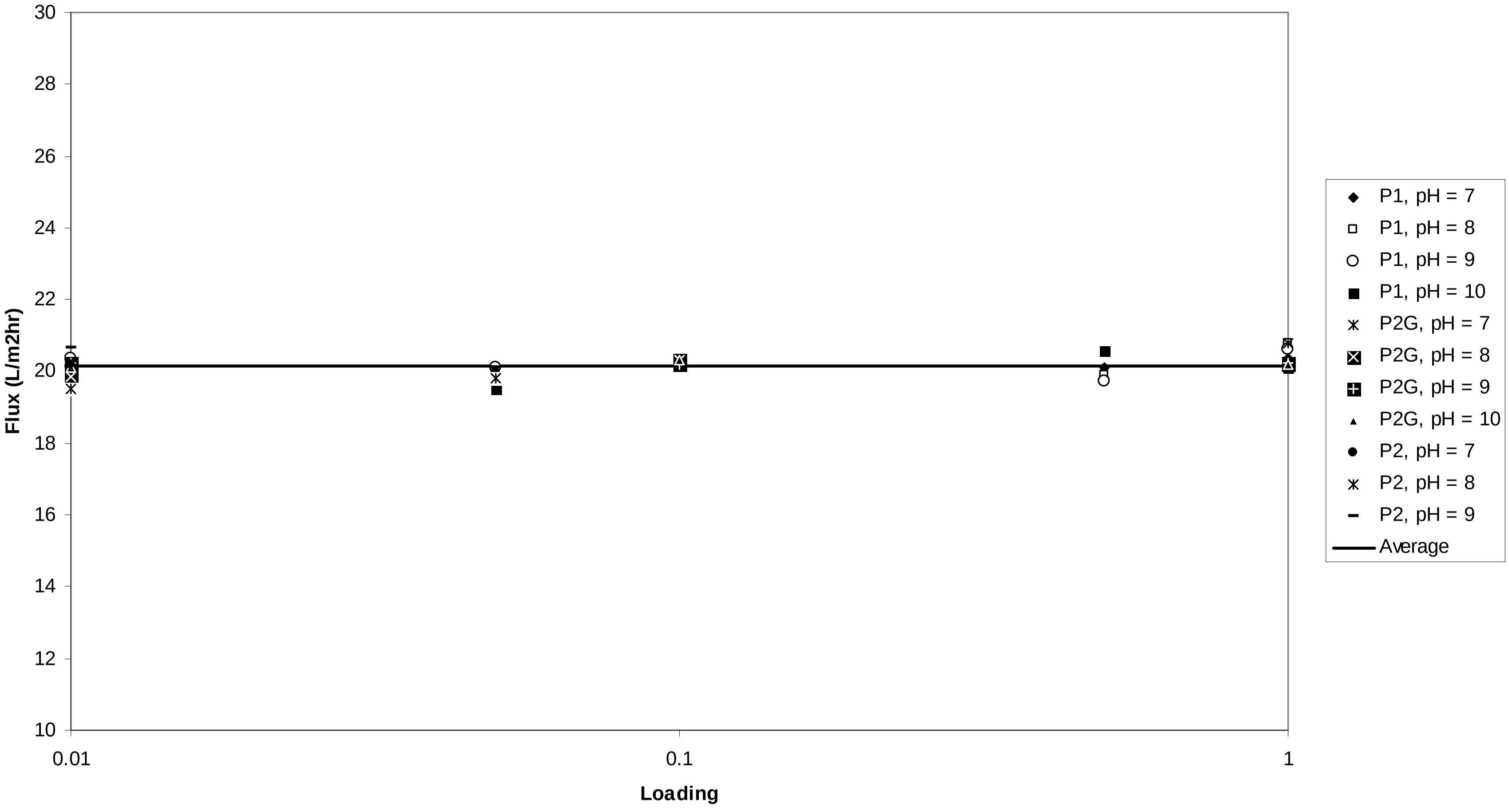

Figure 4.2.1. Effect of Loading, pH and Polymer Type on Permeate Flux

Figure 4.3.1 and Figure 4.3.2 (Table C.4 and Table C.5), retention values at different loadings are presented in semi-logarithmic graphs (in Figure C.1 and Figure C.2 those graphs are presented in non-logarithmic scale). In those figures, the lower the loading, the higher the retention is. This increase is exhibited at all pH values that were studied except for P2G at pH 10. This could be attributed to the lower interaction of this polymer with borate ion at high pH values.

The retention of boron increases with decreasing loadings as expected. This means that high polymer concentrations help the boron retention. In the previous studies [83, 85], because of probable solubility problems, even at very high loadings retentions could not be improved significantly. In our study, it is also suspected that there is a solubility problem in molecular level. For P2G and P2 using loadings lower than 0.01, because of the difficulty to dissolve them, is not practical. This also brings low variance of retention at that range. Contrarily for P1 at the studied range very satisfying results were obtained. At a loading of 0.01, retentions were obtained between the range of 79.4 - 90.1 %. These results are the highest values obtained for a continuous process in the literature. Such high values show that there may be no need of utilizing extra processes for the purifications of the stream. Also obtaining high retentions at pH values close to neutrality makes the process economical. All these results show us

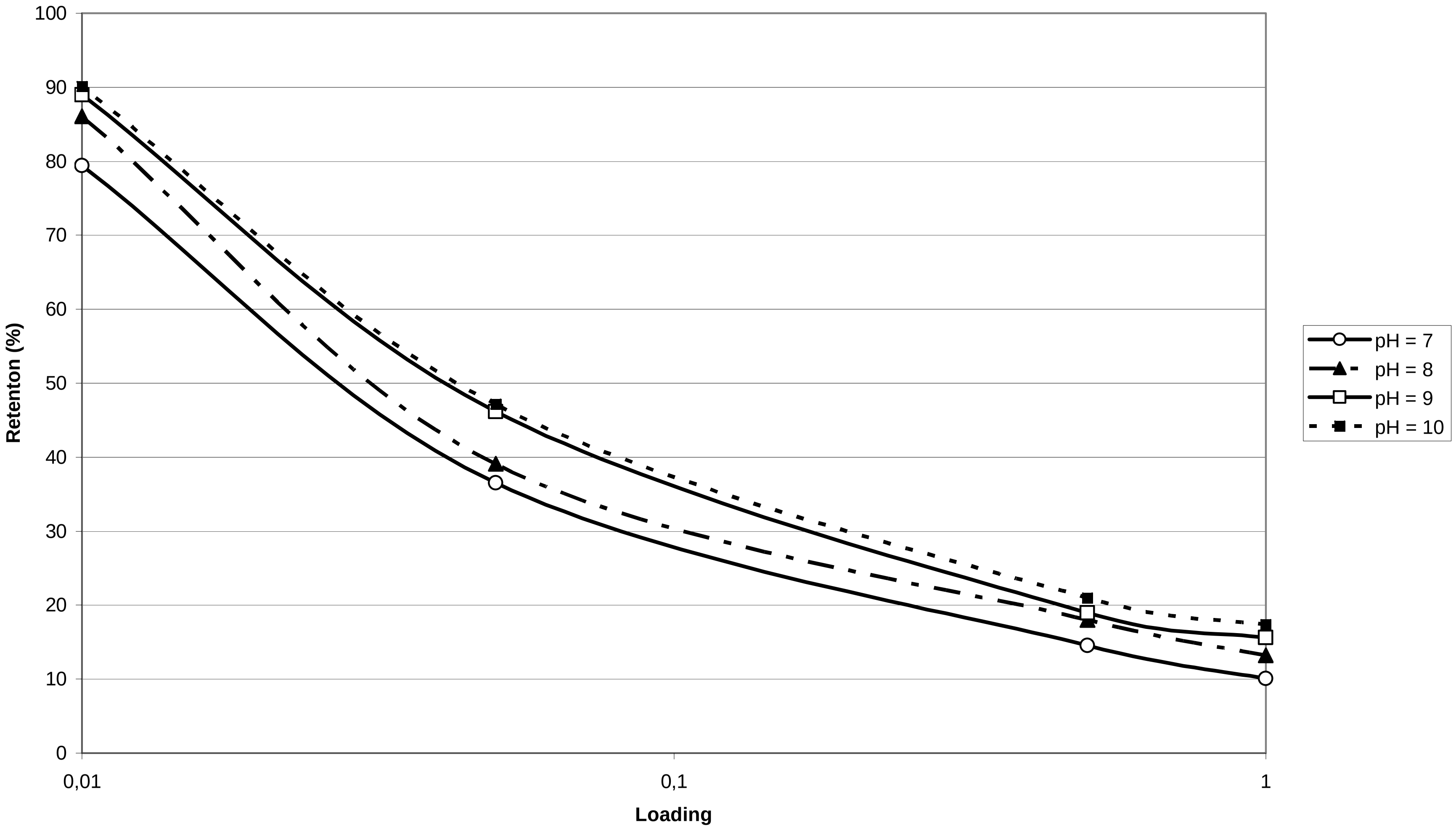

Figure 4.3.1. Effect of Loading on Retention of Boron (with P1)

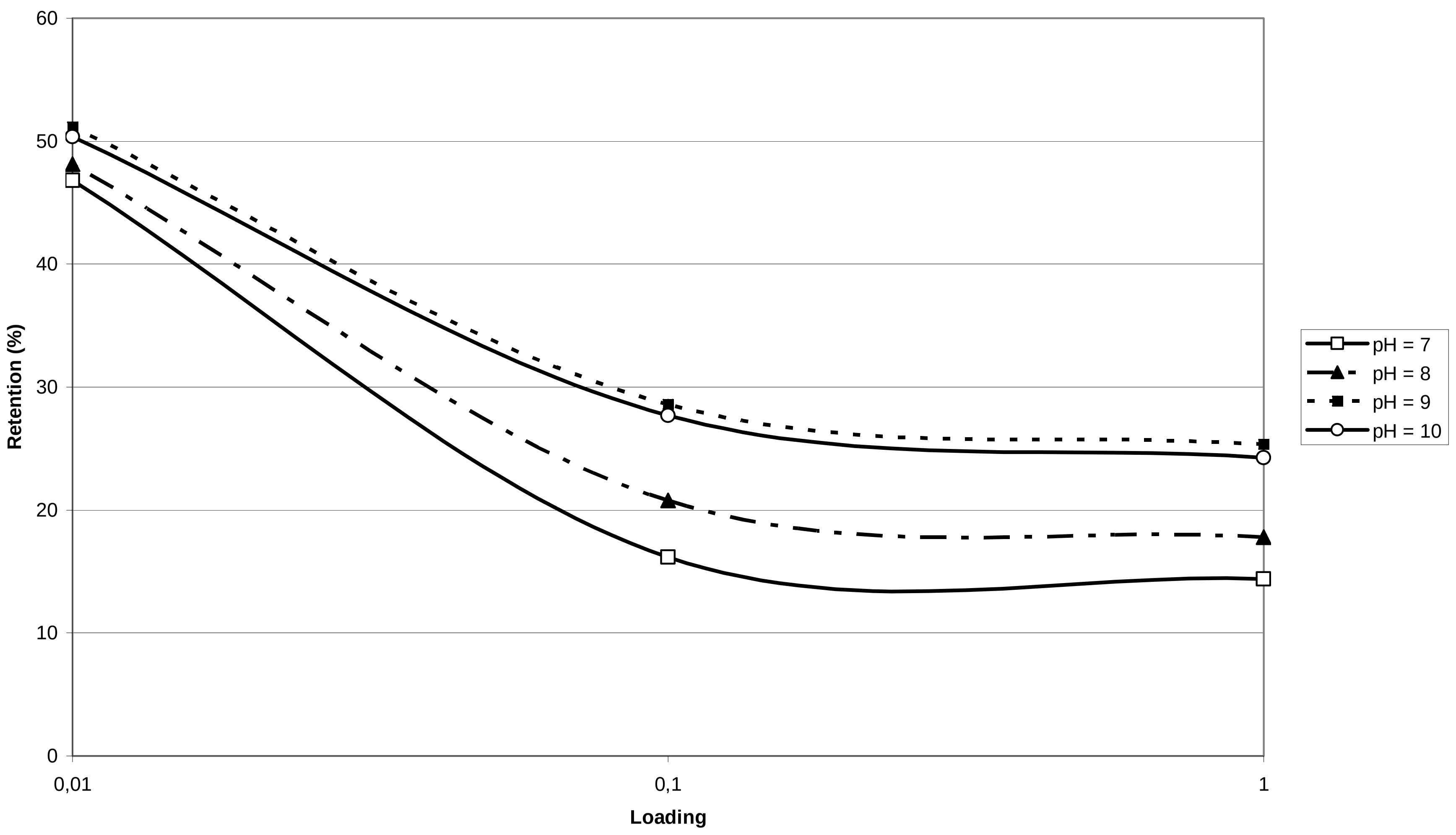

Figure 4.3.2. Effect of Loading on Retention of Boron (With P2G)

that this process may be applicable in an industrial process. In our previous study [83], the effect of loading to retention was lower compared to the current studied polymers. In the studied loading range, in the previous study where commercial polyvinyl alcohol was employed, although loading was decreased dramatically, the increase in the retention was not very pronounced.

In our previous study on the cations [60, 61], retention values close to unity was obtained at relatively high loadings. Furthermore, in those studies a plateau was reached where decreasing the loading did not change the retention very much but increasing the loading further above a critical value caused a sharp decrease in the retention. But when the current results are compared with the previous ones; although there is a sharp change of retention, effect of loading was not that tremendous and a plateau was not reached.

The sharp increase of retention in P1 (Figure C.1) can be explained by the branching of the polymer (Figure A.1). It was proposed by Smith et. al. [72] that for borate ion, during complexation, OH containing chains must arrange themselves in a fashion that can be seen in Figure 2.3.1; borate ion should make cross-links so that most of OH groups in the same repeating unit complexes. This configuration is most likely to occur at low loadings. Figure 4.3.1, which shows retention versus loading, indicates that when loading decreases probability of having that configuration increases logarithmically. This increase reaches to an end when solubility hinders adding more polymer or all of the borate ions are complexed.

4.4 Effect of pH of the Solution on Retention of Boron

pH is the other important factor which affects the complexation thus the retention of the ion. For that reason with loading experiments, pH studies were also carried out. The maximum pH value that was studied was 10 because the maximum allowable pH of the membrane was 11. The results are plotted in Figure 4.4.1 and 4.4.2 (Table C.6 and Table C.7) showing the effect of pH on retention at different loadings. From those figures it can be seen that increase in pH causes the retention to increase. This is observed for all loadings studied except for P2G at pH 10. Although pH has an effect on the increase of retention, this effect is not that high. In our previous study for boron removal [83, 85], separation was obtained at a basic medium and increase in pH enhanced the retention, also pH had a stronger effect than the current study. In our previous studies with cadmium and mercury, retention was also increasing with increasing pH [67]. The system was acidic contrary to the current boron stud. It was observed that retention of cations increased when the system was getting close to normality. The pH effect on retention of boron is weaker with respect to

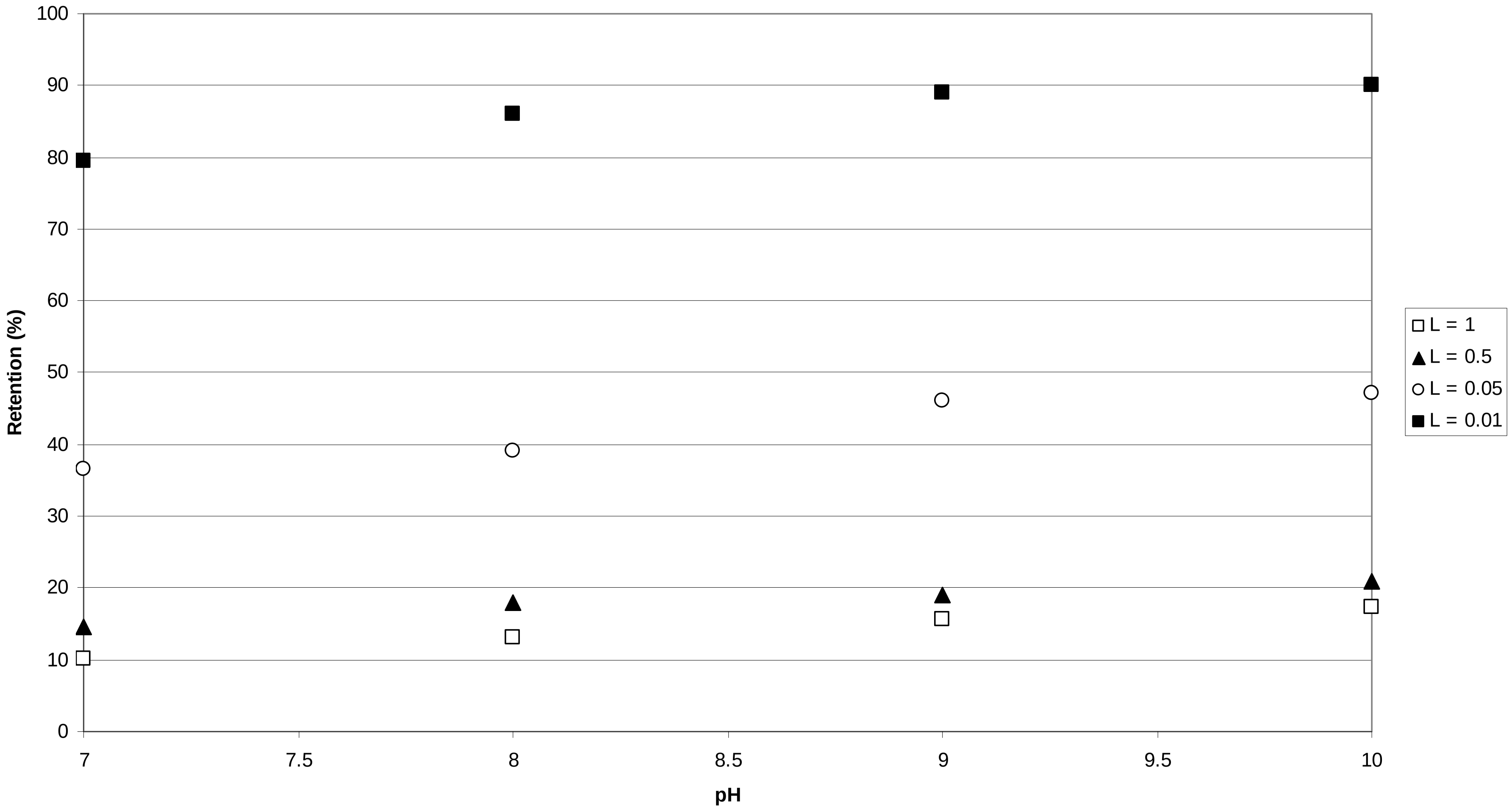

Figure 4.4.1. Effect of pH on Retention of Boron (with P1)

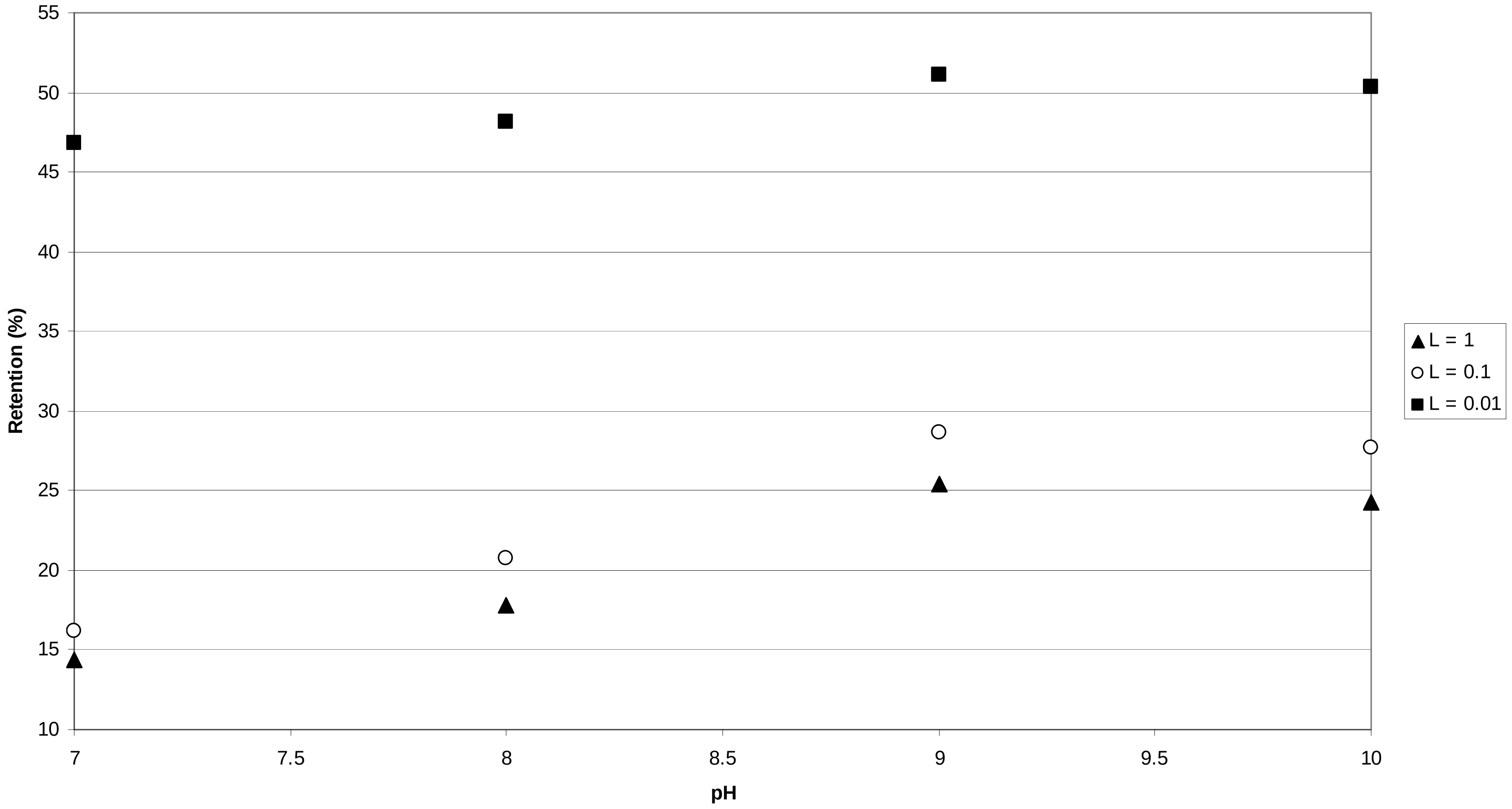

Figure 4.4.2. Effect of pH on Retention of Boron (With P2G)

mercury and cadmium but that does not mean that effect of pH is insignificant.

The effect of pH on retention of boron may be explained by the reactions <2.3.1> and <2.3.2>. It can be seen that production of borate ion is enhanced in basic medium while it is low at acidic medium. So it is unexpected to have recovery of boron at acidic pH values. Polymer enhanced ultrafiltration with pH values in the basic range expected to be more suitable for removal of boron at aqueous solutions. In the results, retention is increasing with the increase of pH. This can also be explained by the mentioned reactions. The more OH^- ion in the solution, the more borate ion is produced, which facilitates the complexation.

The effect of pH is weak with the studied polymers. In fact, in a real life application, changing the pH of a whole waste stream may not be feasible. Additionally P1 had high retentions even at moderate pH values, which may indicate that the waste stream can be treated without changing the pH of the system. Consequently, all these results show us that this process may be economically and industrially promising.

4.5. Retentions with Different Polymers

To find a suitable polymer for the removal of boron three different polymers were studied. These polymers were P1, P2G and P2 (which is a linear version of P2G). All of these polymers are noncommercial, specially synthesized polymers. According to the studies of Bıçak et al. [73, 74], the ligand for the complexation of boron must have two or more hydroxyl functions which are on the adjacent carbon atoms. Also the backbone of the polymer must be as inert as possible. According to those criteria for P1, P2 and P2G, N-methyl-D-glucamine and iminodipropylene glycol, have been used as chelating agents. These agents have many vicinal diol functions. Derivatives of these polymers have yielded good results as a boron sorption resin; they were stable and bound high amounts of boron. The comparative results of P1, P2 and P2G are in Figure 4.5.1.

From the figure, it is obvious that P1 has a great retention performance compared to the other two at all pH values. This huge difference may be due to the structure of the polymers which may have influence the complexation mechanism or probably from some solubility problems in molecular level. Although not much, P2 has an improved performance from its gel version which is again can be related to solubility. As mentioned, for all of the polymers used, effect of pH on retention is not very strong.

For P2, having a higher retention from P2G is an expected result but the main problem for P2 and P2G is suspected to be their solubility in water as indicated by our experiments. The chemical structure of P2 is shown in

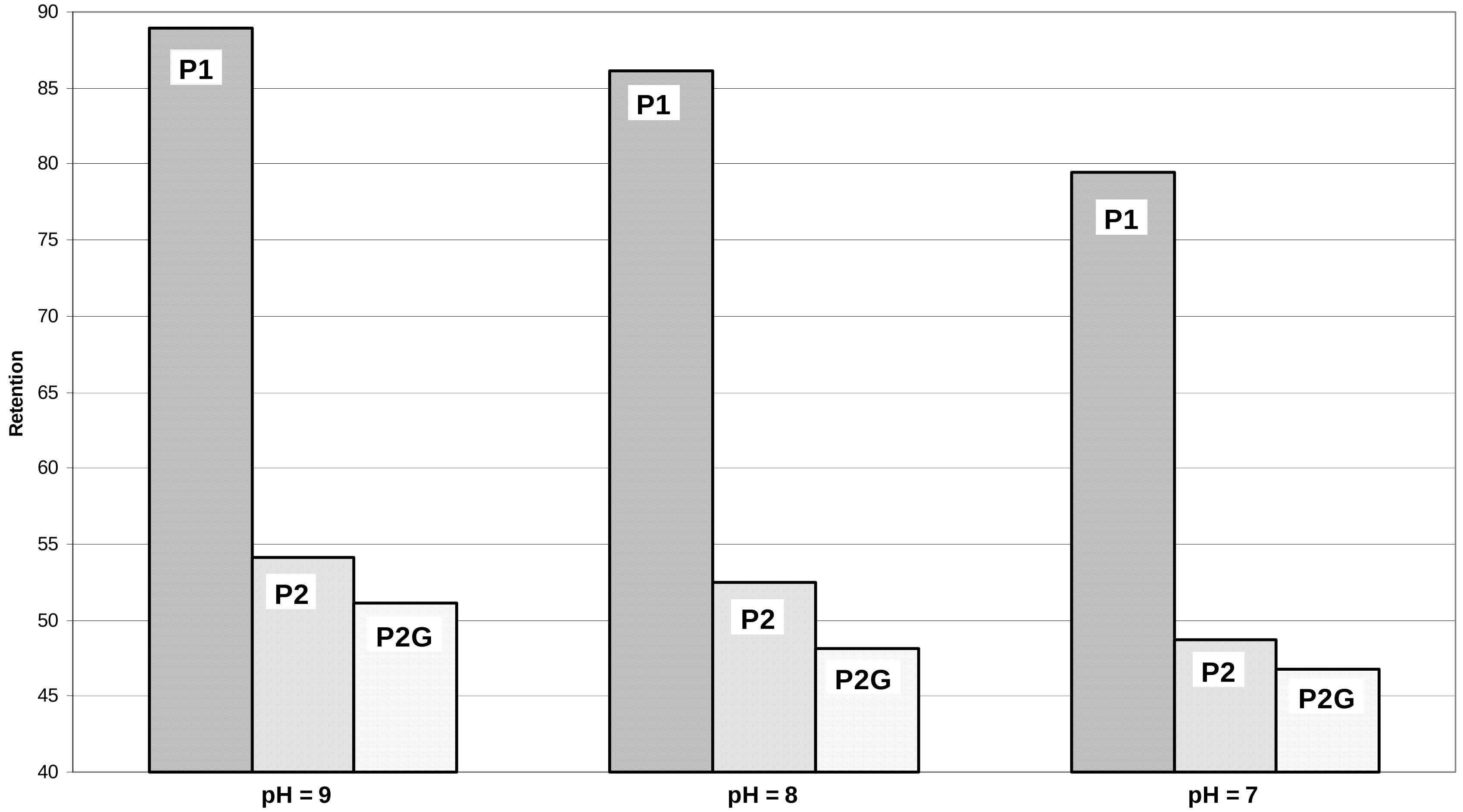

Figure 4.5.1. Comparison of the Retentions of the Polymers at L = 0.01 and Various pH values

Figure A.2. P2G should have a more branched structure. In such a structure, following explanation may be reasonable: because of the narrowness of the space among the hydroxide chains, OH groups cannot interact with water molecules to dissolve in water so although there are lots of hydroxide groups, solubility becomes lower than expected. That results in lower retention values. Also this narrowness may prevent the borate ion to enter through the branches, which also contributes to lower retention. The situation for P1 is different (Figure A.1). The branches are not as closely packed as in P2. They are more linear, which do not complicate the solubility and hinder the interaction of borate ion with hydroxide groups. Also this structure enhances the retention at high polymer concentration.

In our previous study for the removal of boron [83, 85], the ligand used as a chelating agent was polyvinyl alcohol. Polyvinyl alcohol's structure is linear and the OH groups , contrary to the P1, P2 and P2G, are located on the main chain. Maximum retention that was obtained with that polymer was 28 % which is far away from the current results. Also it was stated that, the performance is hindered by the solubility of the polymer.

As a conclusion it is for sure that, besides the amount of OH groups in the chain, position and distribution of these groups in the molecule play an important role in the complexation of boron, thus the retention of the boron.

CHAPTER 5

CONCLUSIONS

A study of continuous PEUF was performed for removal of boron from the aqueous solutions by studying different polymers as complexing agents. The outcomes of several operating parameters on the retention of boron were examined. The process and some of the polymers were found to be suitable for boron removal and repeated experiments showed that the results are reproducible.

The examined parameters did not have any significant effect on the permeate flux. In all of the experiments, flux remained constant. This was proof for the process that it does not have problems such as concentration polarization, fouling and gel formation.

Operating parameters like loading and pH were studied to see how they affect the performance of the polymers for complexation. To find an suitable pH and loading value, experiments were performed in various ranges of experimental parameters for all of the three polymers studied. Decrease in loading, resulted in a higher retention. In P2 series polymers, increase in polymer concentration did not give significant increase in retentions. In P1 on the other hand, the increase in polymer concentration had stronger impact on retention. Although for P1 it seems that it is possible to reach a higher retention value at a lower loading, it is expected that a suitable high retention would be hindered by the low solubility of the polymer. Additionally, the results showed that retention increases with increasing pH.

Three different polymers; P1, P2 and P2G were studied to see their performance on rejection of boron. P1 had very satisfactory results for the removal of boron. Even though P2 and P2G, compared to P1, had less capacity for binding of boron, their retentions are significantly higher from previous similar studies. All of these polymers had low sensitivity to pH, which is demanded if a large quantity of waste stream is to be treated, and the main parameter was observed to be the loading.

The maximum retention that was obtained is 90.1 % at the loading of 0.01 and pH value of 10. This result is the highest retention in the literature obtained in continuous polymer enhanced ultrafiltration of boron.

CHAPTER 6

RECOMMENDATIONS

The removal performance of the process can be furthered by synthesizing polymers which are more soluble in water. By this, loading would have much more effect on retention and higher retentions would be reached at higher loadings.

Second point to be considered is the regeneration of the polymers. These polymers can be considered really effective if they can be separated from the borate ion and reused in PEUF process.

For the development of industrial applications of the PEUF process for the removal of boron, actual wastewater streams or contaminated waters should be studied to understand the effects of other ions on the performance and efficiency of the process. Also if there is some counter ion problems, methodology of the pretreatment of those wastewater steams should be studied.

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APPENDIX A

POLYMERS USED

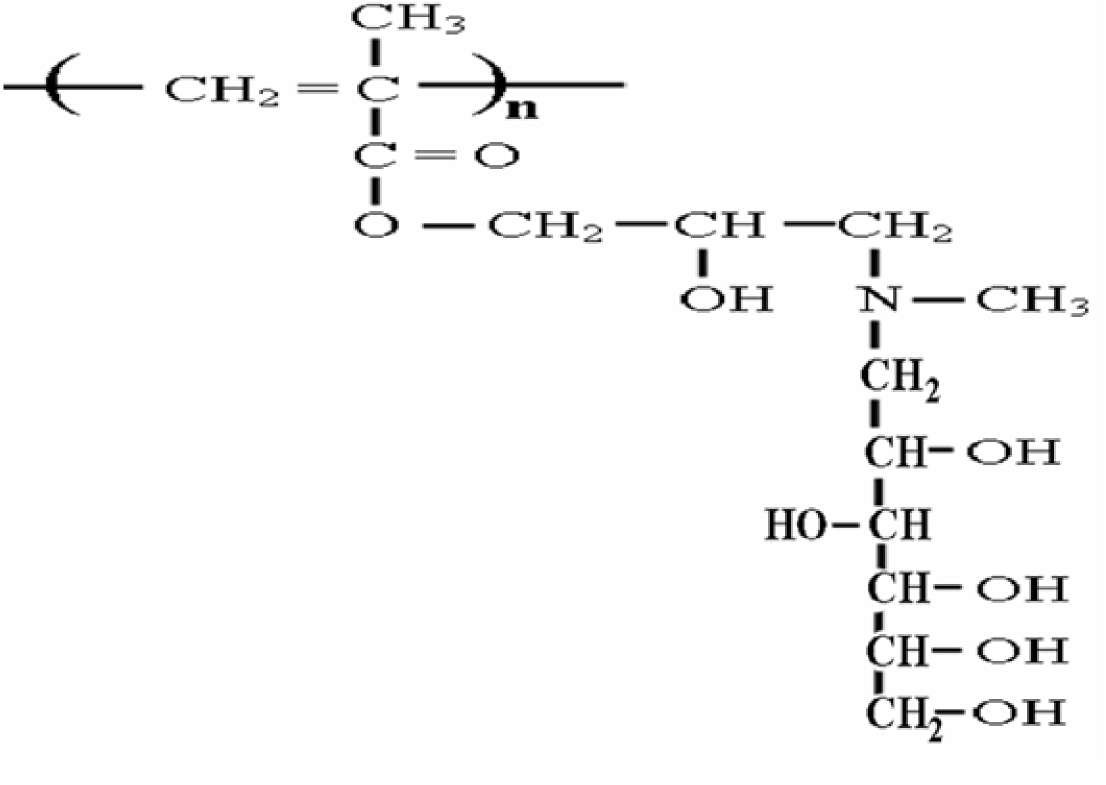

Figure A.1. N-methyl-D-glucamine grafted Polyglycidyl Methacrylate
(P1)

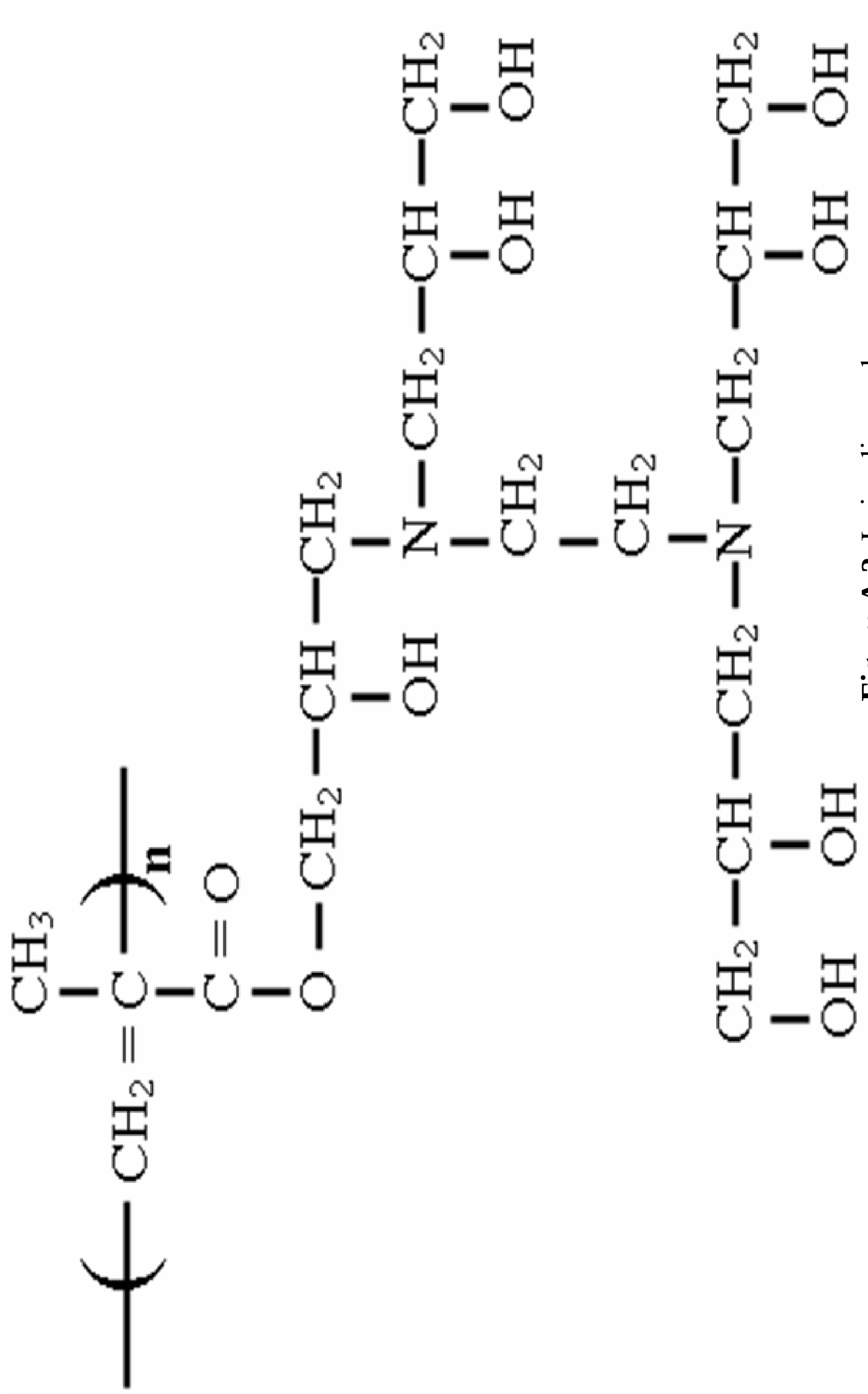

Figure A.2. Iminodipropylene glycol grafted Polyglycidyl methacrylate **(P2)**

APPENDIX B

DIRECT READING ECHELLE (DRE) ICP ANALYSES METHOD AND CALCULATIONS

Before starting up the instrument and igniting the plasma, a protocol should be specified. Protocol is identified by opening a folder and selecting the element or elements that will be analyzed. Afterward, operating conditions such as rinse time, uptake time, the peak line, number of the standards and number of repetitive scannings should be input. Then, a standard solution should be introduced to the system for determining the background points on the wavelength for compensating any possible interferences in ICP (The spectral interferences arise due to the high temperature of the plasma discharge since virtually every species present in the ICP emits light. Also the interferences may arise from viscosity of the solution introduced to the nebulizer. The higher the viscosity, the less amount of solution is transported through the solution. This will cause less light to be emitted. For that reason the background of the standard solution should be as close as possible to the sample solution). After determining the background points, the next step is source peaking for obtaining dependable analysis results. Before the calibration can be initiated, it is required to make certain if the instrument is at the proper height. Mn is selected as the peaking element. The instrument scans the plasma and find outs the best viewing height for analysis, using Mn line. After the Mn peaking, the system is ready for the analysis.

For the purpose of calibrating the instrument, standards for permeate and feed solutions are prepared with distilled water. The permeate standards contain boron and distilled water whereas the feed standards contain additional polymer in the concentration same with the feed solution. Six standard solutions are introduced to system for feed and permeate.

Table B.1. Sample Intensity Data of the Standards for a Feed Analysis

10 mg/L P2G + 10 mg/L Boron, L=1, pH=8

Feed Calibration

Conc.	**Inten. 1**	**Inten. 2**	**Inten. 3**	**Avg. Inten.**	**Correct. Inten.**
Blank	7528	7339	7222	**7363**	
2 mg/L	259649	262016	259778	**260481**	**253118**
4 mg/L	487977	492674	490606	**490419**	**483056**
6 mg/L	885137	883596	883864	**884199**	**976836**
8 mg/L	1059626	1036161	1030098	**1041962**	**1034599**
10 mg/L	1198398	1195376	1199193	**1197656**	**1190293**

x	**y**
2	**253118**
4	**483056**
6	**976836**
8	**1034599**
10	**1190293**

These standards have boron concentrations of 0 mg/L, 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L. 0 mg/L permeate blank contains only distilled water whereas 0 mg/L feed contains distilled water with certain amount of polymer without boron. The standards are aspirated to plasma at the desired replicate numbers and the intensities of the standards are obtained. After that the calibration curves for both permeate and retentate are obtained. Then the samples are introduced and the intensities of the samples are obtained. By the help of the calibration curve and the obtained intensity concentration relation, the concentrations of the samples are found. In Figure B.1 an example of feed calibration is given.

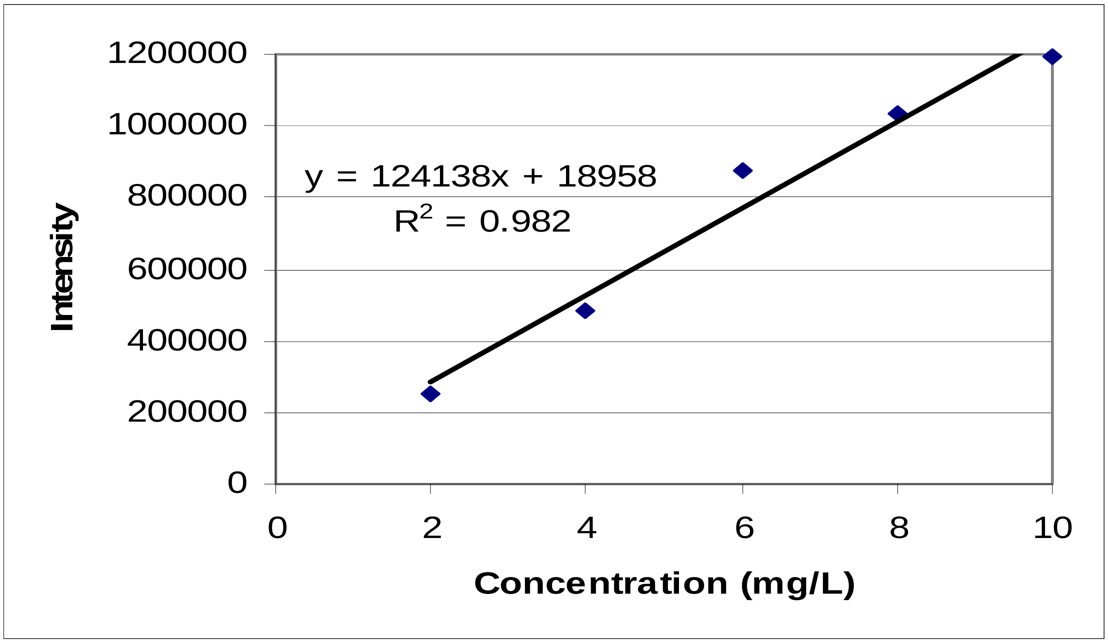

Figure B.1. The Calibration Curve with the Intensity and Concentration Relation of the Related Feed Analysis

Table B.2. Sample Intensity Data and the Determined Concentration Values of the Feed Samples

sample	Inten. 1	Inten. 2	Inten. 3	Inten. 4	Inten. 5	Inten. 6
f0	1193661	1203372	1194731	1183561	1195249	1185517
f60	1075197	1079314	1078162	1085920	1087011	1088500
f85	1115641	1109185	1108513	1101327	1099561	1101037
f110	1111670	1114310	1106341	1103176	1102570	1102983
f135	1090218	1091497	1091016	1092870	1092644	1092913
f160	1055764	1061823	1056920	1059439	1060513	1069500
f185	1059431	1056412	1069877	1059506	1051193	1059641

sample	Inten. 7	Inten. 8	Inten. 9	avg. Int.	corr.Int.	concen.
f0	1196960	1192118	1194518	1193299	1185936	9.40
f60	1083634	1082512	1082276	1082503	1075140	8.51
f85	1114472	1113981	1115743	1108829	1101466	8.72
f110	1106594	1106729	1106646	1106780	1099417	8.70
f135	1093057	1092912	1093155	1092254	1084891	8.59
f160	1062143	1060822	1061131	1060895	1053532	8.33
f185	1058819	1062142	1056798	1059313	1051950	8.32

The concentrations of the feed samples were calculated by the equation which relates intensity to concentration. The equation (B.1) for finding the feed concentration for the run listed at Table B.2 is as below:

$$C = \frac{(I - 18958)}{124138} \tag{B.1}$$

In the Table B.2 the sample data of the feed analysis are given also with blank corrected intensities. The corrected intensities are the average of the intensities determined by the instrument. Both the drawing of the calibration curves and calculations of the concentrations were performed with these corrected intensity data.

APPENDIX C

DATA TABLES OF THE ULTRAFILTRATION EXPERIMENTS

Table C.1. All of the Experimental Data Used in the Results

Polymer Type = P1, Loading = 0.1, Loading$_{TOC}$ = 0.12, pH = 8							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.85	F_{60} = 19.29	F_{90} = 21.72	F_{120} = 18.73	F_{150} = 19.79	F_{180} = 19.14	
CF (mg/L)	6.21	5.29	5.32	5.38	5.31	5.22	5.13
Cp (mg/L)		4.58	4.47	4.50	4.54	4.49	4.48
R (%)		13.4	16.0	16.4	14.5	14.0	12.7
	$F_{P\,Av}$ = 19.75 **$C_{F\,Av}$** = 5.27 **$C_{P\,Av}$** = 4.51 **R_{Av}** = 14.5						

Polymer Type = P2G, Loading = 1, Loading$_{TOC}$ = 0.98, pH = 7							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.73	F_{60} = 22.01	F_{90} = 20.13	F_{120} = 20.21	F_{150} = 19.16	F_{180} = 20.42	
CF (mg/L)	9.40	8.37	8.60	8.70	8.76	8.72	8.65
Cp (mg/L)		7.19	7.34	7.38	7.44	7.43	7.55
R (%)		14.1	14.7	15.2	15.1	14.8	12.7
	$F_{P\,Av}$ = 20.78 **$C_{F\,Av}$** = 8.63 **$C_{P\,Av}$** = 7.39 **R_{Av}** = 14.4						

Table C.1. Continued

Polymer Type = P2G, Loading = 1, Loading$_{TOC}$ = 0.98, pH = 8							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.18	F_{60} = 20.32	F_{90} = 20.10	F_{120} = 19.58	F_{150} = 20.53	F_{180} = 20.28	
CF (mg/L)	9.40	8.51	8.72	8.70	8.59	8.33	8.32
Cp (mg/L)		7.01	6.90	7.07	6.99	7.02	7.05
R (%)		17.6	20.9	18.7	18.6	15.7	15.3
		$F_{P\,Av}$ = 20.17	**$C_{F\,Av}$** = 8.53		**$C_{P\,Av}$** = 7.01		**R_{Av}** = 17.8

Polymer Type = P2G, Loading = 1, Loading$_{TOC}$ = 0.98. pH = 9							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.22	F_{60} = 19.92	F_{90} = 21.02	F_{120} = 20.45	F_{150} = 19.56	F_{180} = 20.32	
CF (mg/L)	9.40	8.31	8.36	8.42	8.37	8.43	8.49
Cp (mg/L)		6.21	6.26	6.26	6.27	6.29	6.31
R (%)		25.3	25.1	25.7	25.1	25.4	25.7
		$F_{P\,Av}$ = 20.25	**$C_{F\,Av}$** = 8.40		**$C_{P\,Av}$** = 6.27		**R_{Av}** = 25.4

Table C.1. Continued

Polymer Type = P2G, Loading = 0.1, Loading$_{TOC}$ = 0.095, pH = 8							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.30	F_{60} = 19.12	F_{90} = 20.73	F_{120} = 20.15	F_{150} = 20.48	F_{180} = 21.13	
CF (mg/L)	4.83	4.58	4.62	4.47	4.54	4.58	4.63
Cp (mg/L)		3.85	3.53	3.54	3.58	3.60	3.62
R (%)		15.9	23.6	20.8	21.2	21.4	21.8
	$F_{P\ Av}$ = 20.32		**$C_{F\ Av}$** = 4.57		**$C_{P\ Av}$** = 3.62		**R_{Av}** = 20.8

Polymer Type = P2G, Loading = 0.1, Loading$_{TOC}$ = 0.095, pH = 9							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.12	F_{60} = 20.47	F_{90} = 20.08	F_{120} = 19.83	F_{150} = 20.35	F_{180} = 20.15	
CF (mg/L)	4.83	4.80	4.79	4.76	4.75	4.76	4.75
Cp (mg/L)		3.32	3.37	3.45	3.47	3.41	3.40
R (%)		30.8	29.7	27.5	27.0	28.4	28.4
	$F_{P\ Av}$ = 20.17		**$C_{F\ Av}$** = 4.77		**$C_{P\ Av}$** = 3.40		**R_{Av}** = 28.6

Table C.1. Continued

Polymer Type = P2G, Loading = 1, Loading$_{TOC}$ = 0.96, pH = 7							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.45	F_{60} = 21.12	F_{90} = 20.87	F_{120} = 20.52	F_{150} = 19.38	F_{180} = 19.73	
CF (mg/L)	9.62	8.73	8.75	8.70	8.65	8.59	8.61
Cp (mg/L)		7.51	7.49	7.43	7.35	7.29	7.28
R (%)		14.0	14.4	14.6	15.0	15.1	15.4
	$F_{P\,Av}$ = 20.18		**$C_{F\,Av}$** = 8.67		**$C_{P\,Av}$** = 7.39		**R_{Av}** = 14.8

Polymer Type = P2G, Loading = 0.1, Loading$_{TOC}$ = 0.095, pH = 7							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.68	F_{60} = 21.29	F_{90} = 20.13	F_{120} = 19.45	F_{150} = 19.77	F_{180} = 20.18	
CF (mg/L)	4.89	4.64	4.56	4.47	4.42	4.38	4.38
Cp (mg/L)		3.95	3.82	3.75	3.71	3.65	3.63
R (%)		14.9	16.2	16.1	16.1	16.7	17.1
	$F_{P\,Av}$ = 20.25		**$C_{F\,Av}$** = 4.48		**$C_{P\,Av}$** = 3.75		**R_{Av}** = 16.2

Table C.1. Continued

Polymer Type = P2G, Loading = 1, Loading$_{TOC}$ = 0.96, pH = 8							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.12	F_{60} = 19.87	F_{90} = 20.31	F_{120} = 19.55		F_{150} = 20.01	F_{180} = 21.09
CF (mg/L)	9.62	8.96	8.89	8.82	8.73	8.67	8.67
Cp (mg/L)		7.26	7.28	7.20	7.13	7.06	7.05
R (%)		19.0	18.1	18.4	18.3	18.6	18.7

$F_{P\,Av}$ = 20.16 $C_{F\,Av}$ = 8.79 $C_{P\,Av}$ = 7.16 R_{Av} = 18.5

Polymer Type = P2G, Loading = 1, Loading$_{TOC}$ = 0.96, pH = 9							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 21.03	F_{60} = 20.52	F_{90} = 20.13	F_{120} = 20.32		F_{150} = 19.89	F_{180} = 19.37
CF (mg/L)	9.62	8.77	8.58	8.47	8.38	8.32	8.32
Cp (mg/L)		6.67	6.45	6.31	6.24	6.18	6.20
R (%)		23.9	24.8	25.5	25.5	25.7	25.5

$F_{P\,Av}$ = 20.21 $C_{F\,Av}$ = 8.47 $C_{P\,Av}$ = 6.34 R_{Av} = 25.2

Table C.1. Continued

Polymer Type = P2G, Loading = 0.01, Loading$_{TOC}$ = 0.01, pH = 7							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.53	F_{60} = 19.68	F_{90} = 20.21	F_{120} = 19.47	F_{150} = 21.14	F_{180} = 22.76	
CF (mg/L)	9.85	9.42	9.23	9.11	9.01	8.95	8.98
Cp (mg/L)		5.18	5.02	4.88	4.74	4.68	4.61
R (%)		45.0	45.6	46.4	47.4	47.7	48.7

$\mathbf{F_{P\,Av}}$ = 20.13 $\mathbf{C_{F\,Av}}$ = 9.12 $\mathbf{C_{P\,Av}}$ = 4.85 $\mathbf{R_{Av}}$ = 46.8

Polymer Type = P2G. Loading = 0.01. Loading$_{TOC}$ = 0.01. pH = 8							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.76	F_{60} = 20.13	F_{90} = 19.38	F_{120} = 19.57	F_{150} = 19.21	F_{180} = 20.01	
CF (mg/L)	9.85	9.39	9.34	9.22	9.15	9.11	9.09
Cp (mg/L)		4.95	4.88	4.83	4.74	4.66	4.63
R (%)		47.3	47.8	47.6	48.2	48.0	49.1

$\mathbf{F_{P\,Av}}$ = 19.84 $\mathbf{C_{F\,Av}}$ = 9.22 $\mathbf{C_{P\,Av}}$ = 4.78 $\mathbf{R_{Av}}$ = 48.12

Table C.1. Continued

Polymer Type = P2G, Loading = 0.01, Loading$_{TOC}$ = 0.01, pH = 9							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 21.30	F_{60} = 20.71	F_{90} = 19.51	F_{120} = 19.89	F_{150} = 19.33	F_{180} = 20.75	
CF (mg/L)	9.85	9.56	9.38	9.15	9.23	9.19	9.12
Cp (mg/L)		4.84	4.67	4.55	4.44	4.37	4.32
R (%)		49.4	50.2	50.3	51.9	52.4	52.6
	$F_{P\ Av}$ = 20.25	**$C_{F\ Av}$** = 9.27	**$C_{P\ Av}$** = 4.53	**R_{Av}** = 51.4			

Polymer Type = P1, Loading = 0.5, Loading$_{TOC}$ = 0.53, pH = 8							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 17.54	F_{60} = 21.01	F_{90} = 20.72	F_{120} = 20.08	F_{150} = 19.73	F_{180} = 20.18	
CF (mg/L)	12.06	11.48	11.35	11.21	11.15	11.08	11.05
Cp (mg/L)		9.30	9.25	9.25	9.19	9.11	9.08
R (%)		19.0	18.5	17.5	17.6	17.8	17.8
	$F_{P\ Av}$ = 19.88	**$C_{F\ Av}$** = 11.22	**$C_{P\ Av}$** = 9.20	**R_{Av}** = 18.0			

Table C.1. Continued

Polymer Type = P1, Loading = 0.5, Loading$_{TOC}$ = 0.53, pH = 9							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.75	F_{60} = 19.33	F_{90} = 19.58	F_{120} = 20.23	F_{150} = 20.05	F_{180} = 19.43	
CF (mg/L)	12.06	11.23	10.83	10.78	10.69	10.53	10.48
Cp (mg/L)		9.16	8.80	8.64	8.59	8.55	8.56
R (%)		18.4	18.7	19.9	18.7	18.8	18.3
	$F_{P\ Av}$ = 19.73		**$C_{F\ Av}$** = 10.76		**$C_{P\ Av}$** = 8.72		**R_{Av}** = 19.0

Polymer Type = P1, Loading = 0.5, Loading$_{TOC}$ = 0.53, pH = 7							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.42	F_{60} = 20.55	F_{90} = 20.73	F_{120} = 19.86	F_{150} = 19.23	F_{180} = 20.75	
CF (mg/L)	12.06	11.56	11.41	11.26	11.21	10.94	10.93
Cp (mg/L)		9.69	9.66	9.62	9.53	9.49	9.50
R (%)		16.2	15.3	14.6	15.0	13.3	13.1
	$F_{P\ Av}$ = 20.09		**$C_{F\ Av}$** = 11.22		**$C_{P\ Av}$** = 9.58		**R_{Av}** = 14.6

Table C.1. Continued

Polymer Type = P1, Loading = 0.5, Loading$_{TOC}$ = 0.53, pH = 10							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.27	F_{60} = 20.78	F_{90} = 21.13	F_{120} = 20.33	F_{150} = 21.13	F_{180} = 20.82	
CF (mg/L)	12,06	11,32	11,07	10,84	10.78	10.69	10.67
Cp (mg/L)		8,91	8,66	8,57	8.53	8.50	8.48
R (%)		21,3	21,8	20,9	20.9	20.5	20.5
	$F_{P\ Av}$ = 20.58		**$C_{F\ Av}$** = 10.90		**$C_{P\ Av}$** = 8.61		**R_{Av}** = 21.0

Polymer Type = P1, Loading = 1, pH = 7							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 17.57	F_{60} = 17.76	F_{90} = 20.86	F_{120} = 22.29	F_{150} = 20.92	F_{180} = 22.68	
CF (mg/L)	9,97	9,15	9,08	9,07	8.96	9.11	8.92
Cp (mg/L)		8,32	8,18	8,13	8.07	8.08	8.05
R (%)		9,1	9,9	10,4	9,9	11.3	9.8
	$F_{P\ Av}$ = 20.35		**$C_{F\ Av}$** = 9.18		**$C_{P\ Av}$** = 8.14		**R_{Av}** = 10.1

Table C.1. Continued

Polymer Type = P1, Loading = 1, pH = 8							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 21.88	F_{60} = 20.34	F_{90} = 20.75	F_{120} = 21.23		F_{150} = 20.16	F_{180} = 20.22
CF (mg/L)	9.97	8.85	8.78	8.93	8.98	8.92	8.95
Cp (mg/L)		7.84	7.75	7.71	7.70	7.68	7.68
R (%)		11.4	11.9	13.7	14.3	13.9	14.2

$F_{P\,Av}$ = 20.77 **$C_{F\,Av}$** = 9.05 **$C_{P\,Av}$** = 7.73 **R_{Av}** = 13.2

Polymer Type = P1, Loading = 1, pH = 9							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.57	F_{60} = 20.15	F_{90} = 19.86	F_{120} = 21.50		F_{150} = 19.79	F_{180} = 21.78
CF (mg/L)	9.97	8.97	8.81	8.81	8.87	8.89	8.93
Cp (mg/L)		7.52	7.42	7.51	7.48	7.53	7.51
R (%)		16.2	15.8	14.8	15.7	15.3	15.9

$F_{P\,Av}$ = 20.61 **$C_{F\,Av}$** = 9.04 **$C_{P\,Av}$** = 7.50 **R_{Av}** = 15.6

Table C.1. Continued

Polymer Type = P1, Loading = 1, pH = 10							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.12	F_{60} = 21.68	F_{90} = 19.36	F_{120} = 20.33	F_{150} = 19.36	F_{180} = 19.68	
CF (mg/L)	9.97	8.82	8.73	8.78	8.82	8.75	8.93
Cp (mg/L)		7.08	7.01	7.43	7.38	7.40	7.36
R (%)		19.7	19.7	15.4	16.3	15.4	17.6
	$F_{P\,Av}$ = 20.09		**$C_{F\,Av}$** = 8.81		**$C_{P\,Av}$** = 7.28		**R_{Av}** = 17.36

Polymer Type = P2G, Loading = 1, Loading$_{TOC}$ = 1.03, pH = 10							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.88	F_{60} = 19.34	F_{90} = 20.12	F_{120} = 21.47	F_{150} = 20.65	F_{180} = 19.56	
CF (mg/L)	9.91	9.62	9.57	9.53	9.42	9.38	9.36
Cp (mg/L)		7.25	7.29	7.14	7.29	7.08	7.03
R (%)		24.6	23.8	25.1	22.6	24.5	24.9
	$F_{P\,Av}$ = 20.17		**$C_{F\,Av}$** = 9.48		**$C_{P\,Av}$** = 7.18		**R_{Av}** = 24.3

Table C.1. Continued

Polymer Type = P2G, Loading = 0.1, Loading$_{TOC}$ = 0.103, pH = 10							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.38	F_{60} = 21.13	F_{90} = 20.40	F_{120} = 19.72	F_{150} = 20.09	F_{180} = 20.22	
CF (mg/L)	9.93	9.67	9.61	9.58	9.52	9.46	9.45
Cp (mg/L)		7.25	6.97	6.88	6.81	6.76	6.76
R (%)		25.0	27.5	28.2	28.5	28.5	28.5
	$F_{P\ Av}$ = 20.32		**$C_{F\ Av}$** = 9.55		**$C_{P\ Av}$** = 6.91		**R_{Av}** = 27.7

Polymer Type = P2G, Loading = 0.01, Loading$_{TOC}$ = 0.01, pH = 10							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.51	F_{60} = 19.40	F_{90} = 20.75	F_{120} = 20.15	F_{150} = 20.26	F_{180} = 20.57	
CF (mg/L)	9.90	9.46	9.31	9.28	9.16	9.07	9.03
Cp (mg/L)		4.66	4.59	4.62	4.57	4.52	4.49
R (%)		50.7	50.7	50.2	50.1	50.2	50.3
	$F_{P\ Av}$ = 20.11		**$C_{F\ Av}$** = 9.22		**$C_{P\ Av}$** = 4.74		**R_{Av}** = 50.4

Table C.1. Continued

Polymer Type = P2G, Loading = 0.01, Loading$_{TOC}$ = 0.009, pH = 7							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.40	F_{60} = 20.29	F_{90} = 20.51	F_{120} = 20.13	F_{150} = 19.87	F_{180} = 20.35	
CF (mg/L)	10.12	9.62	9.44	9.31	9.19	9.08	9.00
Cp (mg/L)		5.23	5.11	4.95	4.88	4.82	4.77
R (%)		45.6	45.9	46.8	46.9	46.9	47.0
	$F_{P\,Av}$ = 20.20		**$C_{F\,Av}$** = 9.27		**$C_{P\,Av}$** = 4.96		**R_{Av}** = 46.5

Polymer Type = P2G, Loading = 0.01, Loading$_{TOC}$ = 0.009, pH = 8							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.19	F_{60} = 20.62	F_{90} = 19.63	F_{120} = 19.20	F_{150} = 19.98	F_{180} = 19.41	
CF (mg/L)	10.12	9.70	9.66	9.54	9.49	9.44	9.44
Cp (mg/L)		5.06	4.99	4.94	4.87	4.80	4.83
R (%)		47.8	48.3	48.2	48.7	49.2	48.8
	$F_{P\,Av}$ = 19.67		**$C_{F\,Av}$** = 9.55		**$C_{P\,Av}$** = 4.92		**R_{Av}** = 48.5

Table C.1. Continued

Polymer Type = P2G, Loading = 0.01, Loading$_{TOC}$ = 0.010, pH = 9							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 18.10	F_{60} = 19.35	F_{90} = 19.78	F_{120} = 19.69	F_{150} = 19.51	F_{180} = 19.73	
CF (mg/L)	10.12	9.79	9.65	9.40	9.31	9.28	9.24
Cp (mg/L)		4.90	4.73	4.61	4.56	4.49	4.47
R (%)		50.0	51.0	51.0	51.0	51.6	51.6

$F_{P\ Av}$ = 19.19 **$C_{F\ Av}$** = 9.45 **$C_{P\ Av}$** = 4.63 **R_{Av}** = 51.0

Polymer Type = P1, Loading = 0.01, Loading$_{TOC}$ = 0.009, pH = 7							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.27	F_{60} = 19.53	F_{90} = 20.09	F_{120} = 20.25	F_{150} = 20.12	F_{180} = 20.40	
CF (mg/L)	9.78	9.43	9.40	9.42	9.40	9.39	9.41
Cp (mg/L)		1.93	1.96	1.94	1.92	1.91	1.93
R (%)		79.3	79.2	79.4	79.6	79.7	79.5

$F_{P\ Av}$ = 19.94 **$C_{F\ Av}$** = 9.41 **$C_{P\ Av}$** = 1.94 **R_{Av}** = 79.4

Table C.1. Continued

Polymer Type = P1, Loading = 0.01, Loading$_{TOC}$ = 0.009, pH = 8							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.25	F_{60} = 20.56	F_{90} = 19.40	F_{120} = 19.88	F_{150} = 20.61	F_{180} = 20.11	
CF (mg/L)	9.78	9.51	9.49	9.48	9.48	9.50	9.50
Cp (mg/L)		1.21	1.28	1.33	1.37	1.36	1.36
R (%)		87.3	86.5	86.0	85.6	85.7	85.7

$F_{P\ Av}$ = 20.14 **$C_{F\ Av}$** = 9.49 **$C_{P\ Av}$** = 1.32 **R_{Av}** = 86.1

Polymer Type = P1, Loading = 0.01, Loading$_{TOC}$ = 0.009, pH = 9							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.60	F_{60} = 20.09	F_{90} = 20.82	F_{120} = 20.53	F_{150} = 20.37	F_{180} = 20.88	
CF (mg/L)	9.78	9.53	9.50	9.50	9.49	9.48	9.48
Cp (mg/L)		1.07	1.03	1.10	1.08	1.05	0.96
R (%)		88.8	89.2	88.4	88.6	88.9	89.9

$F_{P\ Av}$ = 20.38 **$C_{F\ Av}$** = 9.50 **$C_{P\ Av}$** = 1.05 **R_{Av}** = 89.0

Table C.1. Continued

Polymer Type = P1, Loading = 0.01, Loading$_{TOC}$ = 0.009, pH = 10							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.51	F_{60} = 19.18	F_{90} = 20.40	F_{120} = 20.17		F_{150} = 20.81	F_{180} = 20.48
CF (mg/L)	9.78	9.56	9.53	9.54	9.52	9.53	9.51
Cp (mg/L)		0.97	0.91	0.93	0.93	0.94	0.97
R (%)		89.9	90.5	90.3	90.2	90.1	89.8
	$F_{P\,Av}$ = 20.09		**$C_{F\,Av}$** = 9.53		**$C_{P\,Av}$** = 0.94		**R_{Av}** = 90.1

Polymer Type = P1, Loading = 0.05, Loading$_{TOC}$ = 0.051, pH = 7							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 18.91	F_{60} = 19.80	F_{90} = 19.47	F_{120} = 20.25		F_{150} = 20.03	F_{180} = 19.76
CF (mg/L)	10.05	9.39	9.33	9.26	9.22	9.18	9.19
Cp (mg/L)		5.98	5.93	5.89	5.84	5.83	5.81
R (%)		36.3	36.4	36.4	36.7	36.5	36.8
	$F_{P\,Av}$ = 19.70		**$C_{F\,Av}$** = 9.26		**$C_{P\,Av}$** = 5.88		**R_{Av}** = 36.5

Table C.1. Continued

Polymer Type = P1, Loading = 0.05, Loading$_{TOC}$ = 0.051, pH = 8

t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.33	F_{60} = 19.73	F_{90} = 19.56	F_{120} = 20.12	F_{150} = 20.15	F_{180} = 19.52	
CF (mg/L)	10.05	9.42	9.43	9.40	9.38	9.34	9.35
Cp (mg/L)		5.76	5.74	5.73	5.69	5.69	5.68
R (%)		38.9	39.1	39.0	39.3	39.1	39.3

$F_{P\,Av}$ = 19.74 **$C_{F\,Av}$** = 9.39 **$C_{P\,Av}$** = 5.72 **R_{Av}** = 39.1

Polymer Type = P1, Loading = 0.05, Loading$_{TOC}$ = 0.051, pH = 9

t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.12	F_{60} = 22.05	F_{90} = 22.32	F_{120} = 19.86	F_{150} = 18.50	F_{180} = 19.71	
CF (mg/L)	10.05	9.54	9.51	9.53	9.46	9.44	9.42
Cp (mg/L)		5.19	5.15	5.14	5.09	5.03	5.03
R (%)		45.6	45.9	46.1	46.2	46.7	46.6

$F_{P\,Av}$ = 20.09 **$C_{F\,Av}$** = 9.48 **$C_{P\,Av}$** = 5.11 **R_{Av}** = 46.2

Table C.1. Continued

Polymer Type = P1, Loading = 0.05, Loading$_{TOC}$ = 0.051, pH = 10							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.71	F_{60} = 19.58	F_{90} = 19.26	F_{120} = 19.08	F_{150} = 19.47	F_{180} = 20.09	
C_F (mg/L)	10.05	9.57	9.58	9.53	9.47	9.48	9.49
Cp (mg/L)		5.13	5.09	5.05	4.99	4.95	4.96
R (%)		46.4	46.9	47.0	47.3	47.8	47.7
	$F_{P\,Av}$ = 19.53		**$C_{F\,Av}$** = 9.52		**$C_{P\,Av}$** = 5.03		**R_{Av}** = 47.2

Polymer Type = P2, Loading = 0.05, Loading$_{TOC}$ = 0.054, pH = 7							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.47	F_{60} = 19.98	F_{90} = 20.25	F_{120} = 20.11	F_{150} = 20.19	F_{180} = 19.85	
C_F (mg/L)	10.09	9.04	8.95	8.96	8.94	8.91	8.92
Cp (mg/L)		6.94	6.86	6.82	6.78	6.72	6.72
R (%)		23.2	23.4	23.9	24.2	24.6	24.7
	$F_{P\,Av}$ = 19.98		**$C_{F\,Av}$** = 8.95		**$C_{P\,Av}$** = 6.81		**R_{Av}** = 24.0

Table C.1. Continued

Polymer Type = P2, Loading = 0.05, $Loading_{TOC}$ = 0.054, pH = 8							
t (min)	0	60	85	110	135	160	185
F_P (L/m^2h)	F_{45} = 19.79	F_{60} = 19.35	F_{90} = 20.13	F_{120} = 20.22	F_{150} = 20.36	F_{180} = 18.95	
C_F (mg/L)	10.09	9.42	9.22	9.15	9.06	9.05	8.99
Cp (mg/L)		6.93	6.71	6.64	6.59	6.55	6.47
R (%)		26.4	27.2	27.4	27.3	27.6	27.6
	$F_{P\,Av}$ = 19.80		**$C_{F\,Av}$** = 9.14		**$C_{P\,Av}$** = 6.65		**R_{Av}** = 27.3

Polymer Type = P2, Loading = 0.05, $Loading_{TOC}$ = 0.054, pH = 9							
t (min)	0	60	85	110	135	160	185
F_P (L/m^2h)	F_{45} = 19.70	F_{60} = 19.53	F_{90} = 20.28	F_{120} = 20.33	F_{150} = 20.46	F_{180} = 20.32	
C_F (mg/L)	10.09	9.48	9.34	9.16	9.14	9.11	9.11
Cp (mg/L)		6.64	6.37	6.31	6.26	6.22	6.19
R (%)		30.0	31.8	31.1	31.5	31.7	32.1
	$F_{P\,Av}$ = 20.10		**$C_{F\,Av}$** = 9.22		**$C_{P\,Av}$** = 6.33		**R_{Av}** = 31.4

Table C.1. Continued

Polymer Type = P2. Loading = 0.01, Loading$_{TOC}$ = 0.0097, pH = 7							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.36	F_{60} = 19.80	F_{90} = 20.11	F_{120} = 20.48	F_{150} = 20.06	F_{180} = 21.27	
C_F (mg/L)	10.02	9.63	9.51	9.48	9.43	9.41	9.38
Cp (mg/L)		5.01	4.89	4.85	4.84	4.78	4.78
R (%)		48.0	48.6	48.8	48.7	49.2	49.0
	$F_{P\ Av}$ = 20.18		**$C_{F\ Av}$** = 9.47		**$C_{P\ Av}$** = 4.86		**R_{Av}** = 48.7

Polymer Type = P2, Loading = 0.01, Loading$_{TOC}$ = 0.0097, pH = 8							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 19.44	F_{60} = 19.82	F_{90} = 20.10	F_{120} = 19.09	F_{150} = 18.67	F_{180} = 19.93	
C_F (mg/L)	10.02	9.69	9.58	9.54	9.48	9.46	9.44
Cp (mg/L)		4.89	4.80	4.73	4.66	4.62	4.60
R (%)		49.5	49.9	50.4	50.8	51.2	51.3
	$F_{P\ Av}$ = 19.51		**$C_{F\ Av}$** = 9.53		**$C_{P\ Av}$** = 4.72		**R_{Av}** = 50.5

Table C.1. Continued

Polymer Type = P2, Loading = 0.01, Loading$_{TOC}$ = 0.0097, pH = 9							
t (min)	0	60	85	110	135	160	185
F_P (L/m^{2}h)	F_{45} = 20.60	F_{60} = 20.27	F_{90} = 21.46	F_{120} = 20.86		F_{150} = 20.13	F_{180} = 20.55
C_F (mg/L)	10.02	9.72	9.64	9.56	9.51	9.50	9.49
Cp (mg/L)		4.55	4.44	4.41	4.34	4.32	4.31
R (%)		53.2	54.0	53.9	54.4	54.5	54.6
	$F_{P\ Av}$ = 20.65		**$C_{F\ Av}$** = 9.57		**$C_{P\ Av}$** = 4.40		**R_{Av}** = 54.1

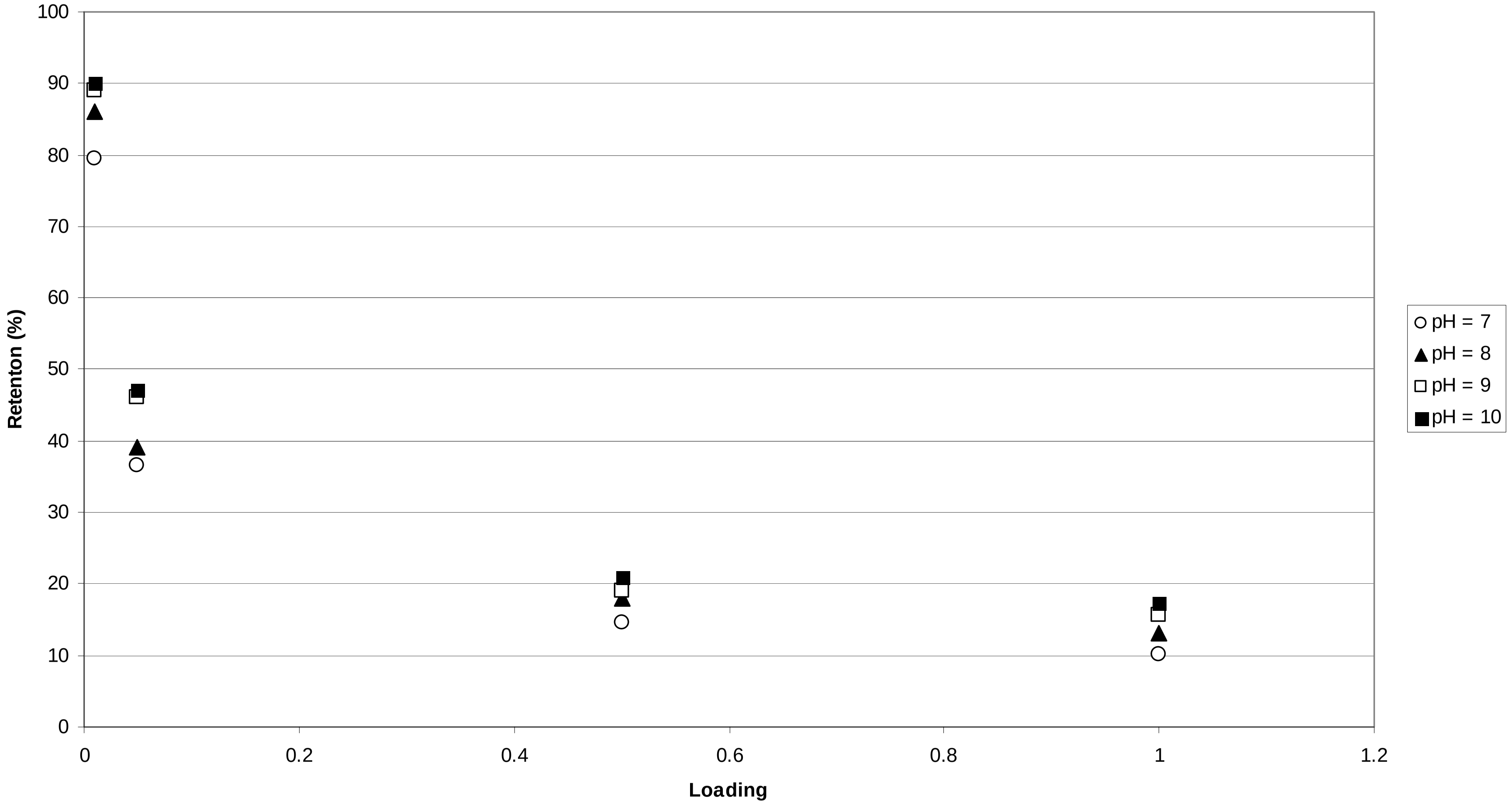

Figure C.1. Effect of Loading on Retention of Boron (with P1)

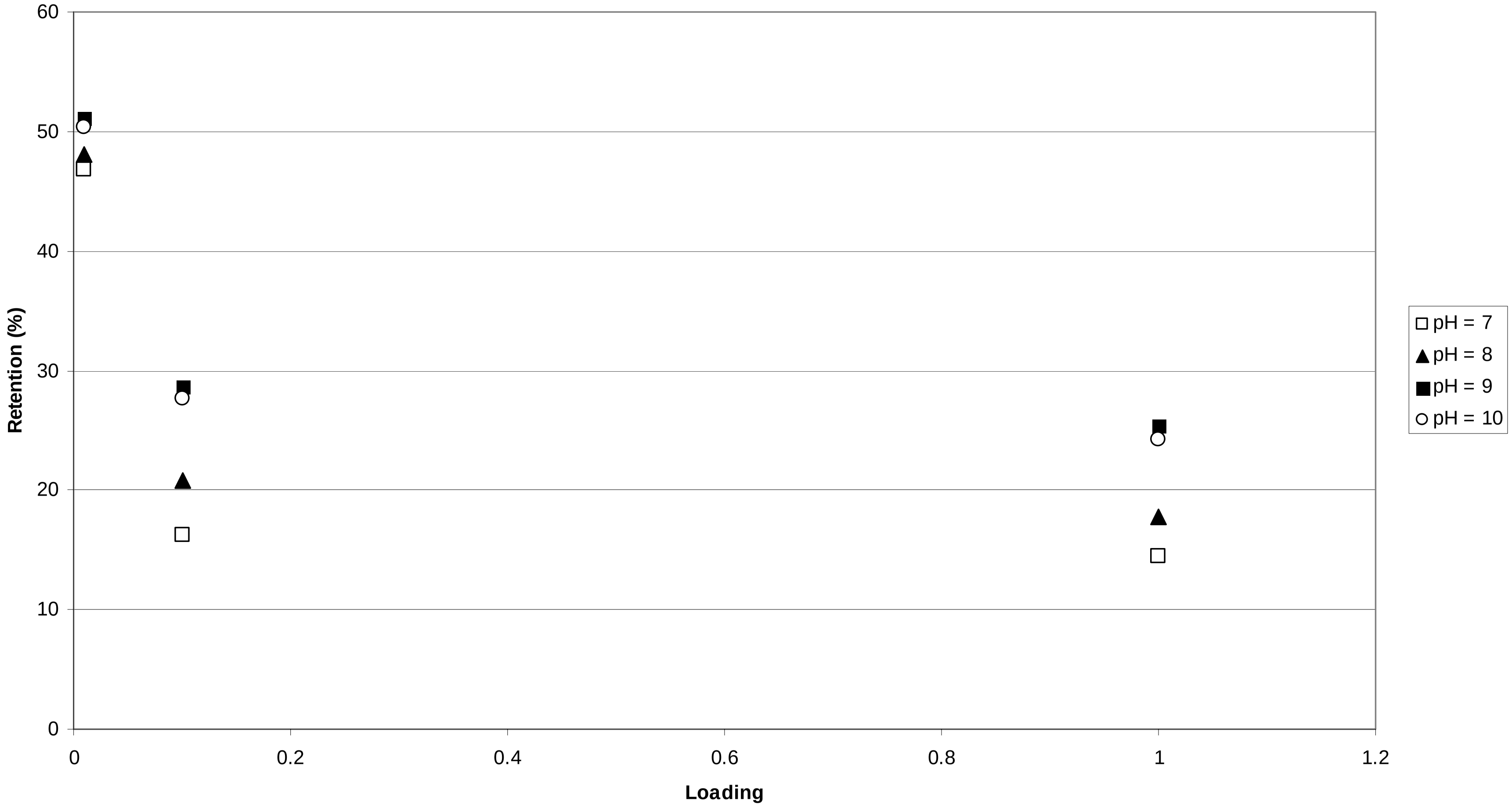

Figure C.2. Effect of Loading on Retention of Boron (with P2G)

Table C.2. Values of Permeate Concentration and Feed Concentration with Respect to Time (Plotted in figure 4.1.1)

Time (min.)	**Permeate Concentration (mg/L)**	**Feed Concentration (mg/L)**
0	-	10.12
60	5.06	9.70
85	4.99	9.66
110	4.94	9.54
135	4.87	9.49
160	4.88	9.44
185	4.83	9.44

Table C.3. Values of pH, Loadings of the Polymers and Permeate Flux (Plotted in Figure 4.2.1)

		Permeate Flux (L/m^2 . hr)			
		pH = 7	**pH = 8**	**pH = 9**	**pH = 10**
L – P1	**1**	20.35	20.77	20.61	20.09
	0.5	20.09	19.68	19.73	20.58
	0.05	19.70	19.74	20.09	19.53
	0.01	19.94	20.14	20.38	20.09
L – P2G	**1**	20.78	20.17	20.25	20.17
	0.1	20.25	20.32	20.17	20.32
	0.01	20.13	19.84	20.25	20.11
L – P2	**0.05**	19.98	19.80	20.10	-
	0.01	20.18	19.51	20.65	-

Table C.4. Values of pH, Loading and Retention of Boron (Plotted in Figure 4.3.1)

Loading	pH = 7	pH = 8	pH = 9	pH = 10
1	10.05	13.21	15.60	17.36
0.5	14.57	18.03	18.97	20.98
0.05	36.51	39.12	46.17	47.18
0.01	79.43	86.11	88.96	90.12

Table C.5. Values of pH, Loading and Retention of Boron (Plotted in Figure 4.3.2)

Loading	pH = 7	pH = 8	pH = 9	pH = 10
1	14.41	17.81	25.37	24.26
0.1	16.18	20.78	28.62	27.70
0.01	46.8	48.12	51.14	50.37

Table C.6. Values of pH, Loading and Retention of Boron (Plotted in Figure 4.4.1)

	Retention (%)			
pH	**L = 1**	**L = 0.5**	**L = 0.05**	**L = 0.01**
7	10.05	14.57	36.51	79.43
8	13.21	18.03	39.12	86.11
9	15.60	18.97	46.17	88.96
10	17.36	20.98	47.18	90.12

Table C.7. Values of pH, Loading and Retention of Boron (Plotted in Figure 4.4.2)

	Retention (%)		
pH	**L = 1**	**L = 0.1**	**L = 0.01**
7	14.41	16.18	46.80
8	17.81	20.78	48.12
9	25.37	28.62	51.14
10	24.26	27.70	50.37

Table C.8. Retention Values According to Polymer Type (Plotted in Figure 4.5.1)

	Retention (%)		
	P1	**P2**	**P2G**
pH = 7	79.43	48.72	46.80
pH = 8	86.11	52.52	48.12
pH = 9	88.96	54.08	51.14

Loading comparison given in Table C.9 is in the order given in Table C.1.

Table C.9. Comparison of the Aimed and Actual Loadings

L_{aimed}	L_{TOC}	L_{aimed}	L_{TOC}	L_{aimed}	L_{TOC}
0.1	0.12	0.1	0.095	0.5	0.53
1	0.98	1	0.96	0.5	0.53
1	0.98	1	0.96	1	1.0
1	0.98	0.01	0.010	0.1	0.10
0.1	0.095	0.01	0.010	0.01	0.010
0.1	0.095	0.01	0.010	0.01	0.009
1	0.96	0.5	0.53	0.01	0.010

Table C.9. Continued

L_{aimed}	L_{TOC}	L_{aimed}	L_{TOC}	L_{aimed}	L_{TOC}
0.01	0.010	0.05	0.051	0.05	0.054
0.01	0.009	0.05	0.051	0.05	0.054
0.01	0.009	0.05	0.051	0.01	0.0097
0.01	0.009	0.05	0.051	0.01	0.0097
0.01	0.009	0.05	0.054	0.01	0.0097

APPENDIX D

TOC CALCULATIONS

For finding the actual loading of the prepared solutions, samples were taken before the experiment starts and at the end of the experiment. As sample calculation, results shown in Table 4.1 will be used. Before introducing the samples to the device, samples were diluted in a ratio of 1/100. Since the results gives us only the carbon amount, these values must divided to the carbon ratio of the polymer. For P2G this ratio is 0.51. Lastly, the initial boron concentration, which is 10.12 mg/L for this experiment, is divided by the average polymer concentration. The results are shown in Table D.1.

Table D.1. Sample Calculation for TOC

	$C_{Carbon,Dilute}$ (mg/L)	**C_{Carbon} (mg/L)**	**$C_{Polymer}$ (mg/L)**	**$C_{Polymer, Average}$ (mg/L)**	**L_{TOC}**
Initial	5.554 ± 0.054	555.4	1089	1077	0,0094
Final	5.432 ± 0.106	543.2	1065		

APPENDIX E

RELATIVE STANDARD DEVIATIONS OF THE RESULTS

With the aim of understanding the consistency of the results of the ultrafiltration experiments, the relative standard deviations (% RSD) of the retentions and the permeate fluxes were calculated. After calculating the average values and standard deviations of the data, the relative standard deviations were found out. In Table 4.1, the retention and permeate flux values of one run are given and in Table E.1 the results of the % RSD calculations are shown.

Table E.1. The Averages, Standard Deviations and Relative Standard Deviations of the Retentions and Permeate Fluxes of One Run (Given in Table 4.1)

C_F (mg/L)	**C_P (mg/L)**	**Permeate Flux (F_P)**	**Retention (R)**
$C_{F,\ Av} = 9.55$ SD = ± 0.112 % RSD = 1.17	$C_{P,\ Av} = 4.92$ SD = ± 0.100 % RSD = 2.03	$F_{P,\ Av} = 19.67$ SD = ± 0.551 % RSD = 2.80	$R_{AV} = 0.485$ SD = ± 0.005 % RSD = 1.03

Some of the experiments were repeated to check the reproducibility of the UF experiments. In Table 4.2, the results of these experiments are given. In order to understand the significance of the differences between the results of the first and the second runs, % RSD values of the retentions and permeate fluxes are determined. The average values, standard deviations and the relative standard deviations of the retentions and the permeate fluxes of the first and second runs are given in Table E.2.

Table E.2. The averages, Standard Deviations and Relative Standard Deviations of the Retentions and Permeate Fluxes of the Experiments Performed for the Reproducibility Study (Given in Table 4.2)

Polymer	**Loading**	**pH**	**Permeate Fluxes (F_P) L/m^{2}hr**	**Retention**
P2G	0.01	9	$F_{P,\ 1st\ Run}$ = 20.25 $F_{P,\ 2nd\ Run}$ = 19.19 $F_{P,\ Av}$ = 19.72 SD = ± 0.750 % RSD = 3.80	$R_{1st\ Run}$ = 0.514 $R_{2nd\ Run}$ = 0.510 R_{Av} = 0.512 SD = ± 0.0028 % RSD = 0.55
P2G	0.01	8	$F_{P,\ 1st\ Run}$ = 19.84 $F_{P,\ 2nd\ Run}$ = 19.67 $F_{P,\ Av}$ = 19.76 SD = ± 0.120 % RSD = 0.61	$R_{1st\ Run}$ = 0.481 $R_{2nd\ Run}$ = 0.485 R_{Av} = 0.483 SD = ± 0.0028 % RSD = 0.56

Table E.2. continued

P2G	0.01	7	$F_{P,\ 1st\ Run}$ = 20.13 $F_{P,\ 2nd\ Run}$ = 20.20 $F_{P.\ Av}$ = 20.17 SD = ± 0.050 % RSD = 0.25	$R_{1st\ Run}$ = 0.468 $R_{2nd\ Run}$ = 0.465 R_{Av} = 0.467 SD = ± 0.0021 % RSD = 0.46

In order to see if the ICP-AES device produce reproducible results, some average values, standard deviations and relative standard deviations of the values listed in Table B.2 were calculated.

Table E.3. The averages, Standard Deviations and Relative Standard Deviations of the Intensities for the Reproducibility Study of the Analysis (Given in Table B.2)

	Average Intensity	**SD**	**% RSD**
F0	1193299	± 5907	0.5
F60	1082503	± 4354	0.4
F85	1108829	± 6668	0.6
F110	1106780	± 3969	0.4
F135	1092254	± 1067	0.1
F160	1060895	± 3888	0.4
F185	1059313	± 5009	0.5

Reproducibility calculations of the TOC device was not made since the device reads the samples until a value under an 2 % RSD value of is obtained.