ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF TRIS(HYDROXYMETHYL)AMINOMETHANE MODIFIED POLYSTYRENE BASED POLYMERIC SORBENT AND REMOVAL OF BORON FROM AQUEOUS SOLUTIONS

M.Sc. THESIS

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Department of Polymer Science and Technology

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

TRİS(HİDROKSİMETİL)AMİNOMETAN İLE MODİFİYE EDİLMİŞ POLİSTİREN ESASLI POLİMERİK SORBENTİN HAZIRLANMASI VE SULU ORTAMDAKİ BORUN GİDERİLMESİNDE KULLANILMASI

YÜKSEK LİSANS TEZİ

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ARALIK 2017

Arzu Ersoy, a M.Sc. student of İTU Graduate School of Science Engineering and Technology student ID 515151004, successfully defended the thesis entitled "SYNTHESIS OF TRIS(HYDROXYMETHYL)AMINOMETHANE MODIFIED POLYSTYRENE BASED POLYMERIC SORBENT AND REMOVAL OF BORON FROM AQUEOUS SOLUTIONS", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family

FOREWORD

There are many people who encourged me to educate on polymer chemistry and science. I am appreciated to all peopele who have guided me, gave opportunities to me and made this work possible.

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Arzu ERSOY
Chemist

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ABBREVIATIONS

FTIR **:** Fourier-Transform Infrared Spectroscopy
MENA **:** Middle East and North America
WHO **:** The World Health Organization
NOAEL **:** No Observed Adverse Effect Level
RO **:** Reverse Osmosis
PEUF **:** Polymer Enhanced Ultrafiltration
AMF **:** Adsorption Membrane Filtration
NMDG **:** N-methyl D-glucamine
PS-DVB **:** poly(styrene-divinylbenzene)
SGDHB **:** 2,3-dihydroxylbenzaldhyde modified silica gel
PVA **:** Poly(vinyl alcohol)
PAA **:** Poly(allylamine)
PAA-Glu **:** Poly(allylamine)-Glucose
EGDMA **:** Ethyleneglycole dimethacrylate
AIBN **:** 2,2′-Azobis(2-methylpropionitrite)
NMP **:** 2-methyl -1-pyrrolidone
PVBC **:** Poly(vinyl benzyl chloride)
PVBC-tris OH: PVBC with tris(hydroxymethyl)aminomethane

SYMBOLS

pKa	**:** Acid dissociation constant
q_e	**:** The amount of adsorbed adsorbate at equilibrium
q_t	**:** The amount of adsorbed adsorbate at certain time
k_1, k_2	**:** The rate constants
t	**:** Time
K_i	**:** The diffusion rate constant
q_{exp}	**:** The capacity as experimentally
$q_{theoretical}$	**:** The capacity as theoretically
R^2	**:** Coefficient factor
q_m	**:** The maximum capacity
K_L	**:** The Langmuir isotherm constant
K_f, n	**:** The Freundlich isotherm constant
R	**:** Universal gas constant
A, b	**:** The Tempkin isotherm constants
T	**:** Temperature

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SYNTHESIS OF TRIS(HYDROXYMETHYL)AMINOMETHANE MODIFIED POLYSTYRENE BASED POLYMERIC SORBENT AND REMOVAL OF BORON FROM AQUEOUS SOLUTIONS

SUMMARY

Boron is placed in-group 13 of periodic table and found at low concentration in a wide area range such as rock, soil and water in nature.

Boron is used in many industrial applications, especially in insulation, retardant fiberglass and ceramic industry. In addition, boron is an essential element for living organism systems. Excess amount of it causes water and other environmental pollution. As high concentration causes adverse effects, boron level is limited in irrigation or drinking water. The World Health Organization (WHO) currently recommends the concentration of boron in drinking water to be 2.4 mg/L. Consequently, boron removal from wastewater is an important topic.

Various removal methods are available for boron separation. Some of them are; precipitation-coagulation, solvent extraction, membrane filtration, reverse osmosis, electro dialysis and adsorption. Adsorption is completely different from others because it is a very useful method and needs low price equipment for removal of boron from wastewater.

In the first part of this study, tris(hydroxymethyl)aminomethane was interacted with poly(vinyl benzyl chloride) resin to obtain boron selective sorbent. The resin was characterized with FT-IR spectroscopy to determine the functional groups important for boron sensitivity. Total amine content of the resin was calculated analytically as 2.45 $mmol.g^{-1}$ sorbent.

In the second part of the study, experimental measurements were performed on modified resin about boron adsorption. Adsorption capacity of the sorbent was investigated for different boron concentrations. Boron loading capacity of the sorbent is 2.17 $mmol.g^{-1}$ resin, in non-buffered conditions. Sorption behavior was also observed in the presence of different concentration foreign ions such as Ca^{+2} and Mg^{+2}. Besides that, boron adsorption was further studied at varying pH in the range of 2.0-10.0.

Kinetics of boron sorption was performed at low concentration to investigate the efficiency of the modified resin at this condition. For this purpose, pseudo-first order, pseudo-second order and intraparticular diffusion kinetics models were used. Regeneration of the loaded resin was also studied. 2.10 $mmol.g^{-1}$ boric acid was recovered of the loaded sample, which showed that the resin was able to desorp nearly completely.

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ÖZET

Bor, periyodik tablonun grup 13 kısmında yer alan, yüksek erime noktalı, elektrik iletkenliği düşük olan bir elementtir. B_{10} (%19,8) ve B_{11} (%80,2) olarak iki kararlı izotopu vardır. Ayrıca az değerlilik elektronlarına sahip olduğundan, metalik bağdan daha çok kovalent bağ yapmayı tercih eder.

Borun yerkürede bulunma oranı %0.01 ve 100 ppm gibi düşük bir konsantrasyon olduğundan nadir elementlerden biri sayılır. Tabiatta yaklaşık 230 çeşit bor minerali vardır. Oksijenle bağ yapmaya yatkın olması sebebiyle pek çok değişik bor-oksijen bileşimi bulunmaktadır. Bor-oksijen bileşimlerinin genel adı borattır. Bu nedenle bor, saf element formunda değil; ya boraks, kolemanit, kernit, üleksit gibi mineraller halinde, ya da borasit, borik asit gibi bileşikleri halinde bulunur. Borun buna benzer metal veya ametal elementlerle yaptığı bileşiklerin gösterdiği değişik özellikler, endüstride pek çok çeşit bor bileşiğinin kullanılmasına imkan sağlamaktadır. Su kaynaklarındaki baskın formu ise, (denizler, göller, vs.) borik asittir. Borik asit pKa değeri 9.1 olan zayıf bir asit olup, 25°C'de çözünürlüğü 55 $g.L^{-1}$'dir ve içme suyunda 0.1 ppm veya daha düşük konsantrasyonda bulunur. Bor tüm dünya için önemli olan ve geleceğin petrolü olarak nitelendirilebilecek bir madendir. Ülkemizin de en önemli yer altı zenginliklerinden biri belki de en önemlisi ve tek stratejik önemi olan doğal kaynaklardan birisidir. Bu nedenle maden ihraç ürünleri arasında birinci sırada yer almaktadır. Bor ve bileşiklerinin endüstride çok çeşitli kullanım alanları bulunmaktadır. İnşaat ve çimento sektöründe mukavemet arttırıcı ve izolasyon amaçlı olarak, ağartıcı ve bakterilere karşı koruyucu özelliği nedeniyle deterjan sektöründe, yumuşaklık, yapışkanlık ve dayanıklılık kazandırma özellikleri nedeniyle kozmetik sektöründe, verimi arttırması bakımından tarım sektöründe, seramiğin pişme sıcaklığını düşürmesi bakımından seramik sektörü gibi çok çeşitli endüstriyel alanlarda bor mineralinden faydalanılmaktadır.. Ayrıca bor, malzemelere küçük miktarlarda bile eklenmesi halinde iletkenlik özelliğini geliştirdiğinden yarı iletken endüstrisinde de (transistor ve diyot üretimi, vb.) kullanılmaktadır. Bor insanlar, hayvanlar ve bitkiler için de önemli bir elementtir. Az miktarlarda alındığı zaman canlı hücrelerinde işlevsel bir özelliğe sahiptir. Örneğin bitkilerin büyümesi, hücre oluşumu ve enzimatik reaksiyonlarında önemli işlevlere sahiptir. Ancak, canlıların boru yüksek konsantrasyonlarda alması halinde bıraktığı etkilerin çoğu tam olarak aydınlatılmamış olmakla birlikte, oluşturduğu tehlikeli sonuçların bazıları bilinmektedir. Örneğin gerektiğinden fazla alındığında bitkilerde yaprak kenarlarının sararmasına, fotosentez hızında düşmeye, kökteki hücrelerin bölünmesinde azalmaya, kök dokularında büyüme geriliğine; insanlarda ve hayvanlarda ise zehirlenmeye, deri döküntülerine, böbrek, karaciğer ve merkezi sinir sisteminde hasara, hücresel gelişmede yavaşlamaya ve üreme sistemi üzerinde olumsuz yan etkilere sebep olduğu söylenebilir.

Sonuç olarak bor, aşırı dozda maruz kalındığında olumsuz hatta ölümcül etkilerine rağmen, canlıların yaşamsal faaliyetleri için minimum bir miktarda da mutlaka alınması gereken bir element olarak karşımıza çıkmaktadır.

Endüstride kullanılan bor sebebiyle endüstriyel atıksulardaki bor konsantrasyonu yukarıda sözü edilen aşırı doz seviyesine ulaşmaktadır. Bu durumdan sularda yaşayan canlılar, sulamada kullanıldığında bitkiler ve içme suyu olarak kullanımında insanlar olumsuz etkileneceğinden, atıksulardan boru neredeyse tamamen uzaklaştırmak veya konsantrasyonunu azaltmak gerekmektedir. Sulardan ve atık sulardan bor giderimi için yapılan çalışmaların amacı borun giderilmesi ya da geri kazanılmasıdır. Diğer bir amaç ise çevre kirliliğinin önlenmesi ve bor kirliliği giderilen suların sulamada tarımsal amaçla kullanılmasının sağlanabilmesidir.

Sulardan ya da atık sularından borun uzaklaştırılması zor ve karmaşık olsa da, uzun bir süreçte yapılan araştırmalar sonucunda bazı yöntemler ön plana çıkmıştır. Bu yöntemleri kimyasal çöktürme, iyon değiştirici reçineler veya/ve ters ozmos membranlarla ayırma, sıvı-sıvı ekstraksiyon, elektrodiyaliz ve adsorpsiyon olarak sıralayabiliriz. Adsorpsiyon yönteminin diğerlerine kıyasla daha basit ve ucuz bir yöntem olduğu söylenebilir. Cis- pozisyonunda hidroksil gruplar olan fonksiyonel grupları içeren şelatlayıcı reçineler, borat-diol kompleksleri oluşturarak borun uzaklaştırılmasında yüksek seçimlilik gösterirler.

Adsorpsiyon, gaz veya sıvı parçacıkların katı veya sıvı bir yüzeye tutunması olayıdır. Burada yüzeye tutunan atomik veya moleküler haldeki maddeye adsorbat adı verilirken, tutunulan yüzey ise adsorban olarak adlandırılır. Adsorbat ve adsorban molekülleri arasında elektrostatik etkileşim, Van der Waals etkileşimi yada kimyasal etkileşim yoluyla gerçekleşmektedir. Gözeneklilik, yüzey alanı, adsorbentin ve adsorbatın kimyasal yapısı, basınç, sıcaklık, ortamın pH değeri gibi etkenler, adsorpsiyonu etkileyen faktörlerdir. Polimerik adsorban kullanılması sentez ve adsorpsiyon aşamasında avantaj sağlar. Örneğin sentez aşamasının görece pratikliği, kolaylıkla tekrar kullanılabilmesi, şekillerinin uygun formlarda olması, gözenekli veya gözeneksiz olabilmesi bunlardan bazılarıdır.Bu çalışmada borun sudan giderilmesi için adsorpsiyon yöntemi kullanılmıştır. İlk olarak bor-seçici özellikte polimerik adsorban hazırlanmış; bunun için etilenglikoldimetakrilat ile çapraz bağlı poli(vinil benzil klorür) polimeri, tris(hidroksimetil)aminometan ile modifiye edilmiştir. Adsorbanın yapısı Fourier dönüşümlü Infrared Spektrometri (FTIR) ile incelenmiş, fonksiyonel gruplardaki amin miktarı analitik yöntemle tayin edilmiştir. Yapılan analitik ölçümlerle reçinenin içerdiği amin miktarı 2.45 $mmol.g^{-1}$ reçine olarak bulunmuştur.Reçinenin bor adsorpsiyonu çalışmalarına, optimum adsorban miktarı belirlenerek başlanmıştır. Bunun için 0.02 – 0.12 g arasında değişen miktarlardaki reçineler, 0.485 M borik asit ile oda sıcaklığında, sürekli karıştırılarak 24 saat süre ile etkileştirilmiştir. Adsorpsiyon kapasitesinin optimum olduğu miktar 0.1 gram olarak bulunmuştur. Ardından, bu optimum miktarda alınan reçineler ile 0.128 M - 0.500 M konsantrasyonları arasında değişen borik asit çözeltileri etkileştirilip boru tutma kapasiteleri hesaplanmıştır. Konsantrasyon artışı ile birlikte reçinenin kapasitesi artarken, kapasitenin belirli bir değerden sonra sabit kalıp dengeye ulaştığı gözlenmiştir. Tampon çözelti kullanılmadan yapılan ölçümlerde reçinenin bor tutma kapasitesi 2.17 $mmol.g^{-1}$ olarak tespit edilmiştir.. Ayrıca elde edilen veriler doğrultusunda Langmuir, Freundlich ve Tempkin izoterm modelleri uygulanmış; reçinenin bor adsorpsiyon davranışının Freundlich ve Tempkin izoterm modellerine uygun olduğu belirlenmiştir.

Daha sonra, ortamda Mg^{+2}, Ca^{+2} iyonlarının bulunmasının reçinenin bor adsorpsiyonuna etkisinin incelenmesi için, borik asite göre 0.485 M, Mg^{+2} ve Ca^{+2} 'a göre 0.14 M olan çözeltiler ile 0.1 gram reçine etkileştirilmiştir. Sonuç olarak bu iyonların varlığının reçinenin bor adsorpsiyon kapasitesi üzerine etkisinin tolerans edilebilecek düzeyde olduğu bulunmuştur.

Buna ek olarak, reçinenin bor adsorpsiyonuna pH etkisinin araştırılması için, 0.1'er gram reçine, değişen pH (pH 2, 4, 6, 8) değerindeki ortamlarda 0.485 M borik asit çözeltileri ile oda sıcaklığında 24 saat süreyle etkileştirilmiştir. Farklı pH'larda ki denemeler ise bor adsorpsiyonunun yüksek pH değerlerinde daha kararlı olduğunu göstermiştir.

Reçinenin bor adsorpsiyon hızını inceleyebilmek için reçine kapasitesindeki değişim zamana bağlı olarak eser miktarda bor varlığında incelenmiştir. Yalancı birinci dereceden, yalancı ikinci dereceden ve parçacık içi difüzyon kinetik modelleri uygulanıp, reçinenin kinetik davranışı tartışılmıştır. Sonuç olarak bor adsorpsiyonunda parçacık içi difüzyon basamağının mekanizmada yer aldığı gözlenmiştir.

Reçinenin rejenerasyonu özellikle endüstriyel kullanımda önemli olduğundan, bor yüklü reçinenin desorpsiyon özelliği de incelenmiş, reçineden 2.10 $mmol.g^{-1}$ borik asidin desorbe olduğu görülmüştür. Bu da reçinenin adsorpladığı borun neredeyse tamamının desorbe olduğu anlamına gelmektedir. Ayrıca, desorbe edilen reçinenin bor ile bir kez daha etkileştirilerek tekrar kullanılabilirliği test edilmiş, reçinenin tam rejenarasyonunun sağlanıp tekrar kullanılabilir olduğu tespit edilmiştir.

1. INTRODUCTION

Boron is found in widely areas in more than 200 boron mineral compounds. Generally the amount of boron minerals are changing according to percentage of other minerals such as calcium, sodium etc. Also water content in boron mineral affect boron compound type and quantity. The most common boron compounds are tincal, colemanite, ulexite and kernite. Largest boron reservoir of all world have found in Turkey. There are about 90 billion tons boron in Turkey. This amount is occurred about 72% of all boron reserves. Emet, Bigadiç, Kırka and Mustafa Kemal Paşa is four most known borate mineral reservoir [1].

Boron is used many industrial application. Especially, boron is very important for ceramic industry. Because boron is enhancing mechanical strength of tiles. Except for this, boron used in glass, fiberglass, detergents, flame retardant, agriculture, cosmetic, construction (especially cement production) industries. During industrial processing, many of boron compounds are introduced into environment in form of waste. Metal pollution is a serious problem compared to benefits of boron. Because boron compound has high solubility in water when it is mixed with water. Moreover, metals are non-biodegradable. They lead to serious disorders when living organism expose to boron compounds [2].

Boron salts and boric acids are the form of boron which is caused environmental pollution because of industrial wastewaters. Industrial wastewaters from surfactants, detergents and different chemicals include boron. These waters are used in agriculture industry [2]. The range of 20-30 $mg.L^{-1}$ of boron is found in geothermal wastewater. Boron toxicity in living organism such as human, plants and animals result from this higher concentration of boron [3].

Adsorption is a popular boron removal method. Boron selective resins are used in adsorption methods. For obtaining boron sensitive resin, main resins type can be modified with N-methylglucamine functions. If polymer resin has the vicinal polyalcohol groups, these groups lead to more effective for boron removal. Because,

boric acid is adsorbed by polyolsgroups which are included in 1,2 or 1,3 position hydroxyl gropus. These groups capture boron ions on hydroxyl groups and make a stable boron-chelating complex [4]. For example, Amberlite IRA-743 with N-methylglucamine modified resin is suitable commercial resin for boron adsorption since 1960s [5]. In addition, chelating type resins have high sensitivity against boron. As a result, the resin is necessary to have at least one vicinal cis-diol pair and a tertiary amine group, which is critical for boron chealating to capture proton [6].

In today, polymer supported resins are used for boron removal and has limited efficiency because of their strong hydrophobic properties. Especially copolymers of styrene and divinylbenzene based polymers are used for boron removal process [7]. Amberlite IRA-743, crosslinked glycidyl methacrylate-based polymers [8], sorbitol-modified poly (N-glycidyl styrene sulfonamide) [9], poly (N-glucidol-N-methyl-2-hydroxypropyl Methacrylate) hydrogel [10] are examples of polymer based resins for using boron removal.

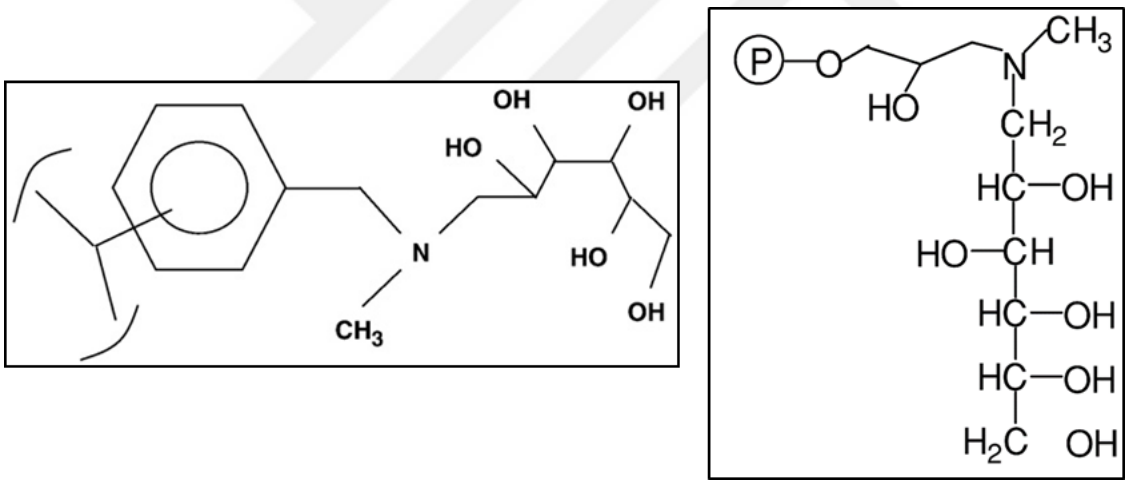

Figure 1.1 : Chemical structure of Amberlite IRA-743 and crosslinked glycidyl methacrylate-based polymers.[5,8]

In this study, polystyrene-based polymer is functionalized with N-methylglucamine and it is used for boron removal. This crosslinked polymer is obtained from reaction between poly(vinyl benzyl chloride) and tris(hydroxymethyl)aminomethane with suspension polymerization. Afterwards, the ability of boron adsorption, kinetics, capacity equilibrium and regenerations are investigated on it. In experimental part, the details are involved about all reaction mechanisms and boron adsorption experiments.

Finally, the results, which belongs to adsorption performance, are discussed. The optimum capacity is determined 2.17 mmol/g resin. It can be seen from the results that he synthesized resin can be easily used in industrial application because of high capacity, high regeneration property and simple polymerization process.

2. THEORY

2.1 Boron Chemistry

Boron is situated in-group 13 of the periodic table. Thus, the boron atom's electron configuration is $1s^2$, $2s^2$, $2p^1$ with an oxidation state of +3. Boron atom is elementally unstable in nature and also shows a tendency to form anionic complexes instead of cationic complexes. The BO_2^-, $H_2BO_3^-$,$(BO(OH)_2)^-$, and $B(OH)_4^-$ are examples of anion formation which may be classified depending on pH values, boron concentration, and temperature [11].

Boric acid is a weak acid with a dissociation constant (pKa) of 9.2. The pKa value is determined by distribution of two components, which are boric acid and borate ion. In seawaters, the concentration of affect boron species dissolved in them. Mononuclear boron species, that are mainly $B(OH)_3$ and $B(OH)_4^-$, are found in dissolved form at low concentration ($\leq$ 216 $mg.L^{-1}$). On the other hand, polynuclear boron species such as $B_2O(OH)_6^{2-}$,$B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4^-$ are formed at higher concentrations, which is also affected by increasing pH values [12].

Boron is found in non-dissociated form when pH is under 7 value. However, boron dissociates into borate form at above 10.5 pH values. The accurate amount of boric acid and borate in aqueous system change according to pH value of medium. As a matter fact that $B(OH)_4$ is formed at high pH as shown in Eq. 2.1, in contrast, boric acid is non-ionized at low pH [13].

$$B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+ \quad pKa = 9.2 \text{ at } 25°C \qquad (2.1)$$

The formation of water soluble polyborate ions such as $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^-$, $B_5O_6(OH)_4^-$ is obtained at high concentration(>0,0025 mol/L) in the range of pH 6 and pH 11 values[14].

Moreover, boron dissociation is approaching 100% when pH value is 10.5. Most of boron molecules show tendency to form borate ions. Effect of pH on boric acid and borate distribution in seawater is illustrated in Figure 2.1[15, 16].

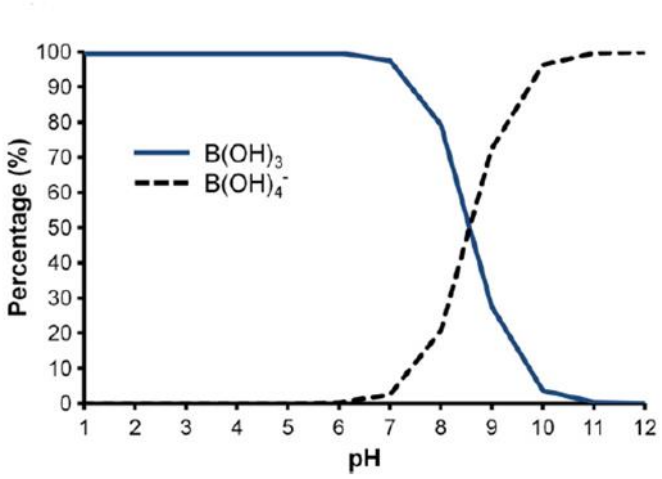

Figure 2.1 : Effect of pH on boric acid and borate distribution in seawater. [15]

2.2 Boron: Source and Distribution

Boron is widely placed in nature. Primary boron sources shown in table 2.1 [17]. The inorganic forms of boron, which water, soil and atmosphere include, commence from natural and anthropogenic sources. Boron is in silicate minerals form in Earth and atmosphere and its concentration is approximately 10 $mg.kg^{-1}$. Igneous, metamorphic and sedimentary rocks can consist of boron silicate. Krauskopf (1972) made this classification (Table 2.1). Especially, sedimentary rocks are the main source of boron. These rocks weathering is the main source of boron. During rock weathering, boron goes easily into solution, forming several anions, including BO^{2-}, $B_4O_7^{2-}$, BO_3^{3-}, $H_2BO_3^-$, and $H_4BO_4^-$ .The boron concentration in soil interstitial solutions is relatively high, ranging from 0.067 to 3 mg L^{-1}.

Boron compounds are released into oceans (65–85%), volcanoes and geothermal steams [18]. Boron reserves are located in particular parts of America, Australia, Chania, Russia and Argentina. Turkey boron reserves constitutes around 72% of all global boron sources. Known boron deposits in Turkey are primarily found in Kırka (Eskişehir), Bigadiç (Balıkesir), Kestelek (Bursa) and Emet (Kütahya). The most common boron ores reserve in Turkey are tincal ($Na_2B_4O_7.10H_2O$) and colemanite ($Ca_2B_6O_{11}.5H_2O$). Major important tincal deposits of Turkey are found in Kırka and major colemanite deposits are around Emet and Bigadiç (Figure 2.2).

Table 2.1 : Boron major reservoirs. [17]

Rock Class	Rock Type	Boron (mg/kg)	Mineral Class	Mineral Type	
Igneous	Granite	15	Hydrous borates	Borax	$Na_2B_4O_7 \cdot 10H_2O$
	Basalt	5		Kernite	$Na_2B_4O_7 \cdot 4H_2O$
				Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$
Sedimentary	Limestone	20		Ulexite	$NaCaB_5O_9 \cdot 8H_2O$
	Sandstone	35			
	Shale	100	Anhydrous borate	Ludwigite	Mg_2FeBO_5
	Soils	7-80		Kotoite	$Mg_3(BO_3)_2$
			Complex borosilicates	Tourmaline	$Na(Mg, Mn, Li, Al)_3 Al_6Si_6O_{18}(BO_3)_3(OH)_4$
				Axinite	$(Ca, Mn, Fe)_3Al_2BO_3Si_4O_{12}(OH)$

In atmosphere, the amount of boron is approximately 20 $ng.m^{-3}$. The source of boron in atmosphere is vaporization of boric acid from sea, volcanic activity, ceramic manufacturing and agricultural activity. In addition, the anthropogenic release of boron to the atmosphere is considered to occur mainly in the vapour form of boric acid. Some boron halogens, such as BF_3, BCl_3, and BBr_3, may be produced during biomass burning, fossil fuel combustion, incineration and manufacturing boron concentration is changing from 10 to 300 $mg.kg^{-1}$ in soil; while in water surface is changing from 0.01 to 2 $mg.L^{-1}$ [19].

In seawater, boron is found that weakly dissociated boric acid is the predominant species, but that weakly associated ion pair neutral and positively charged borate complexes of sodium, magnesium and calcium also exist. The metaborate ion

undergoes rapid hydrolysis in seawater to form borate ions and weakly dissociated boric acid.

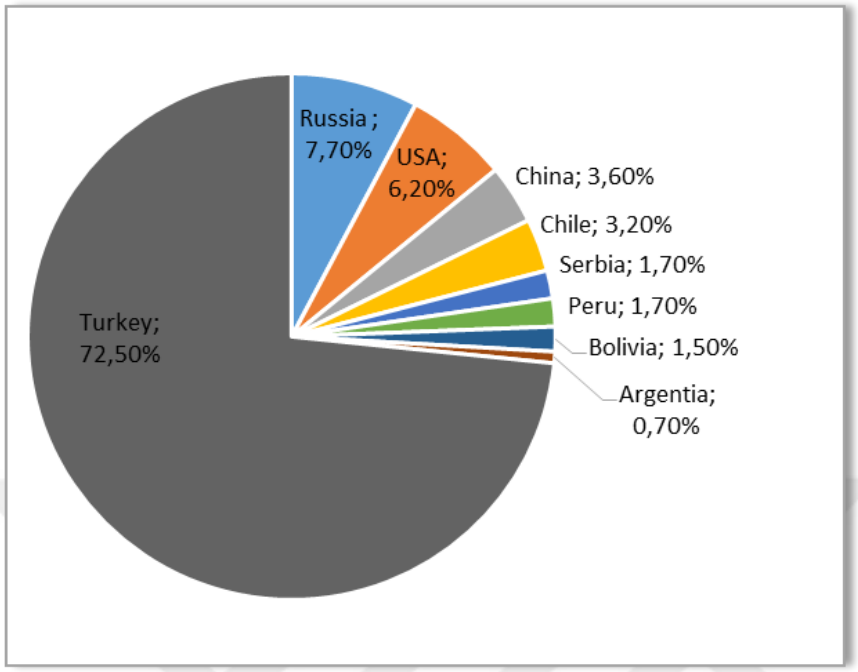

Figure 2.2 : Distribution of boron reserves around the globe (2012).(Eti Maden's Report for Boron Industry)

2.3 Boron Toxicity Effect

Boron is a crucial element that must be taken in a minimum amount for vital activities in living organism systems. However, although boron is important in many respects for plants and animals, there are adverse and even fatal effects of exposure to the high concentration of boron, which are largely unknown for animals and humans. In other words, although boron has a vital feature for living organisms when taken in a small quantity, some side effects or symptoms are observed when they are exposed to over dose, where the toxic or adverse effects of boron itself and/or their mechanism are not known exactly. Yet, the known toxic effects are enough for an alarm to reduce excess boron amount into a safe range. To give an example of this situation, decreasing in the rate of photosynthesis and division of the cell, retarded growth in the root cell are observed for plants; poising, damaging to the kidney, liver, central nervous system and side effects on the reproductive system are observed for

humans and animals. In the following section, these toxicity effects will be mentioned.

2.3.1 Boron toxicity effect on humans

Humans and animals are exposed to boron toxicity generally as boron dusts. These dusts might be found as boric acid, boron oxide, or various hydration states of sodium borate salts (pentahydrate, namely borax) or other borate salts (magnesium borate)[20]. Other ways of exposure might be via consumption of geothermal water or seawater, and/or respiration or contact through the skin might cause human acquire boron.

In human blood, boron exists in boric acid form mainly (98.4 %); only a small percentage of it is (1.6%) in borate form [20]. Normally, optimum boron content of the various body organs alters as given in Table 2.2. When exposed extendedly, boron would be dispersed through the body by blood transport and would be accumulated in lethal amounts in various organs in different amounts.

Table 2.2 : Boron concentration per organ (ppm boron/organ). [20]

Organ	**Boron Concentration (ppm)**
Heart	28
Ribs (hard water area)	10.2
Liver (dry weight)	2.31
Spleen	2.57
Lung	0.6
Kidney	0.6
Muscle	0.1
Brain	0.06

Another point is that the fatal average amount of boron, which is taken in by humans on a daily basis, shows differences depending on gender and age [21]. For example the average daily boron intake in infants (aged 0–6 months), males (aged between 51–70 years), and females are 0.75 ± 0.14 mg/day, 1.34 ± 0.02 mg/day, and 1.39 ± 0.16 mg/day, respectively [22].

2.3.2 Boron toxicity effect on plants

Boron is vital for plants. If boron concentration is low in soil, this concentration comprises no risk to plant. Furthermore, this amount of boron is necessary for plant or crop growth. If the amount of boron exceeds the required one, this situation can be toxic for plants. Between 0.3 $mg.L^{-1}$ and 0.5 $mg.L^{-1}$ magnitude of concentration is optimum for agricultures and soil water; yet, this range is different for all agricultural crops [23]. For example, sunflower requires 0.5 ppm for growth, but 1 ppm concentration can be toxic for this plant [24]. Table 2.3 gives limit amounts of boron in soil.

Table 2.3 : Boron tolerance for agricultural crops. [25]

Tolerance	Concentration of Boron in Soil Water (mg/L)	Agricultural Crops
Extremely sensitive	<0.5	Blackberry, Lemon
Very sensitive	0.5–0.75	Avocado, orange, peach, cherry, plum, grape, onion
Sensitive	0.75-1.0	Garlic, sweet potato, wheat, sunflower, strawberry
Moderately sensitive	1.0-2.0	Broccoli, red pepper, carrot, potato, cucumber, lettuce
Moderately tolerant	2.0-4.0	Cabbage, turnip, Kentucky, barley, cowpea, oats, corn
Tolerant	4.0-6.0	Purple vetch, parsley, red beet, sugar beet, tomato
Very tolerant	6.0-10.0	Sorghum, cotton, celery
Extremely tolerant	10.0-10.5	Asparagus

The lasting, frequency and level of exposure are parameters of tolerance to boron toxicity [26]. In relation to hazardous effect of boron on plants, excess amount of boron might reduce cell root division, photosynthesis, leaf chlorophyll and lay down of lignin and suberin, and retard inhibited root growth, etc. In many other plants, yellow leaves trip, accelerated decay effects might be the symptoms of boron toxicity [27]. In other words, boron toxicity symptoms are different depending on the type of the plants: Other than damage to the foliage, some plants may ooze a gummy

substance from the branches or trunk. Stunted growth is common, and fruit trees may be less productive.

Figure 2.3 : Sterile wheat heads from boron deficient plants.
[cropit.net/q=content/nutrition/boron-deficiency]

In addition to this, high concentration of boron has important effects on cell division in plants. This situation causes to reduce mitotic division, change chromosome bridges of cell and chromosome fragments [28].

2.3.3 Boron toxicity effect on animals

In animals, boron toxicity affects directly on male reproductive system. Many studies on animals such as rats, mice and dogs show that reproductive system incurs many vital effects by exposure to boron toxicity. Especially, boron toxicity cause shrunken scrota, inhibition of spermiation, atrophy of seminiferous tubules, degeneration, with an absence of gem cells in male rats. In addition to this, some adverse effects such as renal lesions in mice, reduction in ovulation in rats, are also seen in female reproductive system [29].Boron has also vital dermal effects on animals. For example, a study carried out in New Zealand on ten rabbits about the dermal effect of boron toxicity showed that the upper limit for irritation was 2.0 $g.kg^{-1}$. In this study, ten rabbits were exposed to borax (sodium tetra borate decahydrate) as a single dose by attachment on rabbits' skin for 2 hours. At the end of this research, the limit dose was determined as 2.0 $g.kg^{-1}$; below of which irritation was not observed [30]. In another study where a 0.1 g dose of borax (sodium tetra borate decahydrate) was

injected in the eyes of six rabbits, eye irritation as a damage of iris, corneal opticity and conjunctival redness, chemosis was observed. [31].

2.4 Boron Problems and Drinking Water Standards

In the MENA (Middle East and North America) countries or areas, the most important problem is water shortage, namely the lack of clean water. In addition to this, population in this area is increasing compared to available water sources. For this reason, desalination technology has been an important development in this area since 1957 [32].

For a long while, boron toxicity effects could not been known and emerged. Boron even did not have a place in the World Health Organization (WHO) international standards in 1958, 1963, 1971. In 1984, boron standards were firstly involved in drinking water quality document; however, harmful effects were not mentioned in any parts of it since they had not been tested on animals at laboratory conditions until 1993. Allowed boron concentration in drinking water was firstly determined also in 1993 as 0.3 $mg.L^{-1}$ based on NOAEL (No Observed Adverse Effect Level). Afterwards, this value increase to 0.5 $mg.L^{-1}$ in 1998, which was still acceptable in 2010 [33].

According to data from the UK and the USA, the amount of boron from taken from air and food is less than expected. Therefore, this value could increase from 0.5 to 2.4 $mg.L^{-1}$ [34].

2.5 Removal Technology of Boron from Aqueous Solution

Because of the adverse effects of boron mentioned in the previous section, treatment for seawater to reduce boron concentration in the WHO's allowed amount is a must. Thus, substantial efforts focus on new treatment methods or effective boron removal methods. High influence of boron on environment shows importance of research in removal boron from aqueous medium. Unfortunately, there are no simple and economical removal systems for boron. This situation arises from the fact that various concentration of chemical compounds are found in presence of boron at seawater and this value differs from place to place [35].

Commonly used water purification methods are sedimentation, coagulation and adsorption, but these methods are effective for fewer types of boron compound and do not remove all boron compounds [35, 36].

Evaporation, crystallization or solvent extraction methods are suitable for high concentration of boron. These methods are suitable to formation of boric acid rather than removing process [37].

There is no doubt that most commonly used and important methods for removal of boron from aqueous media are membrane separation, ion exchange, adsorption and hybrid methods.

- **Reverse osmosis membrane separation:** This method is most commonly used type of membrane separation for boron removal system. Because of that, among the membrane methods only reverse osmosis membrane method will be viewed in this section. Reverse osmosis (RO) is an effective and suitable removal method for drinking water. When boron concentration is more than 2.4 $mg.L^{-1}$, RO method is used to reduce boron concentration for making are suitable to the water standards according to WHO drinking water quality guidelines value [38].
  In reverse osmosis, a semi-permeable membrane separates the two solutions, but pressure is applied to the reverse direction from the natural flow of the water. The forces make the water to move from the more concentrated solution to the weaker. Thus, the contaminants end up on one side of the semi-permeable membrane and the pure water is on the other side. RO membrane has non-porous, homogenous layers. Both solute and solvent dissolve in membrane layer and diffuse from one part to across. RO method occur from four stages. These stages are pre-treatment, pressurization, separation and post-treatment.
  Among the important factors to affect reverse osmosis, pressure, suitable temperature, salt concentration and pH could be counted.
  Ionic substances are easily dissolved in RO membrane. Boron makes negatively charged borate ion ($B(OH)_4^-$) for passing easily through membrane. On the other hand, non-dissociated or neutral charged boric acid passage is difficult in RO membrane. The rejection of boric acid is 40-60% at pH ranges of 5.5-9.5. Removal of borate ion is 95% higher than boric acid in same pH condition [39].
- **Ion exchange method:** First ion exchange resin was developed in 1970s for boron removal. This resin was used in the ceramic industry for borate removal from

magnesium brine [40]. Boron sensitive resins work with complexation reaction principle. Boric acid reacts with molecules, which consist of one or more functional alcohol groups to form borate esters that relatively easily dissociate and release protons [34]. This ester formation monitor the reaction in eq.2.2.

$$B(OH)_3 + 3ROH \leftrightharpoons B(OR)_3 + 3H_2O \quad (2.2)$$

The huge factor is the type of diol to form stable boron esters complex. According to Power and Woods [34], the important point is the strength of the formed complex. At this point, the orientation of hydroxyl groups in a tetrahedral coordinated boron is important. For instance, the reaction of cis-diol and boron forms stable boron complex, which is illustrated by, for instance, *D*-mannitol, *D*-sorbitol, and *D*-ribose [41]. In addition, cis-diol monoborate ester or bis-diol borate complexes are examples of such strong complexes as stable borate esters and shown in Figure 2.4.

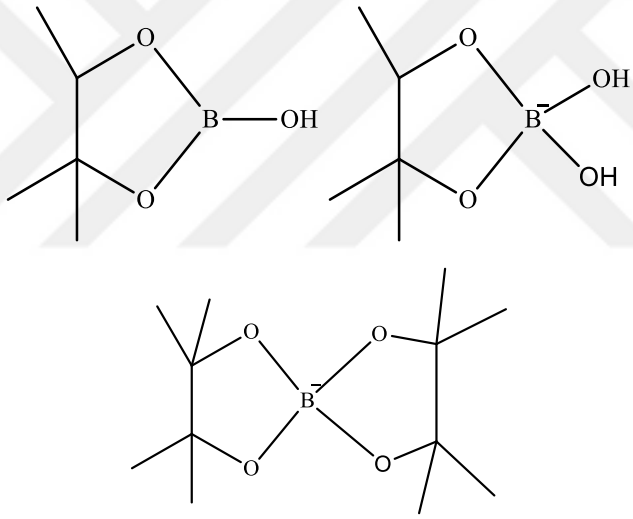

Figure 2.4 : Schematic drawings of the neutral cis-diol monoborate ester (left), the monoborate complex (middle) and the bis(diol) borate complex (down). [42]

Boron removal mechanism with ion exchange resins has several steps. These steps are solution diffusion, film diffusion and particle diffusion on heterogeneous surface resins [43]. In an ion exchange process, film diffusion or particle diffusion steps determine reaction rate.

• **Hybrid method:** This method is one of the popular boron removal methods from seawater or drinking water. It is an effective combination of adsorption and membrane separation methods suitable for decreasing boron concentration down to 0.5 ppm. The separation process includes two phenomena, which are sorption and membrane separation of boron-sorbent material. Hybrid systems are divided into

two groups: (i) polymer enhanced ultrafiltration (PEUF) and (ii) adsorption membrane filtration (AMF) method[44].

PEUF method is especially preferred in separation of pollutant ions from seawater [42–45]. In this method, borate is complexed with a suitable agent, usually by a water-soluble polymer with a polyol structure, the resultant complex of which will have a bigger diameter than the membrane's pores prior to the membrane. Thus, the cost of ultrafiltration is determined by type of borate and water-soluble polymers, molecular weight of which must be higher than that of the membrane [46, 48, 49]. The ratio of the latter to the borate amount could be kept generally as low as 1% [46]. Polymers in PEUF methods are poly(vinyl alcohol) [48], glucoheptanamide derivatives of poly(glycidylmethacrylate), alkyl monol, diol or triol containing poly(ethyleneimine) [46].

AMF consists of micro spherical sorbents and microfiltration membrane. In this method, prior to the microfiltration membrane, the wastewater to be cleaned is mixed with micro spherical sorbents to capture the boron. Then the membrane separates this complex. High pressure is not necessary and AMF works below critical flux conditions [50]. Another advantage of this method is its readily adaption into use in a bioreactor [51]. The effecting parameters are resin particle size, slurry rate delivery and resin concentration in suspension [52].

2.6 Adsorption Method

Adsorption technology is the commonly used one not only for boron removal processes but also for many separation processes. This is due to its practicality, rather low cost and availability of many adsorbents. Since it was the method used in this thesis work, it is going to be in a more detailed way addressed in this part, which will be followed by widely used adsorbents for boron removal.

2.6.1 Adsorption in solid/liquid interphases

All substances include forces for the requirement of nature. Solid substances comprise some molecular forces, which might produce a field around all small molecules, atoms or ions, together. Because of having these unbalanced forces, other atoms in gas or liquid phases might attack easily on its surface. The substance to attack on a solid substance's surface is adsorbate and this solid substance is called

adsorbant [53]. Adsorption is a spontaneous process that adsorbate molecules in a liquid keep themselves that are on the surface of a solid substance called as adsorbent (Figure 2.5). When these adsorbate molecules is released from or through adsorbent surface, this process is called desorption. For a permission of adsorption, an adsorbent must have a very high internal surface area. Commonly used adsorbents for removal process in industrial wastewater are natural or synthetic zeolites (alumina-silicate-polymers), natural clay minerals, silica gel and activated aluminum, activated carbon, polymers and resins, activated alumina [54]. The adsorbent properties such as mechanical (abrasion resistance, etc.), thermal stability, pore size and distribution, surface properties (surface area, etc.) are very important for a good adsorptive separation.

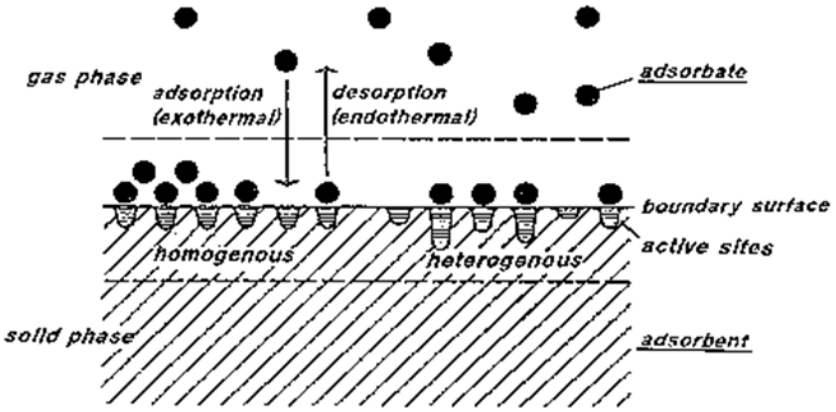

Figure 2.5 : General representation of adsorption process. [54]

2.6.2 Types of adsorption

Adsorption contains two types of process according to bond interaction between adsorbate and adsorbent molecules. If the Van der Waals forces are more dominant than other, then this is a physical adsorption (physisorption). On the contrary; when chemical bond forces are much stronger, this is a chemical adsorption (chemisorption).

In physical adsorption, the adsorbate and the adsorbent are protected with all distinctive properties. A transferring and sharing of electron is available for chemical adsorption.In physical adsorption firstly starts as monolayer and might continue with two or multilayer. If adsorbate's pore and size of the molecules are similar to each

other, these molecules cover in all adsorbate pores and the adsorption rate increases. To end of this event, the physical adsorption makes as multilayer. Because of that, the adsorption capacity of adsorbent is directly associated with surface area of its.

Table 2.4 : Differences between physisorption and chemisorption. [55]

Physisorption	Chemisorption
Low heat of adsorption usually in the range of 20-40 kJ mol^{-1}	High heat of adsorption in the range of 40-400 kJ mol^{-1}
Force of attraction are Van der Waal's forces	Forces of attraction are chemical bond forces
It usually takes place at low temperature and decreases with increasing temperature	It takes place at high temperature
It is reversible	It is irreversible
It is related to the ease of liquefaction of the gas	The extent of adsorption is generally not related to liquefaction of the gas
It is not very specific	It is highly specific
It forms multi-molecular layers	It forms monomolecular layers
It does not require any activation energy	It requires activation energy

In comparison with physical adsorption, in chemical adsorption adsorbate molecules attack to pore of adsorbent molecules and chemical bonds are formed between them which leads to a formation of monolayer. this process is irreversible also; and the rate of adsorption is slow [55].

2.6.3 Factors affecting adsorption

There are same factors to affect adsorption. These factors are given in below.

- *Nature of adsorbate:* Generally in hydrophobic (less dissolve in water) adsorbent, solubility and adsorption process are inversely proportional. If solubility increase, solute-solvent connect ions will be stronger and the degree of adsorption is low. Inorganic compounds give less adsorption compared to other compounds [56]. Because, an inorganic compound has a hydrophilic (dissolve in water) structure The gases which are more easily liquefiable or soluble in water are more readily adsorbed than others. For example, under similar conditions, the amount of

SO_2 or NH_3 adsorbed by charcoal is much more than that of H_2 or O_2 gases. Because the inter-molecular forces are stronger in more easily liquefiable gases, they get adsorbed more strongly.

- *Nature of adsorbent*: Different solids might adsorb the different quantity of the same gas even under similar conditions. Substances like charcoal and silica gel are excellent adsorbents. The substances that are porous in nature and have rough surfaces are better adsorbents.
- *Pressure*: At a constant temperature the extent of adsorption increases with increase in the pressure of the gas (adsorbate).
- *Temperature*: The extent of adsorption decreases with rise in temperature. Adsorption is an exothermic process. The change in enthalpy when one mole of a substance is adsorbed, is called enthalpy of adsorption. The adsorption process is similar to the condensation process. The reverse process is called desorption and is endothermic in nature.
- *pH*: Both acidic and basic medium affect adsorption process. Because, at under same conditions hydrogen (H^+) and hydroxyl (OH^-) hold with same forces on surface of resin . Moreover, different anions adsorb at different pH values [55].

2.6.4 Adsorption isotherms

Studies of adsorption isotherm models might be derived by assuming a thermodynamic equilibrium relationship between the amount of absorbed molecules by the unit mass of adsorbent and equilibrium solution concentration or pressure at constant temperature and pH. The relationship generates adsorption isotherms [56]. An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent, q_e, to the concentration of the solute in the liquid, C_e, with which it is in contact. It not only gives information about distribution of adsorbed molecules between two phases, but also the pore volume and surface area of adsorbent and the hat of adsorption is known by searching adsorption isotherm. Moreover isotherms' constant values can be determined for each system, since all adsorption isotherms and process are different from each other [56].

There are different mathematical models for adsorption isotherm such as Freundlich, Langmuir, Temkin and BET (Brunauer, Emmett, Teller) isotherms. However, Freundlich and Langmuir isotherms are commonly used isotherms to compare to

other isotherm models. In addition, these models are generally applicable for physical adsorption [56].

2.6.4.1 Langmuir isotherm

Langmuir isotherm is useful for most models of adsorption and has many application in surface kinetics and thermodynamics for chemical and physical adsorption. In Langmuir isotherm, the molecules adsorbed on the surface as monolayer which is a smooth and homogenous layer. Moreover, the state of adsorption energy is the same on all sides of surface and independent from other adsorbate molecules. These molecules attack to the surface at definite localized sites that it associates just one of the adsorbate molecule [57].

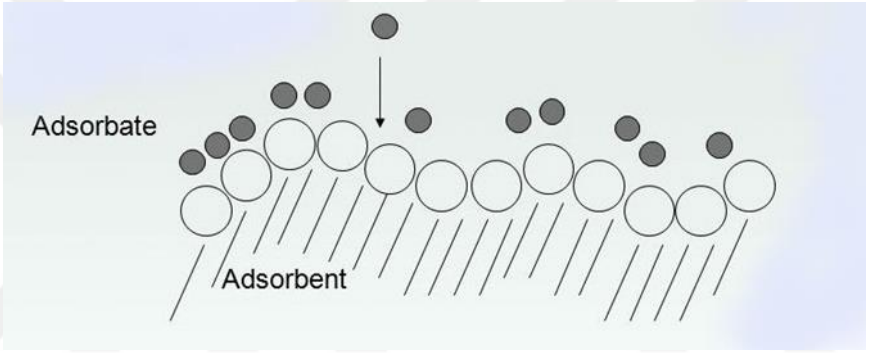

Figure 2.6 : Adsorbate molecules adsorption for Langmuir isotherm model.[57]

The equation of Langmuir isotherm is;

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2.3}$$

where q_m is maximum capacity of adsorbent and K_L refer Langmuir constant. C_e is equilibrium concentration and q_e refer to equilibrium capacity.

If this equation is linearized to obtain the following equation;

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \tag{2.4}$$

Plotting a Graph C_e versus C_e/q_e , q_m and K_L values are determined.

2.6.4.2 Freundlich isotherm

The equation of Freundlich isotherm is;

$$q_e = K_f C_e^{1/n} \quad (2.5)$$

where K_f is freundlich constant and n (n>1) is another constant value which are depends on the nature of the adsorbent and the gas at a particular temperature.

If logarithm of this equation is taken for linearization, the following equation is obtained.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2.6)$$

According to this equation, $\ln q_e$ is plotted $\ln C_e$; n and K_f values are determined.

2.6.4.3 Tempkin isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage.

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad (2.7)$$

where A ($L.g^{-1}$) is Tempkin isotherm equilibrium binding constant and and b is Tempkin isotherm constant. In addition, R is universal gas constant (8.314 $J.mol^{-1}.K^{-1}$) and T is temperature.

2.6.5 Adsorption kinetics

Adsorption process occurs from four stages in solution:

1. Film Layer Diffusion
2. Boundary Layer Diffusion
3. Particle Diffusion
4. Sorption

As a beginning, the adsorbate molecules diffuse and accumulate at the boundary of film layer on the adsorbent molecule. This step is called as film layer diffusion and is generally neglected. Afterwards, the movement of these molecules is started toward the pores of the adsorbent also; particles diffuse into its pores. The movement is

happened at the boundary layer diffusion and is called as intra-particle diffusion; likewise, the diffuse of these particles is happened at particle diffusion step. Finally; adsorbate molecules adhere to adsorbent's surface (Figure 2.7).

There are many different kinetic models like pseudo-first order, pseudo-second order and intra-particular diffusion models. Three kinetic models are tested and investigated below.

The linear form of pseudo-first order kinetic equation for adsorption analysis is

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2.8)$$

where q_e (mmol.g^{-1}) and q_t (mmol.g^{-1}) are the amounts of adsorbed adsorbate at equilibrium and at time t, respectively, and k_1 (min^{-1}) is the rate constant of pseudo first-order adsorption [56].

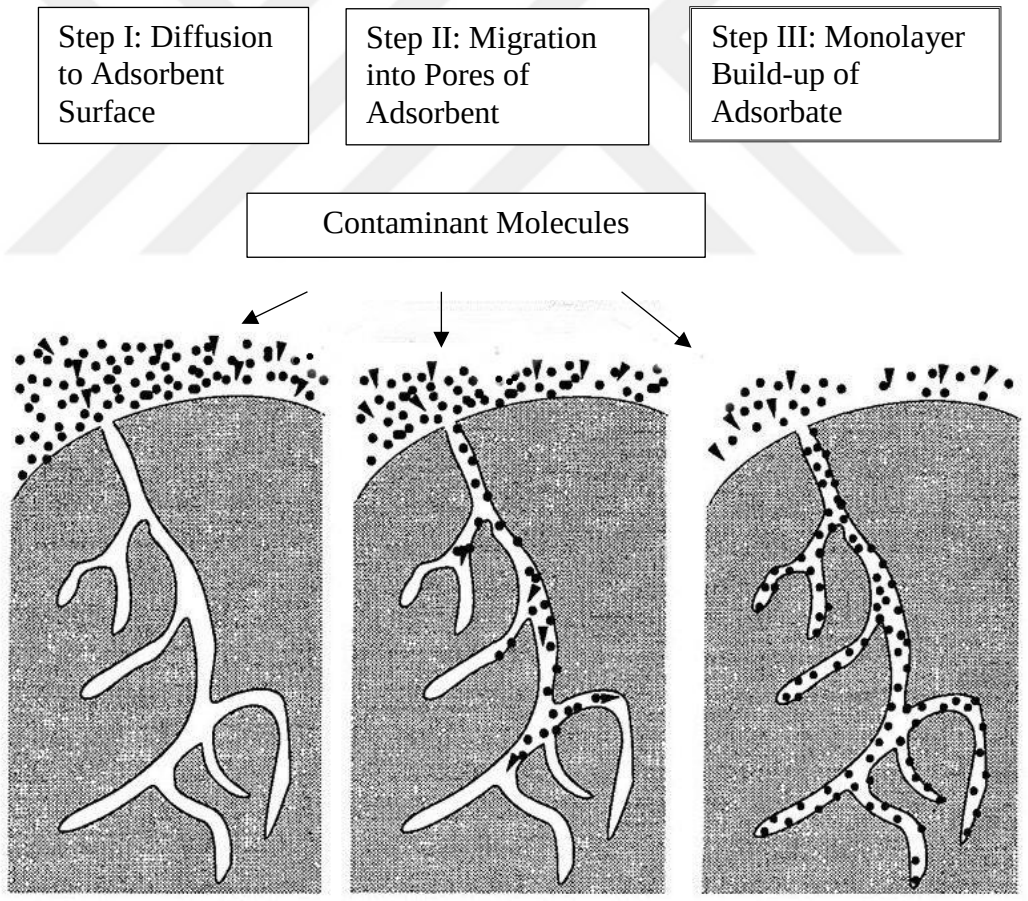

Figure 2.7 : Adsorption kinetic mechanism. [56]

Another commonly used adsorption model is pseudo-second order kinetic model. The linear form of pseudo-second order kinetic equation for adsorption analysis is;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.9)$$

where k_2 (g.mmol^{-1}.min^{-1}) is the equilibrium rate constant of pseudo second-order adsorption. Equation (2.9) does not have the problem of assigning an effective q_e. If there is a linear relationship between t/q_t and t, this should be acceptable for pseudo-second order kinetic. According to this, q_e and k_2 can be determined from slope and intercept of plot which belongs t/q_t versus t graph [57].

Third kinetic model is intra-particle diffusion kinetic model. The intra-particle diffusion equation is given as

$$q_t = k_i t^{1/2} + C \quad (2.10)$$

where q_t is the amount of solute on the surface of the sorbent at time t and k_i is the intra-particle diffusion rate constant (mmol.g^{-1} min$^{-1/2}$). The linear line of q_t versus $t^{1/2}$ graph passes through origin, the rate-limiting step can be determined from only intra-particle diffusion. According to graph, C can be determined from intercept of plot. In addition, it gives the idea on the thickness of the boundary layer [58].

2.7 Boron Adsorption

There are numerous types of adsorbents for boron separation from aqueous media. Since a polystyrene-based resin was prepared and modified for this aim in this study, only polymer-based adsorbents are going to be mentioned in this part. Some of these with their boron sorption capacities are given table 2.5.

Mostly used commercial polymeric resins are Amberlite IRS 743, Purolite S-108, Diaron CRB03 and Diaron CRB05. These polymeric resins have 93-98% boron removal effectiveness.

Generally used commercial boron sensitive resins are macro porous polystyrene based for they are convenient to be functionalized with boron selective groups. Chelating resin has many ligands, which include hydroxyl groups, and these groups are donated with high selectivity to boron [8,35, 65, 66]. Thus, boron-selective resins with different functionalities are gaining attention of researchers at boron removal studies for about three decades. When the functional group is N-methyl D- glucamine (Figure 2.9), the tertiary amine group provides neutralization of the

protons coming from boron-chelation in boron adsorption mechanism. Most synthesized resins were formed by modification with the N-methyl-D-glucamine (NMDG) of copolymer of styrene and divinylbenzene (Figure. 2.8).

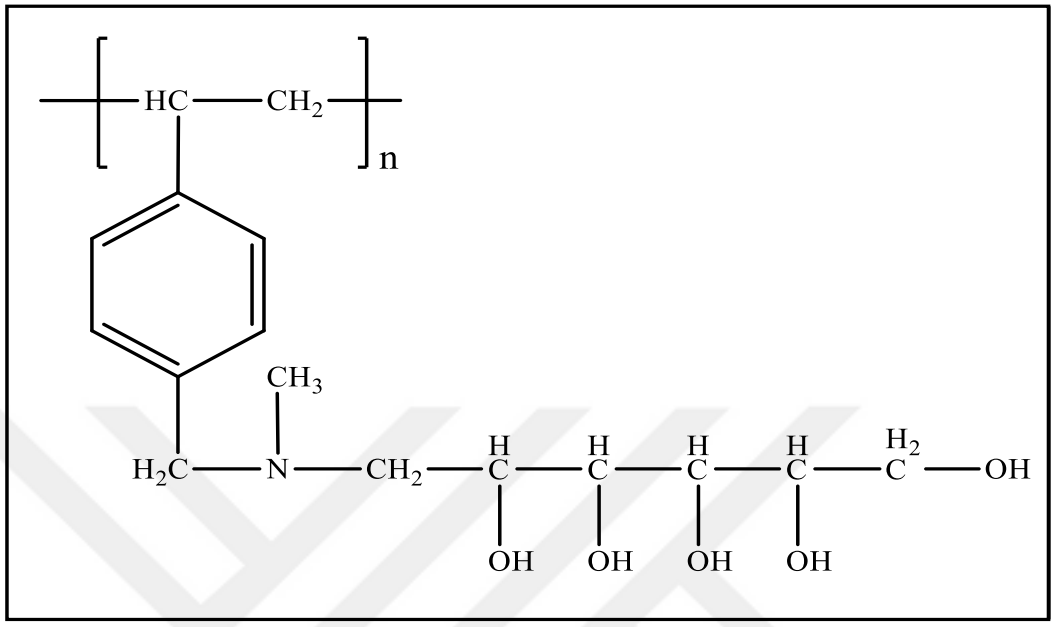

Figure 2.8 : Chemical structure of Amberlite IRA 743.[35]

The functional groups of these resins capture boron through a covalent attachment and form a coordination complex as is shown in Figure 2.9.

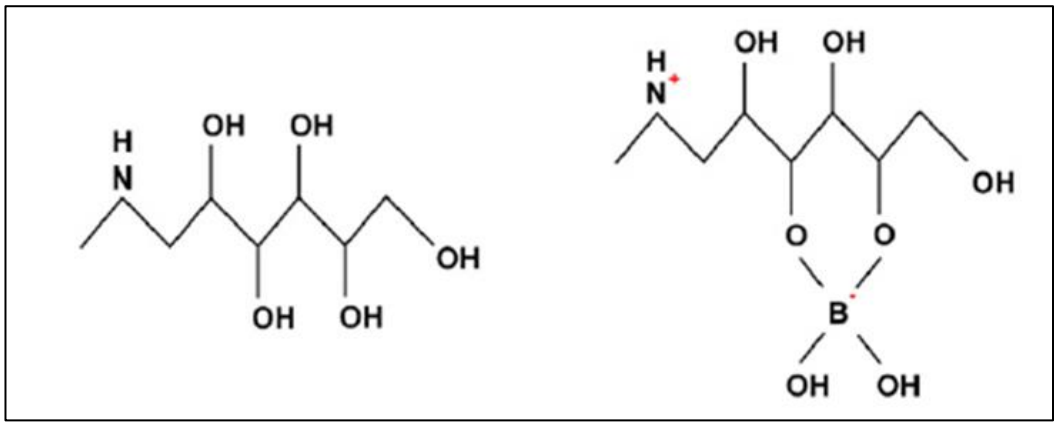

Figure 2.9 : Structural formula of N-methyl-D-glucamine (left) and monoborate complex (right). [35]

To be more specific, the chelating complexes are most important topic for this type of boron removal when using adsorption method. The adsorbent's structure has three or more hydroxyl groups, which are located in cis position. This structure is called as vis-diols. Vis-diols are highly sensitive to boron, but these groups do not react with ordinary metals or elements. Sorption rate of resin depends on the type of boron

source, which is wanted to be removed. Polyoxide structure in chelating resin provides formation of borate ester, where borate-anion and adsorbent chealate and then protons are released [8, 66, 67] (Figure 2.10).

Table 2.5 : Comparison of boron sorption capacities on several synthesized materials.

	Resin	Base Material	Moiety	q (mmol/g)	
Bio-polymer based materials	NMDG-type cellulose derivatives	Cellulose	NMDG	1.1	[59]
	CCTs-NMDG	CCTS	NMDG	2.1	[60]
Organic based materials	Diaion CRB02	PS-DVB	NMDG	≥0.9[a]	[61]
	DOWEX BSR-1	PS-DVB	NMDG	0.7[a]	[61]
	Purolite S108	PS-DVB	NMDG	0.6[a]	[61]
	Polymer supported 2-hydroxyethylamino proplene glycol	GMA-MMA-DVB	2-hydroxyethylamino propylene glycol	1.82	[5]
	poly(GMA-co-TRIM)-NMDG	poly(GMA-co-TRIM)	NMDG	1.84	[7]
	Functionalized mesoporous solid	Mesoporous silica	Glucose	0.67	[62]
			Fructose	0.76	
			Galactose	0.49	
			Mannose	1.85	
Inorganic based materials	NMDG-MCM-41	MCM-41	NMDG	0.8	[63]
	Polyol-grafted SBA-15	SBA-15	Glucose	0.63	[65]

NMDG: N-methylglucamine; GMA-MMA-DVB: glydicyl methacrylate-methyl methacrylate-divinylbenzene; PS-DVB: poly(styreneedivinylbenzene); poly(GMA-co-TRIM): poly(glydicyl methacrylate-co-trimethylolpropane trimethacrylate); MCM-4, SBA-15: silica mesoporous materials. a: Capacity unit (eq/L).

Due to the latter fact, presence of tertiary amine group in the adsorbent's structure makes a significant contribution for removal of boron since this structure easily

captures protons with its neighbourhood position to the hydroxyl functional groups [8]. Most common resins of such adsorbents are the N-methyl-D-glucamine (NMDG) containing copolymer of styrene and divinylbenzene (Figure 2.10).

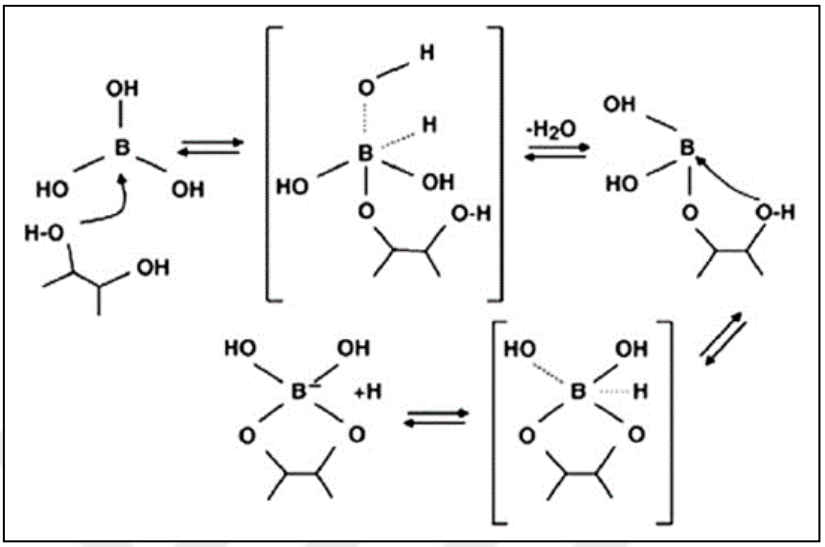

Figure 2.10 : Mechanism of boron with chelating resin. [8]

This chelating structure easily capture protons with covalent bond and gives a coordination complex (Figure 2.11) [56].

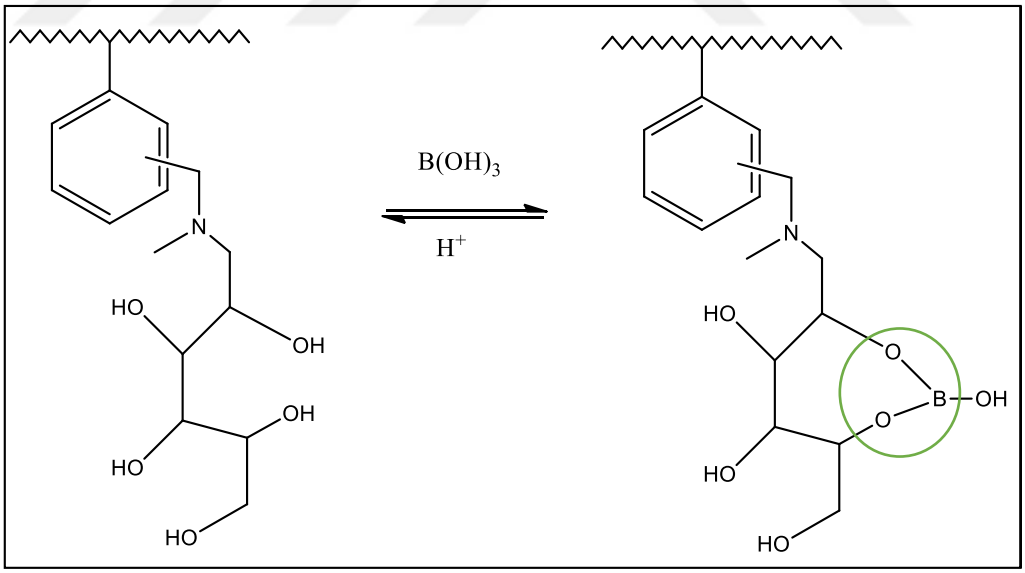

Figure 2.11 : Mechanism of boron by NMDG-type chelating resin. [68]

For example, there are such polymeric supports as natural polymers like polysugars, cellulose [59], cellulose fiber [69], pretreated sawdust [70], chitosan [60] in crosslinked structure (which is polymerized with radical polymerization), also even

silica-polyallyamine composites, polymer layered silicate nanocomposites[71,72] and polyethyleneiminide polymer in alginate hydrogel beads.

Nowadays, the most popular commercial resin is Amberlite IRA743, which is a macro-porous polystyrene-based resin with N-methyl glucamine functionality. At one of the studies using this resin, the effect of initial concentration of boric acid (40-2000 $mg.L^{-1}$), initial pH of medium and the mass of the adsorbent (10-110 $mg.L^{-1}$) were investigated. In conclusion, it could be said that the boron removal efficiency increase in proportion to boron concentration. The optimum sorption conditions were said to be pH 9.5 and 40 $mg.L^{-1}$ initial boron concentration. Langmuir isotherm was found to fit for equilibrium relation between the resin and liquid phase. According to results, the adsorption process was fast when boron was kept at low concentration [73].

In another study, two boron sensitive resins, with different number of alcohol functional groups, were obtained from crosslinked polyethyleneimine based polymer. The base PEI beads were functionalized, respectively, with 2-oxiranylmethanol and glucono-1,5-D-lactone to produce two resins (BSR-1 and BSR-2) with boron-chelating groups. Then, FT-IR spectroscopy, scanning electron microscopy, particle size distribution characterization were made on BSR-1 and BSR-2 resins besides determination of amine and water content. In conclusion, BSR-2 was the resinwith higher has high density of chelating groups. Moreover, sorption capacity was 1.93 $mmol.g^{-1}$ for BSR-2 and 1.23 for BSR-1 in aqueous solution from obtaining Langmuir isotherm. Also second boron sensitive resin showed excellent regeneration efficiency because of many alcohol groups and these resin were compared to Amberlite IRA 743 [74].

Recently; 2,3-dihydroxylbenzaldhyde modified silica gel (SGDHB) resin was functionalized and adsorption capacity, pH medium and kinetic measurement were made on this resin for testing performance for boron removal. This resin's functional groups were almost the same as other commercial chelating resin used for boron removal.

From the results, it could be shown that 25 mL of 0.01 M boric acid solution was completely removed within 30 minutes with using 0.1 g resin in the pH range of 7 and 9. Furthermore, the SGDHB resin had excellent sorption capacity, which is

3.812 mmol.g^{-1}, and all experiments showed that this resin was very effective for boron removal [72].

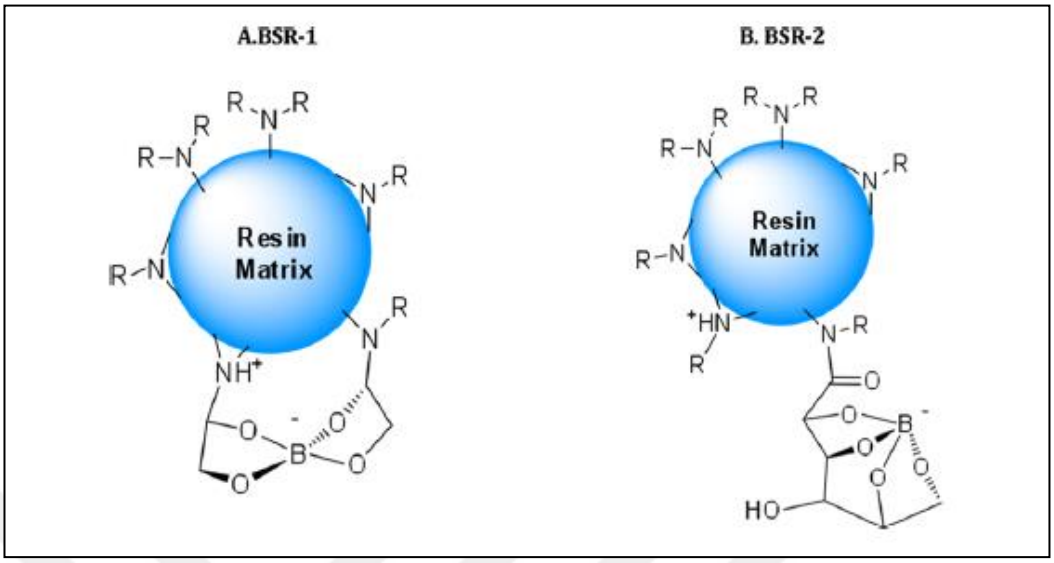

Figure 2.12 : Postulated mechanisms of boron coordination with the BSR- 1 and BSR-2 PEI resins in aqueous solutions. [74].

In another study, polyvinyl alcohol (PVA) based polymeric adsorbent was used for boron. The aim of the research was to investigate the relationship between the number of adsorption site, which is related to the number of hydroxyl group for boron sensitivity, and adsorption capacity.

For this purpose, besides PVA, polyallylamine (PAA) and glucose (PAA-Glu) polymers were synthesized and the hydroxyl contents of them were determined respectively as follows: The molecular weight of PVA was 88,000 g.mol^{-1} and had 2000 hydroxyl units in one molecule (n = 2000). Elemental analyser determined the chemical composition (Carbon/Nitrogen) of CRB03, CRB05 and PAA-Glu. In the second part of that study these polymers were used for boron adsorption. The different amount of polymers (0.0200–1.25 g) were mixed with 250, 125, 62.5 and 31.25 ppm boron solutions at pH 2-13, then to determine capacity, these solutions were filtered and measured by inductively coupled plasma atomic emission spectroscopy. The optimum pH range for boron adsorption was 13 for PVA, 5-7 for CRB03 and CRB05, and 8-9 for PAA-Glu. It could be seen from the boron capacity from Freundlich isotherm that adsorbent structure had a important influence on boron adsorption: PAA and PAA-Glu polymers had 15% and 35% respectively adsorption site availability; but PVA

had only 6% . Besides, the boron adsorption capacities were calculated 27 $mg.g^{-1}$ for PAA-Glu, 13 $mg.g^{-1}$ for CRB03 and CRB05 and 7.5 $mg.g^{-1}$ for PVA polymers. [75].

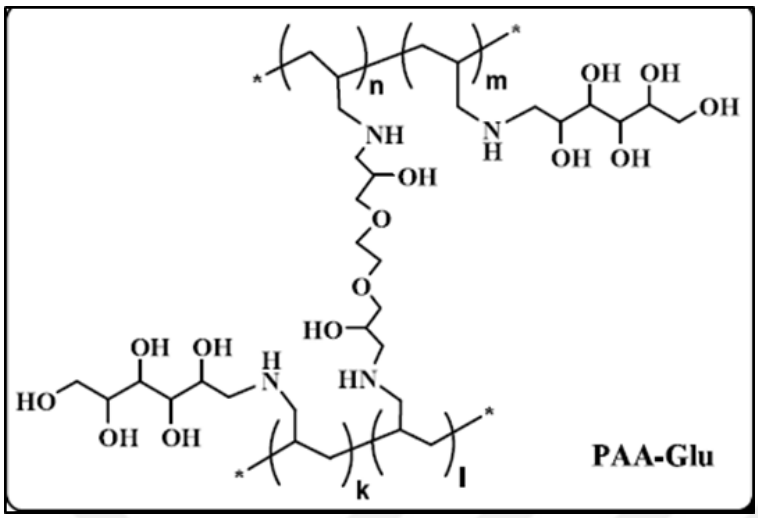

Figure 2.13 : Chemical structure of PAA-Glu. [75]

3. EXPERIMENTAL

3.1 Material and Instruments

3.1.1 Materials

Poly(vinyl alcohol) (Fluka), vinyl benzyl chloride (Sigma Aldrich), ethyleneglycole dimethacrylate (EGDMA), tris(hydroxymethyl)aminomethane (Sigma Aldrich), Sorbitol (Fluka), Boric acid (E-Merck), Magnesium sulphate anhydrous (Fluka), Calcium chloride dehydrated (Fluka) and all the other chemicals, solvents utilized were analytical grade commercial products.

3.1.2 Instruments

UV-Vis Spectrophotometer (Perkin-Elmer Lamda 25) and FT-IR Spectrometer (Nicolet) were used in spectroscopic characterization of the polymeric sorbents

3.2 Preparation of Poly(vinyl benzyl chloride) (PVBC) Resin

Crosslinked PVBC microspheres were prepared by suspension polymerization according to the literature. The details are as follows:

Vinyl benzyl chloride (5.00 mL, 31.90 mmol) as monomer, EGDMA (1.50 mL, 7.80 mmol) as a crosslinker, and 2,2′-Azobis(2-methylpropionitrile) (AIBN) (0.120 g, 0.710 mmol) as initiator were mixed and added to toluene (7.2 mL) as porogen. The resulting organic solution was poured drop wisely into an aqueous medium, composed of poly(vinyl alcohol) (0.25 g) in water (80 mL). The suspension polymerization was performed in a magnetically stirred glass flask (100 mL) at 78 °C for 8 h. At the end of the polymerization, the PVBC microspheres formed were washed with excess water, and then with ethanol to remove inorganic and organic contaminants. They were subsequently dried in vacuum at room temperature for 24 h. The microspheres were sieved and a proper size fraction (200-500 μm diameter) was isolated.

3.3 Modification of PVBC with Tris(hydroxymethyl)aminomethane (PVBC-tris OH)

5 g of PVBC resin was added to 30 mL of NMP. 4 g of tris(hydroxymethyl)aminomethane in 30 mL of NMP was added , which was shaken with a continuous shaker at room temperature for 24 h and 60 ^{o}C for 4 h . The reaction content was poured into water (500 mL), filtered and washed with excess water and methanol respectively. The modified resin dried under vacuum at room temperature for 24 h. The yield was 7.0 g.

3.4 Determination of Amine Content

0.10 g of the PVBC-tris OH resin was added to 10 mL of 0.10 M HCl solution. This mixture was shaken with a continuous shaker for 18 hours at room temperature. And then, the resin was removed from the mixture by filtration and 2.0 mL of filtrate was taken and the acid concentration of the solution was determined by titration with 0.05 M NaOH solution in the presence of phenolphthalein as a colour indicator. Amine content of the resin was determined with respect to the differences between the NaOH consumptions in titrations.

3.5 Determination of the Optimum Amount of Sorbent

The optimum resin was determined as follows: 0.02 g between 0.12 g of the PVBC-tris OH samples were mixed with 10 mL of H_3BO_3 solution (0.485 M) and stirred for 24 h at room temperature. After filtration of the mixtures, 2.0 mL of filtrates were mixed with 10 mL of 0.50 M D-sorbitol solution. Then, the mixtures were titrated with 0.10 M NaOH solution in the presence of phenolphthalein as a colour indicator in the literature. According to result, the optimum and suitable amount of PVBC-tris OH resin was determined. This amount of the sorbent was used for boron sorption experiments.

3.6 Determination of the Boron Loading Capacity of Sorbent

The boron sorption capacity of the sorbent was determined by batch method as follows: 0.10 g of the PVBC-tris OH sample was mixed with 10 mL of H_3BO_3 solution (0.485 M) and was stirred for 24 h at room temperature. Determination of

boron content of the solutions was investigated by using described above. Boron sorption capacities of the resin were also studied by using different boron concentration.

3.7 Determination of Boron Sorption Capacity of The Resin Depending on pH

The adsorption capacity of the resin was studied at various pH values (pH 2, 4, 6, 8). Also, pH values of the boric acid mixtures were arranged with 0.10 M NaOH and 0.10 M HCl solutions. And boron sorption capacities of the resin was determined colorimetrically at (λ=585 nm) by using the carminic acid method [76].

3.8 Effect of Foreign Ions on Boron Adsorption Capacity of Sorbent

To investigate any interaction of the resin with foreign ions, 0.1 g of the resin sample was mixed and stirred with 10 mL of 0.140 M of $CaCl_2$ and $MgSO_4$ solutions separately for 24 h. Analysis of filtered solutions were carried out by EDTA titration. From the difference of metal contents of the initial and final solutions of the sorbent Ca(II) and Mg(II) ions were found. Boron adsorption capacity of sorbent was also determined in the presence foreign ions. The boron content of the solutions concentration was assayed by the titrimetric method, as given above.

3.9 Boron Sorption Kinetics of Sorbent

0.10 g of the sorbent was added to 5 mL of water and left for 2 h. Then, 90 mL of H_3BO_3 solution (4.9×10^{-3} M) was added to the wetted sorbent at room temperature. The mixture was stirred with a magnetic stirring bar. 5 mL of aliquots were taken and transferred to sample-bottles at appropriate time intervals using a filter paper. The carminic acid method was used to determine boron content of the solutions [81] (λ=585 nm)

3.10 Desorption of the Boron from Loaded Sorbent

0.10 g of the boron loaded PVBC-tris OH resin was mixed with 10 mL of HCl solution (4 M) and stirred at room temperature for 24 hours. Then, the solution was filtrated. 2 mL of the filtrate was titrated with 0.10 M NaOH solution in the presence of phenolphthalein indicator. After neutralization of the excess of HCl, 10 mL of

0.5 M D-sorbitol solution was added to the mixture. Additional NaOH solution reveals a 2.10 mmol of desorbed boron per gram of loaded sample. Adsorption and desorption cycle was repeated 2 times.

4. RESULT AND DISCUSSION

In this study, crosslinked PVBC resin was prepared by using suspension polymerization method in the presence of toluen as porogen and AIBN as initiator at 78°C for 8h. The PVBC resin was reacted with tris(hydroxymethyl)aminomethane to obtain tris hydroxy amine functions (Figure 4.1).

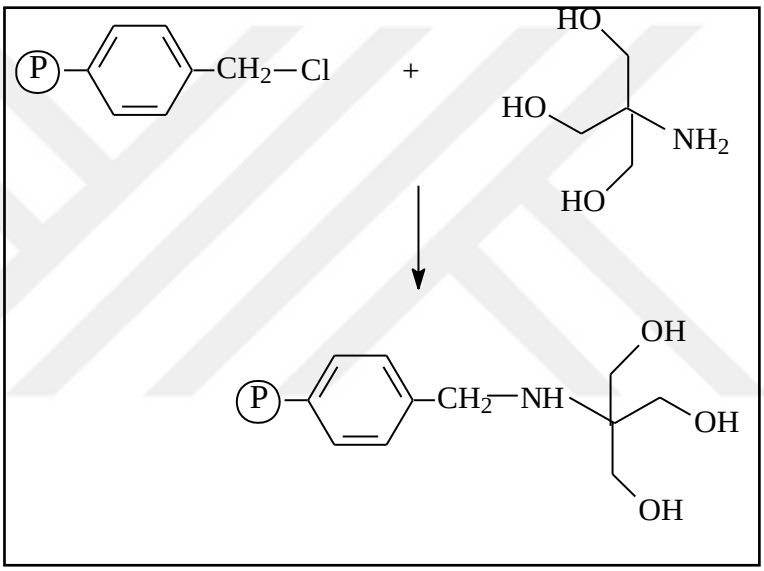

Figure 4.1 : Preparation of PVBC-tris OH resin.

Resins were characterized spectroscopic method by FTIR spectra . According to the Figure 4.2, PVBC resin showed a sharp band 1720 cm^{-1} corresponding to the ester carbonyl group of EGDMA.

In addition, resin showed characteristic C-Cl stretching at about 671 cm^{-1}. Figure 4.2 shows the FT-IR spectrum of the PVBC-tris OH sorbent. The broad band in the 3310 cm^{-1} indicates OH stretching vibrations in the sorbent. The disappearence of the characteristic C-Cl vibration at 671cm^{-1} was observed after modification of PVBC resin with tris(hydroxymethyl)aminomethane.

The reaction of PVBC resin with tris(hydroxymethyl)aminomethane gives amine containing resin with 2.45 $mmol.g^{-1}$.

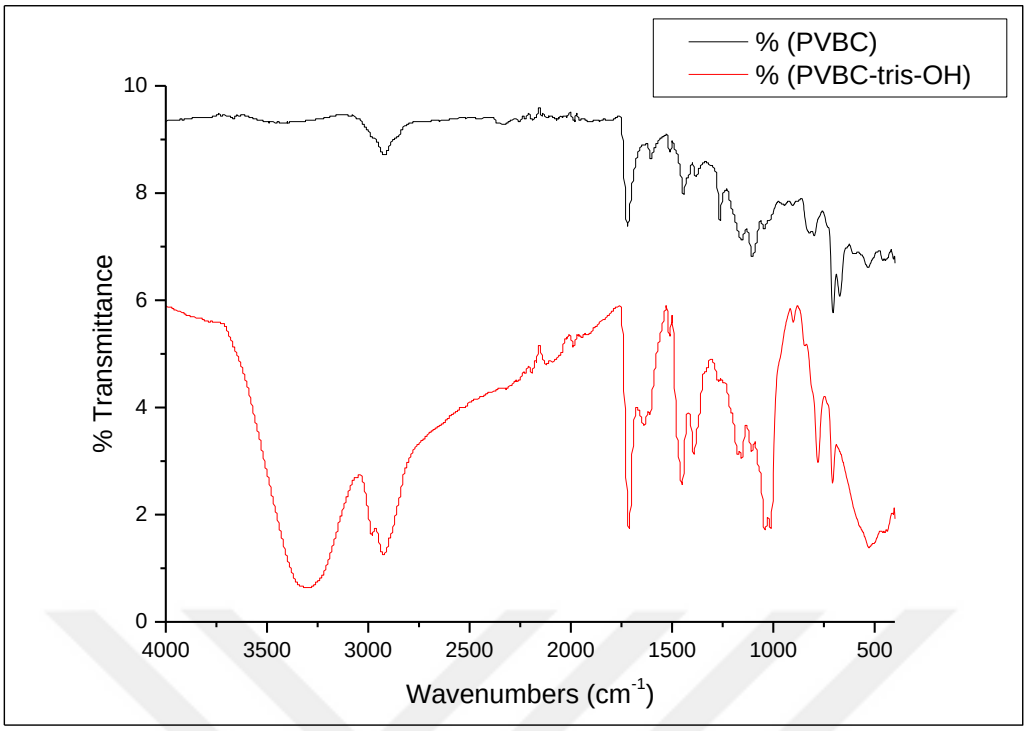

Figure 4.2 : FT-IR spectra of the resins.

4.1 Effect of Dosage

The boron sorption was investigated as a function of adsorbent amount. The results in Figure 4.3 show as the amount of sorbent increases, boron removal capacity increased, which can be attributed to the increase of the sorbent surface area and adsorption sites.

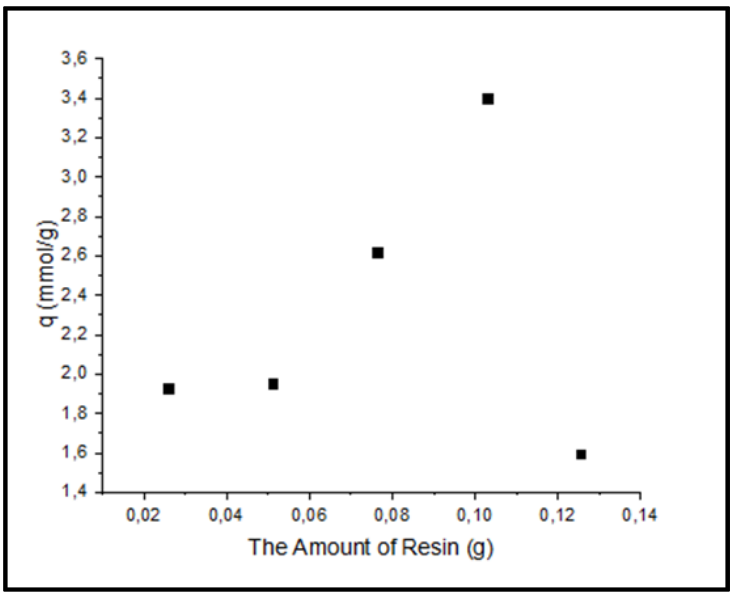

Figure 4.3 : The plot of boron sorption capacity of resin against amount of resin.

However, boron sorption capacity decreased with increasing amount of sorbent, which can be explained by the aggregation of adsorption sites and the difficulty of diffusion. Considering above phenomenon, 0.10 was used as the fixed optimum amount of sorbent in this research.

4.2 Boron Sorptions

Boron sorption experiments were carried out depending on different boron concentrations and different pH medium (Table 4.1 and Table 4.2). Experiments showed that the resin with hydroxy functions is a boron-specific sorbent. These hydroxy functions incorporated into the polymer structure act as chelating agent for boric acid, by forming boron esters. Boron loading capacity of the sorbent is 2.17 mmol g^{-1} in non-buffered conditions.

Table 4.1. Maximum boron sorption capacities of the resin.

Boric Acid Concentration (M)	**Capacity (mmol.g^{-1})**
0.128	0.437
0.150	0.739
0.250	1.420
0.332	1.738
0.376	1.776
0.500	2.170

According to Table 4.1, boron sorption capacity depends on boron concentration and loading capacity of the resin increases with increasing boron concentration.

4.3 Sorption Isotherms

The study of sorption isotherm is used to to determine the maximum sorption capacity of the sorbent. In this study, different isotherm models such as Langmiur, Freundlich and Tempkin were used.

The linearized form of Freundlich isotherm is given as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4.1)$$

where, qe is the amount of boron adsorbed (mmol.g^{-1}), C_e is the equilibrium concentration of the boron (mmol.L^{-1}), K_f and n are known as the Freundlich adsorption constants and they indicate the sorption capacity and measure of the deviation from linearity, respectively.

K_f and n values were determined from the intercept and slope of the linear plots of ln qe vs. log Ce, respectively.

The value of n is not only a measure of the deviation from linearity but also inform about the heterogeneity degree of the sorption sites. As an approaches zero, the surface site heterogeneity increase.

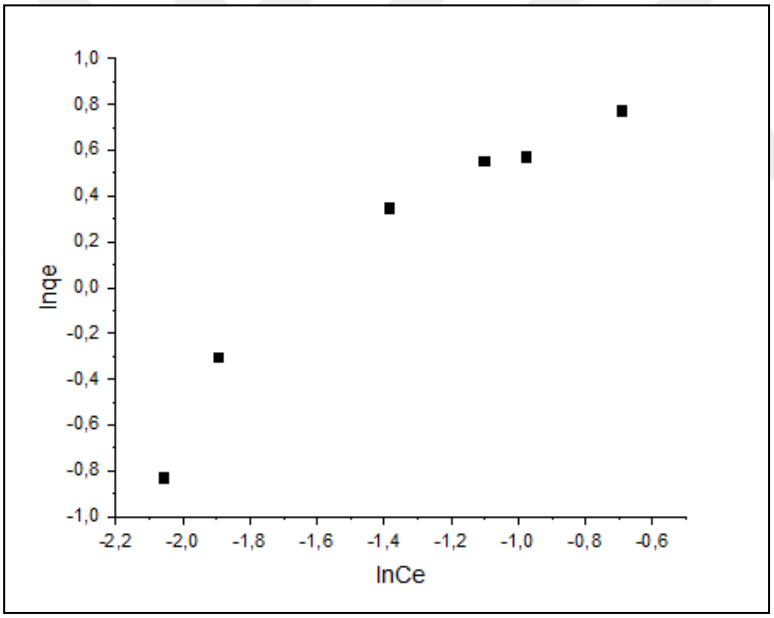

Figure 4.4 : Freundlich isotherm plot of boron adsorption onto PVBC-tris-OH.

The Tempkin isotherm has been generally applied as a linearized form:

$$q_e = B \ln A + B \ln C_e \quad (4.2)$$

where B = RT/b, b is the Tempkin constant related to heat of sorption (J mol^{-1}); A is the Tempkin isotherm constant (L. g^{-1}), R is the gas constant (8.314 J. mol^{-1}. K^{-1}) and T is the absolute temperature (K). Therefore, the constants A and b were calculated from the plot in Figure. 4.5.

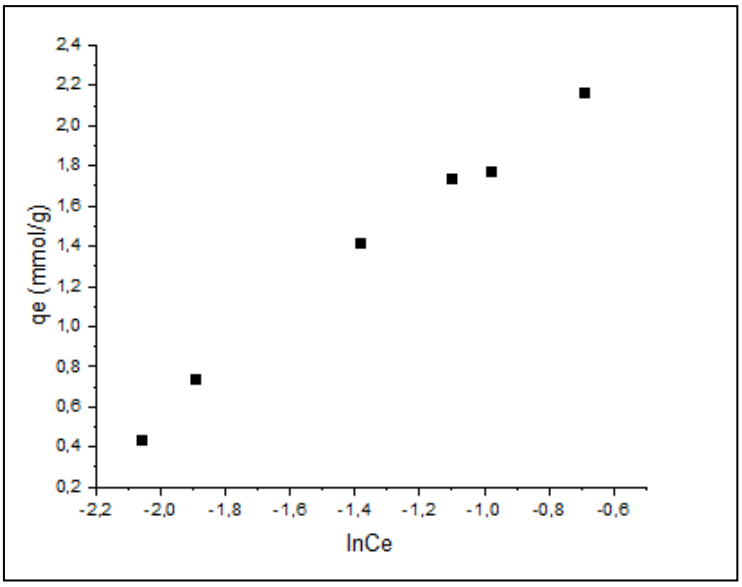

Figure 4.5 : Tempkin isotherm plot of boron adsorption onto PVBC-tris-OH.

The constants A and b are listed in Table 4. 2. It is clear from Table 4.2, the Tempkin isotherm fitted quite well with the experimental data (correlation coefficient $R^2 > 0.99$), whereas, the low correlation coefficients showed the poor agreement of Freundlich isotherms with the experimental data.

Table 4.2 : Freundlich and Temkin isotherm constants and correlation coefficients of isotherm models for the adsorption of boron.

Freundlich Isotherm Model				**Tempkin Isotherm Model**		
q_e (mmol.g^{-1})	**n**	**K_f**	**R^2**	**A**	**b**	**R^2**
2.17	0.895	5.467	0.9295	2.718	3091.170	0.9909

4.4 The Effect of pH on Adsorption

pH value affects the surface charge of the adsorbent [77-79]. Therefore, boron sorption experiments were examined at the initial pH range of 2.0 to 10.0 and the results were given in Table 4.3.

According to the Table 4.3, the boron sorption capacities of the sorbent increased with the increasing initial pH of boron solution in the pH range of 2.0 to 10.0. When boron oxide (B_2O_3) reacts with water, Boric acid, which is very weak Lewis acid, formed.

Table 4.3 : Boron sorption capacity of the resin depending on pH.

pH	Capacity (mmol.g^{-1})
2.01	1.66
4.03	2.35
6.02	2.80
8.03	3.20
10.01	3.75

In acidic conditions, the sorption capacities were small because H_3BO_3 was the main existing form of boron. Boric acid acts as an acid by accepting OH^- to form $B(OH)^-_4$ according to the following reaction [80]:

$$B(OH)_3 + H_2O \longleftrightarrow B(OH)^-_4 + H^+ \quad (4.3)$$

In alkaline medium, boric acid transforms to a negatively charged borate ion, and the amount of borate ion increases with increasing pH level.

$$B(OH)_3 + OH^- \longleftrightarrow B(OH)^-_4 \quad (4.4)$$

Meanwhile, both tertiary amine and hydroxyl functional groups on the sorbent surface became protonated [81], resulting in weak electrostatic interactions between the resin and H_3BO_3.

When increasing of the solution initial pH, sorption capacities of the resin increased significantly and reached the maximum at pH 10. Under this condition, H_3BO_3 transformed into $B(OH)_4^-$ and polyanionic species ($B_3O_3(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$) [78,82,83].

It was also seen that the adsorbent could adsorb boron from aqueous solutions at all pH values, and the boron sorption capacity of in a natural solution was very close to the maximum capacity. Therefore, all the boron adsorption experiments were studied in neutral solutions.

4.5 Foreign Ion Effect on Boron Sorption Capacity of The Resin

The boron sorption experiments were also studied in the presence of some common ions such as Ca(II) and Mg (II). For this purpose, binary mixtures of H_3BO_3 with one of the foreign ions were prepared so the concentration of the foreign ion was

0.140 M. Ion sources of the foreign ions were $CaCl_2$ and $MgSO_4$.$7H_2O$. The resin sample (0.10 g) was interacted with 10 ml of the solutions for 24 h at room temperature. The resin was filtered and non-adsorbed boric acid and the metal ion were assayed separately by analysis of each component. Sorption capacities of Ca(II) and Mg(II) ions were determined by complexometric titration with ethylenediaminetetraacetic acid (EDTA) solutions in basic medium (ammonium chloride/ammonia). The boric acid concentration was found by the titrimetric method. These experiments were also repeated in the absence of boric acid to determine the extractability of the foreign ions alone. Collected data were given in Table 4.4.

Table 4.4 : Effect of foreign ions on boron sorption in non-buffered conditions.

H_3BO_3 (M)	**Ion (0.140 M)**	**Boron capacity (mmol/g)**	**Ion Capacity (mmol/g)**
0.485	Mg^{+2}	2.17	0.24
0.485	Ca^{+2}	1.67	0.24
-	Mg^{+2}	-	0.98
-	Ca^{+2}	-	0.69

4.6 Boron Adsorption Kinetics of Resin

To investigate the efficiency of the resin in the presence of low boron concentrations, batch kinetic sorption experiments were studied with highly diluted boric acid solution ($4.90x10^{-3}$ M). The concentration–time plot (Figure 4.6) shows that within about 250 minutes contact time boron concentration falls to zero.

Three kinetic models were applied to investigate sorption kinetics which are pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

The Lagergren first-order rate equation (4.5) is one of the most widely used for the sorption of solute from a liquid solution [84] and the equation can be given as following:

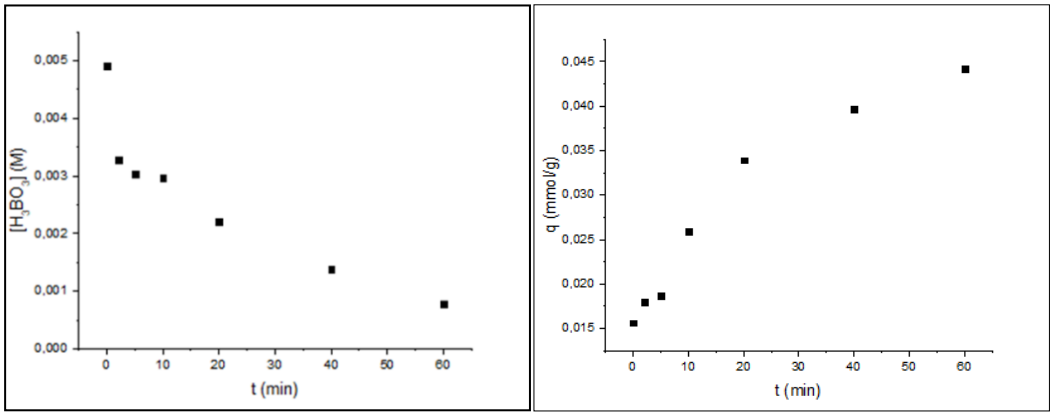

Figure 4.6 : Sorption kinetic of the resin.

$$\log \frac{q_{eq}}{q_{eq}-q_t} = \frac{k_1.t}{2.303} \qquad (4.5)$$

where k_1 is the rate constant (min^{-1}) and q_{eq} and q_t show the amounts of adsorption (mmol. g^{-1}) at equilibrium and at time t, respectively.

The slopes and intercepts of plots of log ($q_{eq} - q_t$) versus t give the pseudo-first-order rate constant k_1 and q_{eq}.

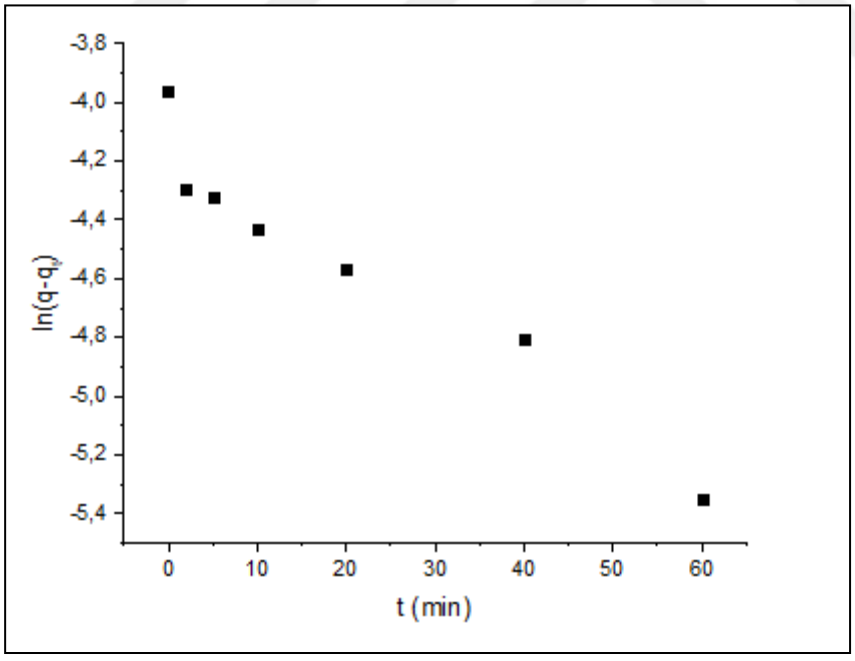

Figure 4.7 : Pseudo-first-order model plot of adsorption of boron on the resin.

The pseudo-second-order kinetic model was given with the equation below :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\, t \qquad (4.6)$$

where q_t is the amount of boron adsorbed at time t (mmol.g^{-1}); q_e is the amount of boron adsorbed at equilibrium (mmol.g^{-1}) and k_2 is the equilibrium rate constant of pseudo-second-order sorption (g.$mmol^{-1}$. min^{-1}). The rate constant k_2 and q_e could be directly obtained from the intercept and slope of the plot of t/q_t versus t in Figure 4.8 and the rate constant k_2 and q_e can be directly obtained from the intercept and slope of the plot.

Sorption kinetics are controlled by different steps including transfer from the sorbent surface to the intra particle active sites, solute transfer to the sorbent surface, and retention on these sites via sorption, complexation and intraparticle precipitation phenomena.

Intra particle diffusion model can be given by Weber and Morris equation [85]. In this model, the initial rate of intra-particular diffusion is calculated by linearization of the curve (4.7),

$$q_t = K_i . t^{0.5} \quad (4.7)$$

where K_i is the diffusion rate constant (mmol g^{-1} $min^{-0.5}$). For intra particle diffusion mechanism, the plot of q_t versus $t^{0.5}$ should be linear (Figure 4.9).

The resulting parameters of these models calculated and the correlation coefficients R^2 were given in Table 4.5

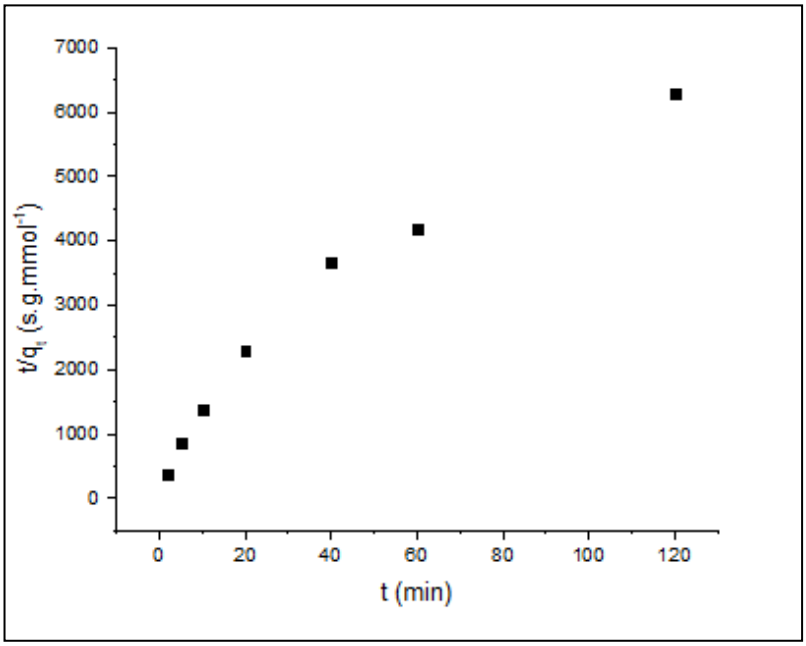

Figure 4.8 : Pseudo-second-order model plot of adsorption of boron on the resin.

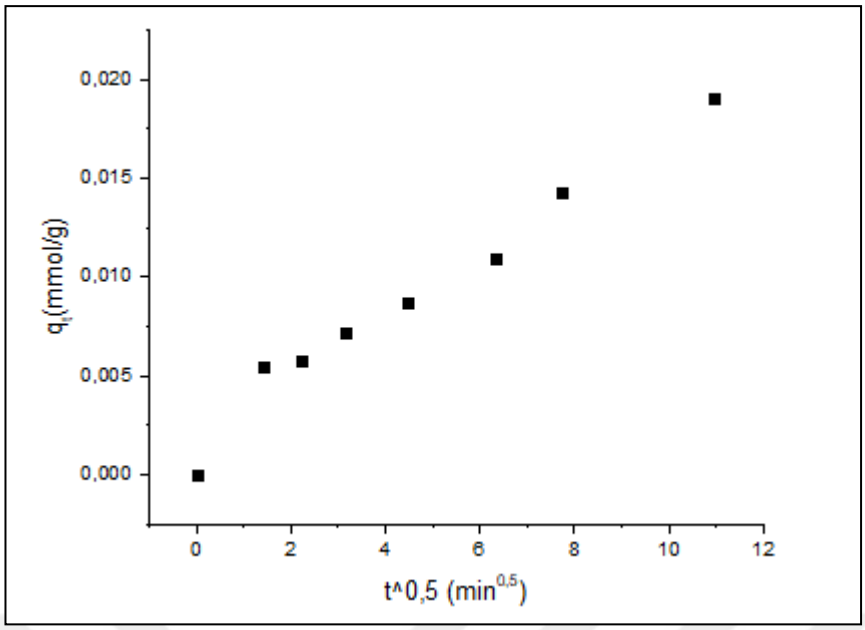

Figure 4.9 : Intra-particle diffusion plots for the adsorption of boron on the resin.

The resulting parameters of these models calculated and the correlation coefficients R^2 were given in table 4.5, where the experimental value of q_e is also presented. The results show that the intraparticle diffusion model was applicable due to the higher correlation coefficients according to the other models.

T**able 4.5** Kinetic parameters for the adsorption of boron.

MODELS	$q_{theoretical}$ (mmol.g^{-1})	q_{exp} (mmol.g-1)	k	R^2
Pseudo First Order	0.0190	0.016	-0.019 min^{-1}	**0.9348**
Pseudo Second Order	0.0190	0.020	0.379 g.min^{1}.mmol^{-1}	**0.9377**
Diffusion Particle	0.0190	-	0.0016 mmol.g^{1}.s$^{-0,5}$	**0.9730**

5. CONCLUSIONS

Crosslinked polystyrene based tris(hydroxylmethyl)aminomethane modified resin has a potential as a sorbent for sorption of boron from wastewater .Also; it can remove boron over a wide pH range.

Desorption experiment was conducted interaction of the boron loaded resin with 1 M HCl for 24 h at room temperature. Then, desorption capacity was found titrimetrically described experimental part and calculated as 2.10 mmol per gram resin. Desorption experiment was repeated with regenerated resin again and the sorbent was desorbed completely.

Trace kinetic results indicate diffusion model is suitable in this resin.

The results indicated that prepared polymeric sorbent demonstrates greater potential for boron removal from aqueous solutions.

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